FUEL ELEMENTS CONFERENCE

**Paris,
November 18-23, 1957**

**BOOK 1
Sessions I, II, and III**

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Preface

The Fuel Elements Conference held in Paris, France, November 18 to 23, 1957, under the joint sponsorship of the U. S. Atomic Energy Commission and the French Commissariat à l'Energie Atomique (CEA), provided an intensive review of fuel-element fabrication practices and behavior of fuel elements under in-pile irradiation and when subjected to corrosive media. The primary mission of the conference, from the standpoint of U. S. participation, was to cooperate with the French, presenting information of value to current and projected atomic energy programs of both the U. S. and France, pursuant to the U. S. Agreement for Cooperation which has been in effect since November 1956. In carrying out this mission, the interests of participants of other countries were also taken into account. The conference served to strengthen cooperative relationships between the U. S. and the European community in the peaceful uses of atomic energy and represented an important activity within the framework of the President's Atoms for Peace Program.

To organize the U. S. effort, the AEC Division of International Affairs selected a Washington Coordinating Committee and a Program Committee early in June 1957. These committees, in addition to naming a 20-man team consisting of 15 AEC contractor and five AEC personnel, reviewed the fuel-element technology field and agreed that the objectives of the conference could be best accomplished by the presentation of papers in the following major categories:

1. Applied Metallurgical Research
2. Natural-uranium Metallic Fuel Elements
3. Enriched-uranium Metallic Fuel Elements
4. Nonmetallic Fuel Elements
5. Corrosion of Uranium Alloys
6. Irradiation Effects on Uranium, Its Alloys, and Its Compounds
7. Plutonium Fuel Elements

Dr. A. J. Vander Weyden, Deputy Director, Division of International Affairs, who led the U. S. team, served as chairman of the conference, which was attended by approximately 125 scientific representatives from the U. S., OEEC (Organization for European Economic Cooperation) countries, Canada, and Israel. The U. S. presented, in addition to 23 technical papers,* two films: (1) "An Adventure in Metallurgy," depicting the mechanism of deformation and fracture in uranium under tensile stress, and (2) "Technology of Enriched Fuel Plate Elements for Research Reactors," treating of the design and preparation of flat-plate fuel elements. Four papers were presented by France, three by the U. K., three by Canada, and two by Sweden.

The AEC is most grateful to the CEA for their effective cooperation and for their expressions of appreciation which attributed the success of the joint conference to AEC participation.

*Two of these 23 papers were in the form of extemporaneous talks and are not included in this cumulation. These talks were given by Dr. Benjamin Lustman, Bettis Plant, Pittsburgh, and were based on Report WAPD-127, Development and Properties of Uranium-base Alloys, Parts I to IV.

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SESSION I

Applied Metallurgical Research

Survey of Basic Engineering Metallurgy Research Programs of the Division of Reactor Development

By J. M. SIMMONS

Division of Reactor Development, U. S. Atomic Energy Commission

ABSTRACT

The Metallurgy Research Program, sponsored by the Engineering Development Branch of the Division of Reactor Development, has one prime objective: to obtain data and information for advancing the understanding and application of the basic laws of metallurgy in the nuclear field.

Five major areas of investigation are covered by this program:

1. Fuel elements
 - (a) Plutonium fuels
 - (b) Advanced types of fuel
 - (c) Fuel for high-temperature operation
 - (d) Radiation damages to fuel elements
 - (e) Basic engineering studies on fissionable and fertile materials
2. Metals, alloys, and materials
3. Components and equipment
4. Control rods
5. Production techniques

Each area is discussed in general, with indications as to the trend and probable achievement in the area.

1 PHILOSOPHY AND SCOPE

Each research investigation sponsored by the Engineering Development Branch of the Division of Reactor Development has, as objectives, the advancement and the application of engineering knowledge to nuclear reactors. Basic engineering metallurgy research, a part of the Branch's activities, has a single aim: to obtain data and information to advance the understanding and application of the laws of metallurgy in the reactor development program.

The scope of the research is (1) to give an integrated scientific and engineering development program on metallurgy and materials, (2) to obtain desired data and to understand fundamental laws, (3) to keep fully informed of the latest discoveries in metallurgical research, and (4) to achieve results that are of specific use in reactor projects.

Advanced thinking is called for, and, by research, concepts are tested rigorously to determine their validity. Projects are undertaken to give answers to current problems in reactor development as well as to obtain data on phenomena that will be of future concern. Surveys of other research in fields of interest to reactor programs are made. If any survey shows that important areas are not being fully investigated, programs to cover these areas are undertaken.

The ultimate goal of this program is to have data available or to have research in progress which will answer all questions reactor designers might ask of metallurgists on fuels, materials, components, and testing methods. Research and development projects are under way at the Atomic Energy Commission (AEC) laboratories, other government laboratories, industrial laboratories, and universities. Criteria for the selection of an organization as a contractor for an investigation are

1. Scientific stature of scientists in charge
2. Active interest of research team in the specific area of research
3. Scientific competence and efficiency of team
4. Data obtained from previous investigations made by the group
5. Support given by laboratory director to the program

The five major areas of research covered by this program are

1. Fuel elements
2. Metals, alloys, and materials
3. Components and equipment
4. Control rods
5. Production techniques

Each of these areas is discussed, with projects in each area being outlined to illustrate the trends of research.

2 FUEL ELEMENTS

2.1 Plutonium Fuels

Reactor technology is at the stage that plutonium can be used as a fuel for the controlled release of energy. A complete fuel core loading of plutonium fuel is being prepared for the Materials Testing Reactor (MTR). Assemblies for the core are manufactured to MTR dimensional specifications. Plates of the assembly containing an aluminum-plutonium alloy approximately 10 wt. % plutonium clad with aluminum are produced by the standard techniques developed for production of MTR cores. Data obtained will be compared with those from previous loadings; operation of the reactor with different fuel composition will be evaluated completely. Several fuel elements of this type have already operated in the MTR. Plutonium utilized in this manner not only produces energy but is a source for large quantities of isotopes of plutonium and of transplutonium elements, materials of great scientific value. General programs on the development of plutonium and plutonium alloys for use as fuel are in effect. Fabrication techniques, cladding procedures, manufacturing and testing of prototype elements—all these phases of plutonium technology are being studied. Production of plutonium core loadings for different types of reactors will result from these studies.

2.2 Advanced Types of Fuel

Reactor development requires the utilization of fuel cores for longer time periods, at higher temperatures, and to greater burn-up of the fissionable atoms. Fissionable fuel, in forms other than normal uranium metal or normal uranium enriched with U^{235} , may be used as energy sources. UO_2 now operates efficiently in reactors. Other compounds of uranium may possess better physical properties and irradiation stability. Combinations of metal and metal compounds (cermets), possessing physical characteristics of metals, corrosion resistance, and irradiation stability of compounds, offer attractive possibilities. In support of the Atoms for Peace program, a more serviceable, economical fuel element of 20 per cent enriched U^{235} is being developed. Fuel elements, formed by powder-metallurgy techniques, of fissionable material dispersed in a nonfissionable material are of prime interest. Different shapes and arrangement of fuel assemblies are being tested under operating conditions in reactors.

Incorporation of fissionable material into glass fibers for use as reactor fuels is being investigated. Mineral fibers, containing fissionable material with diameters up to $60\ \mu$, may be useful as fuel components for existing reactors. One advantage of siliceous fibers is the possibility of developing simplified methods for reclaiming unspent fuel and fission products. Operations included in the investigation are fiber preparation, with careful control of composition; temperature range of operation; resistance to reactor environment; type of fiber; physical testing; and radiation properties of the glass fibers.

Utilization of U^{233} as reactor fuel is desirable. This fissionable metal, obtained from neutron bombardment of thorium, is both an alpha and a gamma emitter. Fabrication of fuel elements from U^{233} will require, for personnel safety, remote controlled operations in shielded, sealed areas. Such an attractive energy source must be used. Techniques for producing fuel from U^{233} are now being investigated.

2.3 Fuels for High-temperature Operation

The possibility of utilizing high temperatures in nuclear reactors has led to an investigation on high-operating-temperature reactors. Temperatures in the range 2500 to 3000°F can be obtained, these temperatures being the surface temperatures of the nuclear fuel core. A gas coolant (helium was selected for design purposes) is assumed to be the heat-transfer medium.

A basic problem is that of developing fuel elements that will function under these conditions. Design parameters for such fuel have been established. These are summarized as follows:

1. Low neutron absorption cross section
2. Mechanical strength to withstand thermal gradients, internal gaseous fission products buildup, differential thermal expansion of components, and external stresses
3. Retention of fuel material and fission products
4. Thermal, chemical, and radiation stability, with no diffusion of core, cladding, or coolants
5. Good thermal conductivity
6. Ease of fabrication and reprocessing

Programs establishing tests for evaluating materials considered as suitable reactor fuel for operation under stated conditions are under way. Data developed indicate that dispersions of uranium compounds in graphite or in refractory metal compounds may be satisfactory core material. Fuel cladding by metallic carbides or by iron-aluminum binary alloys is being investigated.

2.4 Radiation Damages to Fuel

Damage to nuclear fuels from neutron bombardments and formation of fission products remains the most critical area in the efficient, economical operation of reactors. The tendency of uranium to large dimensional distortion under irradiation above 450°C is known to all nuclear scientists. To prevent dimensional changes, heavy cladding, heat-treatment, vented fuel elements, binary and ternary alloys, compounds, dispersions, and many other methods of attack have been used. An intensive program on determining irradiation damage to all types and configurations of reactor fuel is in effect.

Short- and long-term exposures of fuel to reactor fluxes are made. The design and test of experimental equipment for obtaining exact data on burn-up, temperature, total flux, and dimensional changes of samples are constantly being improved.

Postirradiation studies, to compare calculated and actual burn-up, are pursued intensely. Full-sized fuel assemblies of novel design, improved fuel, and unusual operating characteristics are manufactured and run under careful control. After removal from the reactor, these assemblies are studied, measured, tested, and evaluated for use as reactor core loadings.

2.5 Basic Engineering Studies on Fissionable and Fertile Materials

Studies to obtain scientific metallurgical data on fissionable and fertile elements, alloys, and compounds are being made. In particular, the physical properties of uranium, plutonium, and thorium are being studied over an extended range of temperature. Physical constants, diffusion of gases, corrosion in liquids and gases, temperature dependence of physical properties, and other like data are being determined in experiments on high-purity material.

Complete binary- and ternary-alloy phase diagrams are required; an investigation on $UTa_{10}C_4$, believed to be very high melting, has started.

The phenomenon of why uranium worked in the high alpha phase sometimes has good radiation stability is an oddity that warrants the investigation now under way.

3 METALS, ALLOYS, AND MATERIALS

Parallel to the development of fuel elements, a program to investigate properties of materials for use with fuel elements is in effect. The program consists of development of metals and alloys for use as fuel cladding; research on alloys for high-temperature use; physical and mechanical properties of materials over a broad temperature range; corrosion of materials under reactor conditions; and radiation damage studies on materials. All phases of the program contribute to an understanding of materials that are of interest to reactor engineers.

Programs of study and research on beryllium, zirconium, hafnium, niobium, and the rare earths are under way. Properties of these metals and their alloys are studied to enable their effective utilization in reactor construction.

A testing laboratory in which the mechanical properties of metals and alloys can be determined under any gaseous or liquid environment is being operated at one of the AEC laboratories.

4 COMPONENTS AND EQUIPMENT

Reactor system malfunctioning in some degree has been attributed to failure or unreliable operation of standard equipment and components. Research aimed at modifying commercial items for reactor use or developing new types of equipment has demonstrated that equipment more reliable in reactor operation may be obtained. Development of this program has produced pumps, valves, gaskets, heat exchangers, compressors, piping, and thermocouples.

To demonstrate the feasibility of producing heat exchangers of duplex tubing and header material, a 20-tube exchanger has been constructed. The composite tubing was of an Inconel-stainless-steel duplex and was joined into a duplex header by a combination of welding and brazing. Based on this a study of the production of duplex tubing of refractory metals and the construction of duplex heat-exchanger systems is a very meaningful research project.

Programs related to the compatibility evaluation of materials rubbing together in high-temperature liquid metals have been complicated by parameters (surface speed, roughness, load, friction, surface configuration). Design engineers working with problems on pump seals, shaft bearings, and valve stem guides are faced with the need to design around these problems. A basic research project to determine the compatibility of materials rubbing together non-hydrodynamically in high-temperature sodium is under investigation to obtain a better understanding of restrictive parameters. Information obtained will be related to the design of reactor components for sodium-cooled reactors.

No data are available for the design of equipment for compressing helium at 2500°F. No information exists on the operational characteristics of a piping system containing molten salts at a temperature several hundred degrees above solidification. Research to determine these data has been initiated.

Included in this area of research are investigations on the development and construction of equipment that may be operated remotely in highly contaminated areas or under high-inten-

sity radiation. Alpha-gamma facilities, viewing systems, electronic manipulators (the forerunner of the self-repairing robot), hoods, shielding—all these items are being designed, built, and improved.

5 CONTROL RODS

A comprehensive study of reactor physics, metallurgy, instrumentation, and engineering testing on reactor control systems is being developed. The program is a cooperative undertaking by Reactor Physics and Metallurgy. The studies are not aimed at specific reactor concepts but are designed to obtain a sound general knowledge of control-rod requirements, properties, and operational characteristics over the neutron spectrum from thermal- through epithermal-energy ranges for all types of reactors.

The scope and method of development of the program may be summarized as follows:

1. A survey of the data and information developed in previous control system studies.
2. Reactor physics studies and computations to prepare nuclear specifications for control materials. These computations will establish nuclear constants, cross sections, and other nuclear data, and will determine which data are available and which must be obtained to make a complete study.
3. From nuclear specifications materials that are promising as control materials will be selected, and tests will be prepared to determine the control worth of these materials under reactor conditions.
4. From the reactor physics computation tests, metallurgical specifications, including composition of materials, will be derived.
5. Based on the specifications developed under the studies, material will be obtained and fabricated into samples for subsequent tests, i.e., (a) composition and form of material will be determined from physics studies and will be prepared by best metallurgical techniques and (b) tests of fabricated samples before and after irradiation in a reactor will be made. These tests will include but not be limited to physical properties, corrosion, structural strength and integrity, burnout of control material, and control worth. These tests are designed to check physics calculations, fabrication techniques and processes, and changes in material under reactor conditions and to make corrections and changes in specifications.
6. Construction and operation of full-sized experimental control rods in reactors to obtain the engineering data necessary for use in reactor control systems.

6 PRODUCTION TECHNIQUES

A field of research and development usually incorporated into other programs is investigated as a separate area—the development of techniques for improving the production, purity, and testing of metals, alloys, and materials.

Design and development of melting equipment for reactive and toxic metals to obtain the maximum safety of operation; casting techniques for the continuous casting of alloys; more efficient, dependable fabrication of fuel elements; electrorefining of metals to ensure high purity; economical recovery and reuse of scrap—all these projects are being explored.

Nondestructive testing of materials, fabricated fuel elements, and reactor components is of concern in the nuclear field and is being supported.

Studies of the effect of high pressure and high temperature (1,000,000 psi and 3000 to 4000°F) on the production of materials of superior high-temperature properties are being made. Efforts are directed toward obtaining more stable fuel material and also toward understanding the effect of pressure and crystal physics. Initial experiments have been on the evaluation of the effect of pressure on the reaction of UO_2 with metal oxides. Oxides were selected because they are thermodynamically the most stable compounds in the anticipated temperature range and because their normal pressure-temperature behavior is well understood.

Pressure bonding, because of its adaptability, is fast becoming one of the most important fabrication processes for reactor components. Unit parts can be produced, and in some cases entire subassemblies may be clad and joined in one operation. Dimensions may be controlled exactly.

A basic understanding of the pressure bonding process is needed. The process is being approached from several viewpoints. When possible a mathematical model is constructed and used to predict results for specific materials and bonding parameters. Correlations are made with experimental results to determine the validity of the mathematical model. Objectives are to establish sufficient knowledge of the bonding process to predict the desired surface treatment, range of temperature, pressure, and time required for bonding in terms of the materials to be bonded.

ACKNOWLEDGMENTS

All contractors on the metallurgy programs of the Division of Reactor Development have contributed so greatly to all areas discussed in this paper that it is impossible to distinguish and point out specific organizations.

Electronic Welding of Metals

By J. A. STOHR

Commissariat à l'Energie Atomique

The methods of production, acceleration, and focusing of electrons are well known, and numerous applications have been made. Thus, it is easy to produce an impact area of fixed dimensions on an object placed in the path of an electron beam. On that area an amount of energy would be dissipated, depending on the number of electrons (current intensity) and their acceleration potential.

If the impact area along a line corresponding to the line of separation of two pieces of metal to be welded is displaced, it is possible to fuse the metal along this line and thereby obtain a continuous weld identical to that obtained with an argon- or helium-arc welder or an oxyacetylene torch.

The unit power obtainable, expressed in watts per square centimeter, with such an apparatus is considerable, and widely differing types of welds can be made.

In the welding of very thin pieces, it is possible to produce a point of impact of 0.1 mm^2 without difficulty, assuring a welding precision not obtainable with the argon arc, helium arc, or torch. Finally, since the welding is done in a vacuum, any oxidation or deterioration of the material is prevented.

In welding thick pieces of metal, it is possible to produce a considerable energy dissipation on an impact area of 6 to 8 cm^2 , e.g., 5×10^4 watts.

In all cases the localization of the energy and the use of a vacuum permit improvements in welds not obtainable by other methods. In the case of refractory metals (such as tungsten, molybdenum, and tantalum) or easily oxidizable metals (such as zirconium, beryllium, and uranium), the results obtained are remarkable.

1 LIMITATIONS OF THE METHOD

The extent to which it is possible to dissipate energy on the impact surface depends on the ability to accelerate the electrons, i.e., the potential between the electrodes. The maintenance of this potential is not possible if any ionization occurs. The ionization depends, in this case, on the probability of collisions of molecules or atoms of vaporized metal with the electrons provided by the cathode. For a given geometry it depends mostly on the nature of the metal and the size of the impact area.

For a given temperature the melting point, e.g., the quantity Q of metal vaporized per unit area, is

Metal	$Q, \text{ g/cm}^2/\text{s}$	$\theta, ^\circ\text{C}$
Al	$<10^{-8}$	660
Zr	2×10^{-6}	1,750
Ta	$1.4 \text{ to } 1.3 \times 10^{-5}$	2,996
W	1.4×10^{-4}	3,382
Be	4.4×10^{-5}	1,280
Mg	$>10^{-3}$	650

The quantity QS (where S is the area of the point of impact) will define the ionization probability in the path of the electrons, this probability increasing as we approach the point of impact.

In the case of metals (such as magnesium) which yield a very large quantity of metallic vapor, interruption of the anode current assures, with a convenient speed of displacement, a weld at successive points overlapping to prevent the setting up of an arc and accomplishes the electronic weld (see Fig. 1).

Fig. 1—Use of the current chopper.

2 DESCRIPTION OF AN ELECTRON WELDING APPARATUS

Figure 2 shows a welding apparatus that has been used mostly for tube closures.

The equipment consists of a chamber evacuated by a backing pump and a condensation pump and a valve system permitting all the necessary connections between vacuum chamber and pumps.

The pieces to be welded are placed on a mandrel operated by a variable-speed motor; the height of the mandrel is controlled by a gear rack operated by a small motor. Above this piece is an electron-emitting cathode, made up of a tungsten filament and a focusing piece which controls the potential.

A high-voltage rectifier, a current chopper, and a regulating stand feed the welder and control the various welding parameters (Figs. 3-4).

Figure 5 shows some equipment including a cylindrical device that permits 30 consecutive welds without breaking the vacuum.

Figure 6 shows an apparatus used for welding sheet metal and tubes along a generatrix.

3 SOME TYPES OF WELDING MADE POSSIBLE

Figure 7 shows the preparation for welding tube closures for either vertical or horizontal bundles.

Figure 8 shows the preparation for welding sheet metal in a line, one with a metal wire acting as a filler and the other using raised edges. Welding has been done without difficulty on some sheet metal simply brought edge to edge without special preparation.

Figure 9 shows an arrangement for closing a box by the use of a small ball put in place after evacuation and melted.

It is noteworthy that the tube closures in Fig. 7 permit placement as well as sealing under vacuum.

ELECTRONIC WELDING OF METALS

Figure 2

Figure 3

Figure 4

ELECTRONIC WELDING OF METALS

Figure 5

Figure 6

ELECTRONIC WELDING OF METALS

SHAPES OF CAP FOR LATERAL WELDING WITH AND WITHOUT CHAMFERED EDGE

Fig. 7—Some types of welding of fuel elements.

(a)

(b)

Fig. 8—Two methods of welding. (a) Intermediate rod, acting as metal filling. (b) Special design edges.

ELECTRONIC WELDING OF METALS

Figure 9

Thermopneumatic Cladding

By M. GAUTHRON

Commissariat à l'Energie Atomique

The principle of hydraulic cladding is well known. Briefly recalling this principle: the uranium is enclosed in its sheath with a clearance that is then reduced by means of external oil pressure (Fig. 1).

This method mainly permits the cladding of assemblies with complex cross sections (finned tubes) and the fabrication of mountings (e.g., the mounting of the claddings on the uranium of the EL-2 reactor).

Thermopneumatic cladding is based on the same principle but uses a hot gas as the compressing fluid.

Figure 1

A diagram of the installation is given in Fig. 2.

Bonding of Magnesium Cladding to the Uranium of Fuel Elements for Reactors Cooled with Carbon Dioxide Under Pressure. The theory of this operation is studied in detail in the discussion by Ringot concerning the fuel elements of the EL-2 reactor. It is a matter of applying the sheath of magnesium to the uranium at 400°C. Since the magnesium is about twice as dilatible as the uranium, the clad will be reduced to the fuel at lower temperatures. This is done industrially at the relatively low pressure of 40 kg/cm² at 400°C, following the cycle represented in Fig. 3.

Figure 4 is a photograph of the apparatus used in fabricating fuel elements for the Marcoule reactors.

Cladding of a Hollow Bar of Uranium Too Thin To Withstand the Pressure of Hydraulic Cladding in the Cold. This is the case for the fuel elements of the first loading of the EL-3 reactor; a drawing is given in Fig. 5. The cladding has to be done at a temperature such that the aluminum sheath has almost completely lost its mechanical resistance whereas the uranium still has a large part of its own strength. In Fig. 6, the region of practical utilization is represented by the cross-marked area.

THERMOPNEUMATIC CLADDING

Figure 2

Figure 3

Fig. 4—Hot cladding apparatus of the SACM at Annecy.

THERMOPNEUMATIC CLADDING

Figure 5

Figure 6

Fig. 7—Cladding for EL-3.

THERMOPNEUMATIC CLADDING

Fig. 8—Pleated bar.

Figure 9

Fig. 10—Swollen bar.

Fig. 11—Small cladder, 1000 kg/cm², 650°C.

The assemblies of the EL-3 reactor were clad at 400°C and 200 kg/cm² pressure in the machine shown in Fig. 7.

Application of an Aluminum Clad to a Small Bar with an Initial Diametral Clearance Between Uranium and Clad Too Wide To Withstand Hydraulic Cladding in the Cold Without Creasing. When one attempts to apply, by hydraulic pressure, an aluminum clad to a small bar of uranium with an initial clearance that is too wide, a longitudinal pleat is produced as shown in Fig. 8.

The initial diametral clearance that produces a failure may be called *j*. It can be seen from Fig. 9 that the maximum possible clearance increases considerably with the temperature.

Since the clearance anticipated in the fabrication of the assemblies for the EL-3 reactor can exceed 0.3 mm, cladding of these elements in the cold would have been impossible without changing the tolerances.

Detection of Large Leaks in Assemblies. Cladding with heat at high pressure affords an excellent method of detecting large leaks.

In effect it is only necessary to slowly raise the pressure in the apparatus so that the gas being used penetrates the cartridge between the uranium and the clad. Then, if it is violently decompressed in the hot state at the end of the procedure, the internal overpressure is enough to swell the clad at the weakest point. The photograph in Fig. 10 shows the results obtained on such a cartridge for the EL-3 reactor, after cladding at 400°C and 200 kg/cm² pressure.

Other Applications. It is interesting, for the other applications of this process, to go up to the highest possible temperature and pressure. Thus we hope that an apparatus furnishing a pressure of 1000 kg/cm² at 650°C will permit studies of fritting. A diagram of this equipment, which is under construction at Saclay, is given in Fig. 11.

To end this discussion with a view of the future, it is concluded that it is not perhaps impossible to bring about uranium-cladding diffusion on an apparatus with even greater performance.

SESSION II

Natural-uranium Metallic Fuel Elements

Casting and Fabrication of Natural Uranium

By F. L. CUTHBERT

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ABSTRACT

A general review is presented of the important and more critical aspects of technology involved in the casting and fabrication of natural uranium. The preparation of uranium metal suitable for melting stock to produce ingots or other uranium-metal shapes is discussed. Recent development work involved in vacuum-induction casting, centrifugal casting, and melting under a protective salt cover is described. Techniques involved in the preparation of uranium alloys by melting and involving not more than 2 per cent of the alloying ingredient are presented.

The fabrication of natural uranium fuel elements by rolling, swaging, and machining is described, along with the heat-treatment involved in these operations. The preparation of uranium-metal shapes utilizing powder-metallurgy techniques is also described.

1 INTRODUCTION

The suitability and performance in atomic reactors of natural uranium fuel elements depends to a great extent upon the casting and fabrication history of the metal in the element. However, the fuel-element design often dictates a particular process to the exclusion of others. In the last analysis the optimum process and composition for a fuel element of any design is that which provides the best reactor performance at lowest cost.

Considerable research and development effort has been expended to develop and improve casting and fabrication techniques applicable for natural uranium fuel elements of many designs and for many different types of reactors. It is the purpose of this paper to present some of the newest technology in this field.

2 CASTING

2.1 Preparation of Charge Material

The composition of the charge material or melting stock, which is related to the manner in which it is prepared, has been shown to be a very important factor in determining both the best casting technique and quality of casting obtained. Charge material might consist of one or more of the following: (1) derbies of uranium metal resulting from the direct reduction of uranium tetrafluoride with calcium or magnesium, (2) scrap fuel elements not meeting metal quality or dimensional specifications, and (3) fabrication scrap consisting of rod ends, extrusion butts, briquetted machine turnings, etc.

Uranium derby metal obtained by the reduction of uranium tetrafluoride with calcium or magnesium frequently contains some occluded slag, which most often is concentrated at the

surface. This slag, if present, should be removed by chipping or pickling in order to provide good clean charge material. Under some circumstances it has been found advantageous to leach the derby material with boiling water before pickling in order to reduce the amount of uranium metal dissolved in the nitric acid pickle liquor. The hot-water leach aids in removing the magnesium or calcium fluoride, thus decreasing the length of time the derby must remain in the acid.

Fabrication scrap is commonly contaminated with furnace salts, lubricants, and uranium oxide. These contaminants are best removed by degreasing (in the case of machine coolants) or by pickling (for furnace salts or uranium oxides). Some slight degree of contamination can be handled by varying the vacuum melting cycle, but, as in all metal melting practice, the charge material should be as clean as possible.

2.2 Vacuum-induction Casting

Most uranium metal is melted and cast in vacuum-induction furnaces. A typical furnace used for the purpose is illustrated in Fig. 1. Furnace pressures of 500 μ or less are sufficient. Graphite is most frequently used for both the crucible and mold material; however, under some special circumstances, other refractories have been used with success. Graphite, as a mold material, has the advantage of being easily machined.

Fig. 1—Schematic drawing of a vacuum-induction furnace.

A practical melting cycle is one that heats the charge to the liquid state as rapidly as possible; further rapid heating to a temperature of about 1430°C is desirable, yet it must be slow enough so that the melt does not boil violently. The melt may then be held at this super-heat temperature for 20 to 30 min prior to tapping to effect separation of the insoluble compounds.

Only those metallic contaminants that have a high vapor pressure at temperatures less than 1430°C are removed in the melting of the charge, whereas the greater part of the non-metallic contaminants may be controlled by the mechanics of the melting process. The two major nonmetallic impurities are nitrogen and carbon. The derbies are the prime carriers

of nitrogen, whereas the graphite crucible and the scrap used in the charge are the primary sources of carbon.

Nitrogen levels in the ingots can be controlled by the liquation of the uranium nitrides to the surface of the melt. The nitrides are entrapped in the crucible skull or in the top ingot crop, which may be scrapped.

Carbon pickup is associated with the rate of heat input, temperature, and time. Carbides may be liquated, although the apparent rate of carbide removal is dependent upon the effectiveness of the crucible coating in preventing attack on the crucible. In addition to nitrogen and carbon, other nonmetallic inclusions in ingot metal, such as oxides, hydrides, and fluorides, are controlled by the degree of vacuum and by the length of the melting cycle.

Table 1 shows the effect of charge composition and melting cycle on the yield of fuel elements (slugs) meeting a given standard of metal quality with respect to inclusion content and chemical composition.

Table 1—EFFECTS OF CHARGE AND FURNACE CYCLE ON QUALITY

Cycle	Type of charge	Relative yield, %
120 kw to 1400°C; 50 kw for 20 min	100% chipped derbies	93
120 kw to 1400°C; 50 kw for 20 min	100% pickled derbies	93
120 kw to 1400°C; 50 kw for 20 min	20% briquettes; 80% chipped derbies	91
120 kw to 1400°C; 50 kw for 20 min	50% chipped derbies; 20% briquettes; 30% solid scrap	78
120 kw to 1400°C; 50 kw for 20 min	50% pickled derbies; 20% briquettes; 30% solid scrap	92
100 kw to 1400°C	Unpickled rolling mill scrap	64
100 kw to 1400°C; power off 10 min	Unpickled rolling mill scrap	81
100 kw to 1370°C; power off 10 min	Pickled rolling mill scrap	93
100 kw to 1400°C	Reject slugs	80
100 kw to 1400°C; power off 10 min	Reject slugs	87
100 kw to 1400°C	Briquettes	82
100 kw to 1400°C; 50 kw for 20 min; power off 10 min	Briquettes	93

2.3 Centrifugal Casting

Centrifugal casting has been used to produce depleted, normal, and slightly enriched uranium and uranium alloy (zirconium, silicon, and molybdenum) fuel elements. Fuel elements for the Sodium Reactor Experiment (SRE) have been cast in this manner with good results. Cost studies for development purposes, comparing three methods (rolling, extrusion, and centrifugal casting), show an economic advantage for the centrifugal route. This route has the advantage of a higher metal yield from charge to finished fuel element and also eliminates the necessity of more costly primary fabrication facilities, thereby allowing an additional significant saving.

Figure 2 is a schematic diagram of a centrifugal machine that has been used in casting work. Shown are the furnace shell, crucible shell, stopper rod, base refractory, mold chambers, rotor, and drive mechanism. Figure 3 is a photograph of an experimental furnace and its associated parts.

Three different sleeve materials used to line the mold cavities have been used for casting: graphite, copper, and stainless steel. Graphite is somewhat less subject to erosion.

Fig. 2—Schematic diagram of a centrifugal casting machine.

Fig. 3—Exploded view of an experimental centrifugal casting furnace.

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Table 2—DATA FROM CENTRIFUGALLY CAST HEATS

Composition	Alloy addition, wt. %	Pour temp., °C	Mold speed of pour, rpm	Pressure at pour, μ	Yield, %*	Density, g/cm ³
Uranium		1460	25	43		18.9
		1490	25	47		
Uranium-zirconium	2.0	1340	200	11	78.8	18.27
		1370	25	14	75.7	
		1480	25	30	77.7	
		1540	200	17	78.2	
Uranium-silicon	0.5	1300	25	7	78.1	18.33
		1320	200	18	85.4	
		1480	25	95	82.7	
		1480	200	14	81.1	
Uranium-molybdenum	1.2	1340	25	12	86.7	18.68
		1340	200	11	80.5	
		1510	25	12	79.3	
		1510	200	13	81.4	

* Finished element per charge.

Table 2 presents data obtained for centrifugally cast fuel elements under varying conditions of pour temperature, mold speed, and vacuum.

Metallographic samples from several of the cast elements reveal structures as illustrated in Figs. 4 to 7. Fine-grain structures are evident in the cast alloy pieces. The inclusion content of the zirconium and silicon alloys is low, whereas the molybdenum alloy and the unalloyed elements show moderate counts.

Analytical data to show the degree of homogeneity obtained in the alloy castings are presented in Fig. 8. These results indicate no difficulty from segregation or nonuniformity.

2.4 Salt Melting

Some work has been done to demonstrate the feasibility of melting uranium in an open furnace under a protective salt cover. Such a process would be applicable as a means of recovering metal scraps such as machine turnings and saw chips that are normally not desirable as vacuum-induction melting stock.

Preliminary small-scale laboratory tests indicated the feasibility of this method of melting, and slightly larger scale tests confirmed the results. Table 3 presents data obtained in both the small and larger scale tests.

The furnace used for these tests was a 200-lb 50-kw Ajax tilt-pour unit (Fig. 9). A refractory liner of stabilized zirconia was prepared by ramming the zirconia around a 10½-in.-O.D. graphite crucible. The liner was sintered by slowly heating the crucible to a temperature of 1650°C and maintaining that temperature for 2 hr. After cooling, the crucible was removed, and any cracks in the refractory liner were patched. The crucible was coated with MgZrO₃ and was replaced inside the zirconia liner. Both bottom pouring and top-tilt pouring have been tried, with the latter appearing to be more successful.

In the melting of uranium under molten salt, the desired amount of blended salt (CaF₂-MgF₂) was first charged to the crucible, and a stabilized zirconia refractory lid was placed on the top. When the salt was completely molten (at 1260 to 1320°C), the metallic scrap was charged at a rate to maintain the temperature of the salt constant. When the crucible was filled, the heat was held at temperature for ½ hr. The molten metal was poured into a helium-purged mold.

The density of the metal obtained averaged about 18.90 g/cm³. Both the carbon and the nitrogen levels were reasonably low, being about 400 to 600 and 10 to 30 ppm, respectively.

Fig. 4—Uranium—2 per cent zirconium alloy.
(100 x.)

Fig. 5—Uranium—0.5 per cent silicon alloy.
(100 x.)

Fig. 6—Uranium—1.2 per cent molybdenum alloy.
(100 x.)

Fig. 7—Unalloyed uranium. (100 x.)

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Fig. 8—Analytical data of uranium alloys.

Table 3—SALT MELTING, EFFECT OF VARIATIONS

Type of scrap	Condition of scrap	Salt covering	Metal separation	Recovery of metal, %
Coarse turnings	Clean, slightly oxidized	CaCl_2	Good	90+
Fine saw chips	Degreased, slightly oxidized	CaCl_2	Fair	90+
Fine turnings	Degreased, slightly oxidized	CaCl_2	Poor	80
Coarse turnings	Clean, slightly oxidized	CaF_2 -1% MgF_2	Good	90+
Fine turnings	Degreased, slightly oxidized	CaF_2 -1% MgF_2	Good	90+

Fig. 9— Experimental tilt-pour induction furnace used for salt melting uranium scrap.

3 URANIUM ALLOYS

Many of the fuel elements being developed for power reactors require alloys of uranium with high-melting-point metals such as zirconium, molybdenum, and niobium. Such alloys may be made by vacuum-induction melting. Here the alloying element is introduced as fine powder to promote a high dissolution rate. Large particle sizes or pressed powder bars or pellets have been found to be less desirable because of their slower melting rate.

A stirring action in the crucible aids considerably in increasing the dissolution rate of the alloy and tends to keep the powder from floating to the top of the melt. All the alloy additions are much lighter than uranium. The stirring action also helps to promote homogeneity. Induction currents, thermal currents, degassing volatiles, mechanical stirring, and gas lancing are all means of accomplishing some degree of stirring.

The degassing of volatiles in the melt and mechanical stirring have been particularly effective in promoting alloying. Magnesium or calcium, carried with the derby metal and resulting from the reduction of uranium tetrafluoride with either magnesium or calcium, is a principal source of volatiles which, if present, through boiling will result in a stirring action. However, excessive occluded magnesium or calcium in the melting stock must be avoided to prevent the following undesirable effects:

1. Erosion of the protective crucible coating by the violence of the boiling action
2. Condensation of the metal vapors upon the elements of the vacuum gauge within the furnace
3. Electrical short circuiting across the turns of the induction coil by conduction through the metal vapors
4. Condensation of the vapors within the mold, ultimately causing blow porosity and other associated surface defects, as well as contamination of the uranium

Mechanical stirring has been used successfully. Materials of construction for the stirrer are critical. Both zirconium and graphite stirring elements have been used in developing uranium quaternary alloys.

Carbon pickup by the metal as a result of attack on the graphite crucible must be controlled. Two coatings found useful for this purpose are magnesium zirconate and a beryllia coating consisting of a mixture of beryllium oxide and beryllium sulfate. The magnesium zirconate coating has also been found effective in keeping the carbon pickup in normal uranium vacuum-induction melts at a low level, frequently at a level of less than 50 ppm.

Magnesium oxide or the magnesium zirconate coating mentioned above is often used to coat the mold; when the content of the alloying agent has been less than 2 wt. %, these coatings have been found satisfactory for most alloys.

Those practices used in normal uranium induction melting and casting in order to prevent pipe or porosity, keep contaminants at a minimum, and provide good cast surfaces also apply to alloying.

Table 4 presents data obtained in experimental alloying by vacuum-induction melting using the practices outlined above.

Table 4—VACUUM-INDUCTION MELTING TO PRODUCE URANIUM ALLOYS

Alloying agent	Crucible coating	Mold coating	Furnace cycle	Alloy analysis, wt. %	Carbon content, ppm
2 wt. % Mo powder (-80 mesh)	MgZrO ₃	MgO	50 kw for 200 min, pour at 1370-1400°C	2.15 (top) 2.03 (bottom)	100
2 wt. % Zr (ground sponge) (-20, +80 mesh)	MgZrO ₃	MgO	50 kw to 1480°C, then pour	2.17 (top) 2.08 (bottom)	70

A homogeneous quaternary Zr-Nb-Mo-U alloy was prepared, utilizing a mechanical stirrer of zirconium crystal-bar pieces clamped to a stainless-steel shaft, which passed through a vacuum seal provided in the top lid of the furnace. Ground zirconium-metal sponge, niobium-metal powder, and molybdenum-metal powder were blended prior to crucible charging and then added to the uranium in the crucible. By the use of 50-kw input power, the melt was brought to 1400°C; the stirrer was then lowered into the melt and was turned by hand for 10 to 15 sec. This was repeated at 10-min intervals until the melt was stirred three times. Excellent homogeneity was obtained, with an average zirconium content of 0.42 per cent (range, 0.34 to 0.49 per cent), an average niobium content of 0.10 per cent (range, 0.09 to 0.12 per cent), and an average molybdenum content of 0.23 per cent (range, 0.22 to 0.23 per cent). The melt was very fluid and offered no resistance to stirring. The final analysis indicated that no significant amount of zirconium was dissolved from the stirrer. The average carbon content was 80 ppm, the range being 55 to 120 ppm.

4 FABRICATION

4.1 Rolling

Considerable laboratory and pilot-plant development activity has been expended in the fabrication of uranium by rolling. Various roughing pass designs have been investigated, including square, diamond, rectangular, oval, and round. Billets of both square and round cross sections have been used.

Early work indicated that round billets with round pass shapes gave best results. It was also found that light reductions were most favorable but that even under these conditions the uranium heated up very quickly and had to be cooled frequently. Rolling temperatures were varied between 300 and 600°C, as well as rough rolling at 600°C followed by finish rolling at 300°C. The lower temperatures were considered because of reduced oxidation, superior surface finish, and closer dimensional control. The test work demonstrated that a low-temperature rolling (starting with approximately a 5-in.-diameter billet) was difficult in that suitable temperature control could not be maintained. Supplementary data to establish the roll separation force required for rolling cast uranium at temperatures of 250, 300, 400, 500, and 600°C was obtained. The data indicated that at 400, 500, and 600°C the average deformation resistance varies only slightly with the amount of reduction. However, at 300°C, the resistance to deformation increases significantly with increasing reduction.

Owing to friction, the rolling of uranium in the alpha phase results in a significant temperature rise of the material, particularly at high speeds. Attempts have been made to measure this rise by embedding a thermocouple in the starting piece. In this test, during the first five passes (58.7 per cent reduction) at 600°C, there was a 6 to 12°C temperature rise per pass. In the first seven passes (68.5 per cent reduction) at 300°C, there was a 35 to 44°C rise per pass.

Other work has been conducted utilizing various combinations of oval, diamond, square, octagonal, and bullhead pass designs in a rolling mill to break down ingots into billets suitable for finish rolling. A bullhead and box schedule normally used for the reduction of steel ingots was not satisfactory because the uranium would not stand up in the passes but rolled over and finned. Combinations of oval and square or oval, diamond, and bullhead passes also did not result in suitable reduction because of rather severe folding on the unsupported sides of the ingots in the oval passes.

One blooming schedule that did appear to give promising and satisfactory results was made by alternating bullhead passes with box passes. The box passes used differed from those normally used for steel ingots. They were narrower, had smaller side-wall angles, and had a radius on the bottom of the box. The steeper walls provided better support of the ingot during rolling, and the crown in the box pass resulted in the unsupported faces of the section going into the bullhead passes and particularly into the leader oval following the last box pass, being convex and less inclined to wrinkle or fold.

Finish rolling to rounds has been attempted using an oval-round pass schedule in both continuous mills and in manually fed merchant bar mills. Commercial tolerances of less than 10 mils have been obtained.

Alternative methods of heating have been attempted using various heating mediums. Heating in air normally results in excessive oxidation and scaling, with resulting varying temperatures. Molten lead and various salts also have been tried. The temperature pattern of the metal during rolling proved to be different for each medium. Tests at rolling speeds of 100 fpm showed that the metal temperature rose 110°C from a lead-bath heating temperature of 510°C and dropped 30°C from a salt-bath heating temperature of 590°C. Molten salts mixtures of 45 per cent Li_2CO_3 - 55 per cent K_2CO_3 and 25 per cent Li_2CO_3 - 75 per cent K_2CO_3 have been used with some success at temperatures ranging from 540 to 650°C. These salts have been used both to heat ingots prior to rolling and to bring up their temperature during the rolling.

4.2 Swaging of Uranium

Rotary swaging has been utilized as a method of fabricating uranium. In rotary swaging, rod or wire (which need not be of circular cross section) is fed into a tapered orifice formed by grooves in the faces of two dies. These rotate about the rod or wire and hammer the material by a series of rapid blows to produce a circular cross section. It is generally accepted that the most successful results from swaging have been realized with die acceptance angles of 10 or 12 deg maximum.

Uranium has been swaged cold, warm, and hot, the hot swaging involving temperatures ranging into the high alpha phase (650°C). Heating of the uranium prior to swaging has been accomplished in resistance-wound vacuum furnaces, as well as in oil, lead, and salt-bath mediums.

Cold swaging of uranium has been utilized to produce excellent rod surfaces, and rod-diameter tolerances of ± 0.005 in. have been attained on a 0.600- to 0.250-in.-diameter rod. On this size rod, reductions of up to 35 per cent per pass and total reductions of up to 58 per cent (without intermediate anneals) have been attained on a semiproduction basis. Swaging of a 0.810-in.-diameter rod for prestraining experiments has substantiated the fact that single-pass reductions of 30 to 15 per cent are entirely possible, although reductions of 10 to 15 per cent are more commonly used. During reductions of 30 per cent, uranium has a tendency to heat up considerably. Work on smaller diameter rods (0.250- to 0.017-in. diameter) has indicated that total reductions beyond 46 to 55 per cent result in central cracking of the specimen. These central cracks have been associated with overworking or work-hardening of the uranium specimen. Annealing at 650°C for 15 min after 46 per cent reduction has permitted further working of the specimen. Examination of alpha-rolled rod that had been subsequently cold swaged to 58.2 per cent reduction revealed an increase in Rockwell G hardness from 76 to 96 and improved tensile properties. In addition, the swaging produced a preferred orientation of the poles of the (0 0 2), (2 0 0), and the (1 1 3) planes which had a uniform radial distribution. A lubricant consisting of 75 per cent lard oil and 25 per cent kerosene has been commonly used during cold-swaging operations.

Warm swaging at temperatures of 300 to 450°C has been used as a means of reducing uranium at generally higher rates of deformation than are possible by cold swaging while minimizing the amount of oxidation experienced during hot swaging. Oils are often used for preheating rods at warm-swaging temperatures. At warm-swaging temperatures (below 450°C), deformation of uranium is mainly due to twinning processes. At temperatures above about 450°C, a slip system operates. Final reductions of 83 per cent have been attained by swaging at 300°C.

Hot swaging of uranium at temperatures up to 650°C (which represents the high alpha phase) has been quite successful. Uranium is considerably more plastic during hot swaging than during warm or cold swaging, and as a result greater reductions per pass are possible. In addition, since the uranium specimens are continually recrystallized during working at high alpha temperatures, intermediate anneals are not necessary. Oxidation of the uranium during hot swaging is much more rapid than that at cold- or warm-swaging temperatures. One approach that is used to help alleviate this problem is copper jacketing of uranium prior to swaging. Such a method has been used with success to the point where failure of the copper jacket occurs at 25 to 50 per cent reduction, after which the uranium is cold- or warm-worked to final dimensions.

5 HEAT-TREATMENT

The temperature and mechanical history of uranium metal affect both the grain size and the preferred orientation and consequently influence the stability of the fuel element during irradiation.

Heat-treating of uranium is done primarily to achieve random orientation of the grains and thereby obtain optimum dimensional stability. The beta heat-treatment consists in heating

into the beta phase (between 660 and 770°C) until the uranium has transformed to the beta crystal structure and then air cooling or quenching to room temperature. Although this heat-treatment does not give a completely random orientation, the slight final texture (residual or induced) does not seemingly present a problem. However, the control of grain size during beta heat-treatment has been shown to be necessary if dimensional stability is to be obtained; in fact, the grain coarsening that occurs during heat-treating is said to be a shortcoming of that process.

Practical problems in the heat-treatment of uranium are those that are common to the heat-treating of any metal. Additional problems are due to the high monetary value of the metal. Criticality problems may also arise.

The following presents information on the choice of heat-treating mediums: The very early work on the selection of a salt composition to be used in fabricating uranium indicated that the major requirement for the salt was a low corrosion rate of the uranium. The study of the corrosion of uranium by molten salts soon disclosed that an economic mixture that caused little corrosion was the eutectic composition of 46:54 wt. % $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3$.

The use of the mixed carbonate salt as a beta heat-treating medium raised two problems: (1) increases in the alkalinity of the bath, causing high rates of corrosion on immersed stainless-steel electrodes, and (2) an increase in the hydrogen content of the treated uranium.

Both these effects could be detrimental, the former by reason of rapid disintegration of parts by intergranular corrosion and the latter by causing hydrogen gas to evolve from the fuel element during subsequent canning operations. Hydrogen is evolved by the uranium when the compound UH_3 undergoes thermal decomposition above 440°C, even when under 1 atm of hydrogen. Inasmuch as the equilibrium content of hydrogen in uranium in the beta phase is approximately twice the equilibrium content in the alpha phase, beta transformed metal can evolve hydrogen gas when it is held in the high alpha temperature range. The hydrogen may cause poor bonds during the canning of the fuel element.

Extensive development has been directed at improving the carbonate mixture to prevent both the difficulties mentioned above. Sparging the salt with carbon dioxide effectively reduces both the intergranular corrosion and the amount of hydrogen picked up by the uranium.

Concurrently with the studies on the carbonate salt, attention was directed to developing new salt compositions. In a preliminary evaluation of new salt compositions, the following comments were made on various systems:

1. Sulfates—the uranium was rapidly dissolved.
2. Bromides—there was an excessive fuming of these compounds.
3. Fluorides—at the heat-treating temperatures, the salts were too reactive with the uranium metal.
4. Phosphates and silicates—these salts were very hygroscopic and very viscous.
5. Chlorides and carbonates—these showed some promise.

A preliminary survey of 17 salts was made using 6-g buttons of uranium for test specimens. Table 5 lists the compositions of salts and the weight losses obtained when the samples were heat-treated in these salts for 13 min at 730°C. The table shows separately the corrosion loss at each of the three absolute humidity ranges that were investigated (<10, 10 to 25; and >25 but not greater than 80 mm Hg partial pressure of water vapor).

Table 6 shows the hydrogen content of the uranium samples after heat-treatment in the same salt compositions. It also gives a separate listing of hydrogen content for each of the three separate absolute humidity ranges.

As a result of this study it was shown that favorable properties were obtained with the compositions 50:50 wt. % KCl:NaCl and 50:50 wt. % $\text{KCl:Na}_2\text{CO}_3$. These two salts were extensively evaluated by direct comparison with the 46:54 wt. % $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3$ and with the other eutectic of the system that occurs at 25 wt. % Li_2CO_3 . In this evaluation rod sections 1.4 in. in diameter were used, and attention was paid to the 25:75 eutectic mixture of the carbonate because of its lower cost. The specimens were immersed in the molten salt for 11 min at 730°C and then were quenched in water.

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Table 5—AVERAGE WEIGHT LOSS* OF URANIUM FOR THREE LEVELS OF ABSOLUTE HUMIDITY

Salt composition, wt. %	Average weight loss, %		
	<10 mm Hg	>10 to <25 mm Hg	>25 to <80 mm Hg
	P _{H₂O}	P _{H₂O}	P _{H₂O}
44 Li ₂ CO ₃ -56 Na ₂ CO ₃	0	3.4	0
44 Li ₂ CO ₃ -56 K ₂ CO ₃	1.5	2.0	1.3
50 KCl-50 Na ₂ CO ₃	2.8	3.4	3.5
24 NaCl-28 KCl-48 BaCl ₂	0.07	0.69	0
22.5 NaBr-77.5 LiBr	0	3.1	0
50 KCl-50 NaCl	3.4	0.16	2.0
46.2 LiCl-53.8 KCl	0.1	0.75	1.0
32.8 NaCl-67.2 CaCl ₂	1.0	1.0	2.1
21 NaCl-31 BaCl ₂ -48 CaCl ₂	0	1.3	0
25 NaCl-25 LiCl-50 KCl	2.5	0.08	2.6
30 LiCl-70 KCl	0.1	0.06	0.3
33 NaCl-33 KCl-33 Na ₂ CO ₃	2.8	0	3.1
19 NaCl-34 CaCl ₂ -47 KCl	0.21	0.26	0.4
25 Li ₂ CO ₃ -75 K ₂ CO ₃	1.95	1.75	1.85
15 Li ₂ CO ₃ -37 K ₂ CO ₃ -48 Na ₂ CO ₃	3.1	0	2.0
50 Na ₂ CO ₃ -50 K ₂ CO ₃	0	0	0

* Samples were heat-treated for 13 min at 730°C.

Table 6—HYDROGEN CONTENT OF URANIUM AFTER HEAT-TREATING IN VARIOUS SALTS AT THREE LEVELS OF ABSOLUTE HUMIDITY

Salt mix, wt. %	Hydrogen content, ppm		
	<10 mm Hg	>10 to <25 mm Hg	>25 to <80 mm Hg
	P _{H₂O}	P _{H₂O}	P _{H₂O}
44 Li ₂ CO ₃ -56 Na ₂ CO ₃	0	8.0	0
44 Li ₂ CO ₃ -56 K ₂ CO ₃	7.8	8.5	11.9
50 KCl-50 Na ₂ CO ₃	2.3	3.2	4.4
24 NaCl-28 LiCl-48 BaCl ₂	7.0	4.1	0
22.5 NaBr-77.5 LiBr	0	2.2	0
50 KCl-50 NaCl	3.0	2.1	7.0
46.2 LiCl-53.8 KCl	7.5	6.4	6.5
32.8 NaCl-67.2 CaCl ₂	5.1	4.7	4.5
21 NaCl-31 BaCl ₂ -48 CaCl ₂	0	4.0	0
25 NaCl-25 LiCl-50 KCl	9.4	7.6	5.7
30 LiCl-70 KCl	3.4	5.1	9.6
33 NaCl-33 KCl-33 Na ₂ CO ₃	2.7	0	4.2
19 NaCl-34 CaCl ₂ -47 KCl	11.7	12.2	0
25 Li ₂ CO ₃ -75 K ₂ CO ₃	5.0	7.0	13.4
15 Li ₂ CO ₃ -37 K ₂ CO ₃ -48 Na ₂ CO ₃	6.6	0	12.0
50 Na ₂ CO ₃ -50 K ₂ CO ₃	6.7	0	0

Table 7—COMPARISON OF TWO HEAT-TREATING SALTS

25:75 wt. % $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3$		50:50 wt. % KCl:NaCl (contaminated with 6.5 wt. % of 25:75 $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3$)		
Absolute humidity, mm Hg	Hydrogen pickup, ppm	Absolute humidity, mm Hg	Hydrogen pickup, ppm	Uranium weight loss, %
12.0	1.00	10.4	0.23	0.18
12.0	0.67	11.2	0.36	0.16
12.5	1.08	13.4	0.29	0.18
13.0	0.98	9.7		0.21
13.0	0.95	11.2		0.15
13.0	1.13	13.0		0.17
11.5	1.41	15.7	0.34	0.15
11.5	0.75	15.1	0.25	0.20
12.0	1.85	8.1	0.36	0.18
13.0	0.78	8.3	0.37	0.18
13.0	1.00	9.8	0.27	0.18
16.0	1.17	8.7	0.49	0.20
16.0	1.05	10.2	0.25	0.13
15.5	1.07	10.6	0.13	0.17
		19.6	0.54	0.10
		15.7	0.26	0.12
		15.4	0.27	0.11
		14.2	0.25	0.30

Table 7 shows the results of this test comparing the 25:75 wt. % carbonate mixture to the 50:50 wt. % KCl:NaCl composition contaminated with 6.5 wt. % of the 25:75 carbonate mixture.

In the same study the composition 50:50 wt. % $\text{KCl:Na}_2\text{CO}_3$ was compared to the 50:50 wt. % KCl:NaCl . Hydrogen pickup and corrosion data are shown in Table 8. Here the KCl:NaCl showed superiority over the $\text{KCl:Na}_2\text{CO}_3$.

In summary the data of Tables 5 to 8 show that the best salt from the standpoint of hydrogen pickup is a mixture of 50:50 wt. % KCl:NaCl . This salt also shows favorable properties for minimizing the loss of uranium.

Table 9 compares the corrosion rates of various steels when immersed in 50:50 wt. % KCl:NaCl and in 25:75 wt. % $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3$ mixtures at 730°C for 240 hr.

6 MACHINING

The properties or characteristics of uranium which make its machining somewhat of a unique operation in contrast to other metals are

1. Low ductility
2. Low tensile strength
3. High work-hardenability
4. High density
5. High abrasiveness
6. High pyrophoricity
7. Low heat conductivity
8. Toxicity

With respect to several of these characteristics, uranium machines similarly to a 300-series stainless steel. However, the combination of all eight characteristics necessitates special considerations.

CASTING AND FABRICATION OF NATURAL URANIUM

Table 8—HYDROGEN PICKUP AND CORROSION DATA FOR
EXPERIMENTALLY HEAT-TREATED ROD SECTIONS

Composition of salt	Hydrogen pickup, ppm	Absolute humidity, mm Hg	Uranium weight loss, %
93.5% (50 KCl-50 NaCl)	0.51		0.20
6.5% (50 KCl-50 Na ₂ CO ₃)	0.21		0.13
	0.40		0.19
	0.37		0.22
	0.40		0.20
	0.57		0.13
Average	0.41		0.18
93.5% (50 KCl-50 NaCl)	0.42	7.37	0.23
6.5% (25 Li ₂ CO ₃ -75 K ₂ CO ₃)	0.66	7.37	0.21
	0.50	8.69	0.21
	0.67	8.69	0.20
	0.92	12.98	0.20
	0.44	12.98	0.23
Average	0.60		0.21
93.5% (50 KCl-50 NaCl)	0.52	7.29	0.22
6.5% (44 Li ₂ CO ₃ -56 K ₂ CO ₃)	0.47	7.29	0.20
	0.37	7.44	0.22
	0.48	7.44	0.26
	0.29	7.34	0.23
	0.25	7.34	0.21
	0.36	7.34	0.18
	0.20	7.34	0.18
Average	0.37		0.21
93.1% (50 KCl-50 Na ₂ CO ₃)	0.73	5.59	0.20
6.5% (44 Li ₂ CO ₃ -56 K ₂ CO ₃)	1.09	5.59	0.16
	0.95	8.23	0.18
	1.10	8.23	0.16
	0.83	6.05	0.25
	0.49	6.05	0.20
Average	0.87		0.19
93.5% (50 KCl-50 Na ₂ CO ₃)	0.97	7.14	0.19
6.5% (25 Li ₂ CO ₃ -75 K ₂ CO ₃)	0.62	7.14	0.28
	0.61	6.68	0.23
	0.87	6.68	0.19
	0.51	6.05	0.21
	0.48	6.05	0.20
	1.15	5.82	0.82
	1.11	5.82	0.78
Average	0.79		0.38

Table 9—CORROSION OF MATERIALS OF CONSTRUCTION
IN CHLORIDE AND CARBONATE SALTS

Alloy	Average corrosion rate for 50:50 wt. % KCl:NaCl, MPY*	Average corrosion rate for 25:75 wt. % $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3$, MPY*
AISI 310	-53	+9
AISI 430	-116	+25
AISI 446	-78	+10
AISI 311	-46	+16
Hastelloy C	-14	-75
AISI 347	-40	+4
Inconel	-21	-14.5
AISI 1020	-129	-3
AISI 304 L	-54	+9
AISI 316	N.D.	+20

* MPY (mils per year), extrapolated.

Considerable work has been done in the investigation of various commercial cutting fluids for use when machining uranium. Both water-soluble oils and straight cutting fluids have been studied. Water-soluble oils appear superior because of their greater cooling ability and their tendency to minimize fires occurring in the chips produced during the machining operations. The use of water-soluble cutting fluids definitely seems to increase the chances of both localized corrosion of the uranium parts and oxidation of the machining chips. The latter can be disadvantageous if the turnings are to be used as melting charge material, since turnings to be remelted should be as free from oxide as possible. An investigation was performed in which the water to soluble oil concentration ratio was varied over a wide range. A 30 to 1 ratio was satisfactory for general machining operations and appeared to be optimum from a chip-oxidation and tool-life basis. Heavy flows of coolants are frequently used, 30 to 50 gpm being common. These high flow rates aid in removing chips, dissipating heat, and quenching fires that may be initiated in the hot chips produced.

In the special application of deep drilling of uranium, high cutting fluid flow rates and pressures were found to be essential in obtaining satisfactory tool life and good dimensional control. Such pressures may exceed 1500 psi. In a system of this type continuous filtering of the fluid to remove chips and oxide is mandatory.

Carbide tool materials have been demonstrated to be superior to high-speed steel and cast alloy tool materials. Their advantages are (1) longer tool life, (2) increased ease of dressing the tools, and (3) lower costs.

Tool geometry for machining uranium is very similar to that used for machining other materials, but in special applications, such as drilling, broaching, reaming, and milling, negative rake angles on tools greatly increases tool life. When negative rake angles are used, clearance angles should be increased for optimum benefit. On other operations, such as turning and boring, standard tool angles may be employed.

Uranium has been successfully milled, turned, ground, drilled, reamed, bored, threaded, thread-rolled, and broached, much of this to very close tolerances. Each operation has its optimum cutting speed, feed rate, and depth of cut, dependent upon the type of machine used and the desired dimensions of the finished piece. Generally, machines somewhat heavier and more rigid than those used for steel or brass are desirable for machining uranium because of its high density. Their use also permits faster machining rates and closer tolerances. Power requirements are also greater.

7 FABRICATION BY POWDER METALLURGY

7.1 Powder Preparation

The formation of metallic uranium powder suitable for powder metallurgy involves conversion of metallic uranium to the uranium hydride and subsequent decomposition of the hydride to uranium powder. It has been demonstrated that it is essential to start with clean unoxidized metal. This is normally accomplished by pickling the charge material in a solution of 50 to 50 concentrated nitric acid. The pickled metal may then be charged into a stainless-steel pot that is evacuated to a pressure of approximately 25 μ . The pot is then brought to a temperature of about 225°C under a pressure of 8 psi of purified hydrogen. While at this temperature, uranium hydride is continuously forming on the surface of the metal and flaking off, thus exposing a clean uranium surface that in turn is hydrided. This reaction continues until essentially no more hydrogen is consumed. The uranium hydride powder so produced is extremely fine (-325 mesh) and is very pyrophoric.

The uranium hydride powder may be charged to another stainless-steel pot and heated to about 440°C under vacuum for decomposition to uranium. During this operation, the uranium sinters, forming a loose cake. After the cake is formed, it is removed and ground to size by a hammer mill. It has been found necessary to do the grinding under an inert atmosphere such as argon because of the extreme pyrophoricity of the powder. The use of uranium alloy hammers in place of the normal steel hammers also has been found to be helpful in reducing iron pickup.

7.2 Fabrication

Hot pressing, cold pressing, sintering, and powder rolling have all been used experimentally to produce fuel elements.

In one hot-pressing test -12 mesh powder has been used. The die was under an inert atmosphere, and the powder was protected from oxidation by the use of a preparation such as xylene. Temperatures as high as 600°C and pressures of 7 tsi have been used. The work-piece should be under vacuum during application of both heat and pressure and should be allowed to cool under vacuum. Elements or pieces so produced have required little machining, a surface grinding or a light lathe cut generally being adequate. Metallographic studies reveal that material prepared in this manner has a grain size of 8 to 12 μ and is randomly oriented.

In cold pressing and sintering, a finer powder than that used for hot pressing has been found best. Better sintering characteristics have been obtained with -325 mesh material. Pressures of 30 to 50 tsi have been used under inert atmospheres. These compacts have then been sintered under vacuum at temperatures of about 1100°C for 4 to 10 hr. High shrinkage and somewhat lower densities (18.5 g/cm³) than the hot-pressed compacts have been experienced. Grain size has also been larger, being in the order of 500 to 1000 μ .

When powder rolling is attempted, -12 mesh powder is used. A thin steel tube is used to contain the powder, which is loaded into the tube under an inert atmosphere and is vibrated to get good packing. After loading, a plug is welded on the open end, provision being made for evacuating the assembly. While the assembly is heated to temperatures as high as 600°C, it is evacuated to a pressure of 15 μ , after which the tube is sealed. Before it is rolled, the assembly is again heated to about 600°C. Rolling schedules call for 10 per cent reductions, with intermediate heatings as necessary to maintain temperature.

In order to satisfactorily densify the product, an over-all reduction of approximately 75 per cent is desirable. The steel tube or sheath may be removed by milling or by turning on a lathe, whichever is suitable.

Bomb Reduction, Forging, and Extrusion of Uranium and Uranium Alloys

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ABSTRACT

This paper describes a process for the production of pure uranium in 1.5-ton masses by a bomb reaction of UF_4 with magnesium. Similar techniques are discussed for the production of binary uranium alloys by thermite reaction, and the limitations of the process are indicated. Fabrication methods for the hot forming of bomb reguli by forging in the alpha range and by extrusion in both gamma and alpha phases are described. Examples of structure are presented, and the influence of alloy additions on both forming characteristics and product quality are illustrated.

1 INTRODUCTION

The development of thermite bomb reduction of massive charges has offered a means of producing uranium and high-purity uranium alloy metal which does not require a remelting step to convert it to ingot form. The heavy metal reguli of such bomb reactions can be fabricated directly to useful shapes by either forging or extrusion. This paper describes the bomb-reduction practice for both pure uranium and assorted uranium alloys and discusses procedures in press forging and extrusion that are applicable to a variety of uranium grades and compositions.

2 THERMITE REDUCTION OF MASSIVE URANIUM CHARGES

The development of a technique to create a large mass of uranium by a thermite reaction of UF_4 with magnesium^{1,2} was aimed at bypassing the usual production procedure of vacuum melting and recasting of derbies to form ingots. As such the large-scale bomb reaction was planned to produce a direct ingot.³⁻⁶ The term "direct ingot" was promptly shortened by pilot-plant phraseology to the coined word "dingot," which has grown to be the official name of the large-scale bomb product.

The thermite reaction is carried out within a mild steel bomb shell such as shown in the cutaway view of Fig. 1. A mandrel accurately clamped in a centralized position permits the formation of a refractory liner of uniform thickness composed of crushed MgF_2 slag derived from earlier bomb reductions. This is packed firmly to the desired hardness by the action of a conventional foundry jolter of 3 tons capacity. When the proper liner hardness has been achieved, the mandrel is carefully withdrawn, exposing the cavity to receive the bomb load.

Fig. 1—Cutaway view of dingot bomb shell.

Fig. 2—Inverted dingot and attached slag after removal from bomb. Fragments of the liner are visible on and around the mass of product slag.

The lower portion of the cavity has a 1 to 1 height to diameter ratio that favors complete separation of metal from slag.

For a bomb of this size, the charge consists of a careful blend of approximately 4500 lb of UF_4 with an amount of magnesium to slightly exceed the stoichiometric requirement. This is theoretically equivalent to approximately 3400 lb of uranium metal to be formed in one piece. The blend of UF_4 and magnesium is packed to achieve optimum compactness and is then capped with a 4-in. layer of slag before bolting the bomb lid in place. The firing of this bomb has been accomplished in an electrically heated car-bottom furnace using a control temperature in the range between 600 and 700°C. The firing requires a prolonged soak that may vary from 9 to 14 hr. For safety the bomb is usually left in the furnace for an additional hour after firing to ensure that the reaction has gone to completion and is then removed for air cooling, which will last two to three days. The time for solidification of the metal within the bomb is approximately $2\frac{1}{2}$ hr.

The discharge of the bomb contents is easily carried out by inverting the bomb shell after removal of the lid. The dingot with the attached product slag is shown in Fig. 2. The metal is readily separated from the slag mass by impact that can be effected either mechanically or by hand as desired. It is then cleaned of adherent slag with a chipping hammer and is weighed to determine the crude yield. The product slag is broken up and sent to a crushing plant for preparation as new slag liner material. The metal dingots may be seen in Figs. 3 and 4, which show contrasting surface qualities as influenced by the completeness of metal separation from slag in the bomb reaction. Figure 3 shows the dingot after chipping and ready for scalping. The roughness of the top surface (facing the camera) indicates that the separation of metal from slag is not so clean as is desirable. On the other hand, Fig. 4 shows an example of excellent separation of slag from metal. The regulus shown in these photographs is approximately 18 in. in diameter by 18 in. high. At this stage the dingot is ready for surface preparation for the selected method of hot-working.

3 URANIUM ALLOY FORMATION BY THERMITE BOMB COREDUCTION

The formation of a uranium alloy by the thermite reduction of component salts by magnesium offers an attractive means of achieving a high-purity alloy by avoiding the carbon pickup associated with vacuum-furnace remelting and casting in graphite containers. This becomes an important feature in alloy systems where the additive readily forms a carbide that may float to the top of an ingot and contribute to a serious nonhomogeneity. The bomb practice for coreduction is patterned after that for production-grade uranium using similar sizes of shells and mandrels with the same grade of MgF_2 lining.⁶ Figure 5 shows a view of a bomb shell and liner employed to fire a 300-lb derby³ for use as melting stock where vacuum recasting is desired. This size of bomb is useful for small-scale experiments in thermite reduction. The liner is formed between the shell and mandrel by jolting the MgF_2 slag to the desired hardness. Another shape intermediate in size between this and the full dingot can be formed in the bomb shell shown in Fig. 6. The regulus from this bomb weighs approximately 900 lb and measures about 9 in. in diameter by 20 in. in length and is thus a favorable shape for direct fabrication. It was designed to create a billet for extrusion. Losses experienced in scaling have demonstrated that in general a 1 to 1 height to diameter ratio is a shape more favorable for optimum metal yields.

The choice of the components for the bomb charge depends upon considerations involving the heat balance of the reaction, the expected reaction rate, the properties of the compound of the additive, and the melting point and viscosity of the product slag. Under suitable conditions either a salt, an oxide, or even the metallic form of the additive may be employed. If a salt is used, it should be nonvolatile at the bomb temperatures and should react with magnesium without undue violence. The use of the oxide is less desirable since the MgO created by the reaction tends to have an unfavorable effect upon the slag fluidity and therefore on the completeness of the slag and metal separation in the bomb. In cases where a highly reactive salt is under consideration, a portion of the additive may be charged in metallic form to absorb a part of the

Fig. 3—Dingot with a mediocre surface.

Fig. 4—Dingot with a fine surface.

Fig. 5—Derby bomb shell and mandrel. This size of bomb is useful for small-scale experiments in thermite reduction. The liner is formed between shell and mandrel by jolting the MgF_2 slag to the desired hardness.

Fig. 6—Intermediate dingot bomb shell.

heat and diminish the vigor of the reaction to a safe level. The coreduction of a number of specific alloys will be described as examples of the success that may be anticipated for this practice.

3.1 Silicon-Uranium Alloys

The alloying of silicon with uranium may be carried out very easily and successfully by coreduction of UF_4 and SiO_2 of high purity by magnesium in a bomb.^{6,7} Four typical compositions prepared by this technique are given in Table 1, showing a good control of final analysis.

Table 1—RESULTS OF SI-U COREDUCTIONS

Composition aim points, wt. % Si	Derby analyses, wt. % Si
0.14	0.15
0.18	0.18
3.6	3.6
9.5	9.5

In each case an excess of 25 per cent SiO_2 was used, which as may be seen was a very accurate allowance for the distribution of the silicon between metal and slag. The first three compositions gave a successful regulus, but the 9.5 per cent alloy collected as pellets rather than as a derby. It is believed in this case that the MgO created from this quantity of SiO_2 was sufficient to upset the fluidity of the product slag to a degree that complete slag and metal separation was not possible. The behavior indicates that the slag of this reaction froze before the alloy draining to the bottom of the bomb cavity could coalesce.

3.2 Chromium-Uranium Alloys

Experimental preparation of chromium-uranium alloys⁶ by coreduction has been performed successfully with the use of either Cr_2O_3 or $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ as the additive to the UF_4 -Mg blend. Table 2 lists the results obtained with four compositions. The first two were prepared

Table 2—RESULTS OF Cr-U COREDUCTIONS

Composition aim points, wt. % Cr	Derby analyses, wt. % Cr			Ingot analyses, wt. % Cr	
	Top	Bottom	Composite	Top	Bottom
0.077			0.094	0.077	0.080
0.15	0.14	0.14		0.18	0.17
5.0	6.99	4.65			
10.0	8.70	3.98			

as 300-lb derbies using sodium dichromate dihydrate as the alloying agent, and the last two were made using chromic oxide. In this series of alloys, only the two low chromium compositions were remelted and cast as ingots. The uniformity in chromium distribution from top to bottom was encouragingly good despite the tendency of this alloy to form a chromium carbide that might have been expected to float to the top of the ingot and impoverish the remainder of the section. The calculated charges for these bombs employed no excess of equivalent chromium.

3.3 Titanium-Uranium Alloys

A reaction between potassium fluotitanate (K_2TiF_6) and UF_4 -Mg has been employed to produce one experimental composition⁶ aimed at 0.10 wt. % titanium. Derbies (300-lb) produced from bomb reactions using a 25 per cent excess of K_2TiF_6 showed some tendency of the titanium to segregate at the top, averaging 0.17 wt. % at this location and 0.07 wt. % at the bottom. Recasting of this metal, however, produced ingots of good uniformity, analyzing 0.09 wt. % at the top and 0.08 wt. % at the bottom.

3.4 Molybdenum-Uranium Alloys

Table 3 shows the results of five coreductions^{6,8} in which various combinations of molybdic oxide (MoO_3) with molybdenum metal were added to the UF_4 -Mg blend. The metal was used here as a diluent in order to ensure that the higher alloy additions would not incur a dangerous heat evolution. No excess of molybdenum was added in calculating the charges. It is evident

Table 3—RESULTS OF Mo-U ALLOY COREDUCTIONS

Composition aim points, wt. % Mo	Derby analyses, wt. % Mo		Mo charge ratio (metal:oxide)
	Top	Bottom	
2.5	2.4	2.4	0.0
5.0	5.0	5.1	1.0
10.0	9.0	8.7	0.67
12.0	10.6	11.3	0.67
14.0	13.7	12.7	1.0

that, as the size of the alloy addition has increased, both the recovery of molybdenum and the uniformity of its distribution have been impaired. This may be influenced by the quantity of MgO created in the more highly alloyed reactions and the consequent effect of this high-melting constituent on the slag fluidity and thus on the completeness of metal to slag separation.

3.5 Zirconium-Uranium Alloys

Thermite bomb reductions to produce zirconium-uranium alloys^{6,9-11} have employed ZrF_4 as the additive to the bomb charge. This presents a favorable situation where the reaction effects no change in the product slag. Table 4 shows the compositions of a variety of derbies and recast ingots in terms of alloy uniformity. It is evident that in the derby form a somewhat erratic behavior has been experienced. Between 0.6 and 2.0 wt. %, a moderately even distribution of zirconium has been obtained. At both higher and lower zirconium additions, the uniformity has been relatively poor. The usual behavior upon vacuum remelting and casting has been a segregation at the top of the ingot which is attributed to a concentration of zirconium carbides formed by reaction with the graphite crucible and displaced by the difference in specific gravity to this location. A crop of the ingot top of the order of 25 per cent has served to remove this segregated area and leave an ingot that is more nearly uniform in analysis.

3.6 Niobium-Uranium Alloys

Two methods have been tried in attempting to prepare niobium-uranium alloys^{6,12} by coreduction. One of these has been quite successful in small-scale experiments¹³ carried out at Iowa State College, Ames, Iowa. This procedure has employed $NbNa_2OF_5$ and UF_4 with calcium added at 1.3 times the stoichiometric requirement to fire 2- and 4-lb bombs that have given very high yields and excellent uniformity of niobium content.

Table 4—RESULTS OF Zr-U ALLOY COREDUCTIONS

Composition aim points, wt. % Zr	Derby analyses, wt. % Zr		
	At top	1/2 in. below top	At bottom
0.20	1.34	0.11	0.09
0.40	1.61	0.21	0.23
0.60	0.47		0.52
0.80	0.63		0.64
1.00	0.85		0.78
1.50	1.75		1.29
2.00	1.79		1.84
2.00	2.04		1.71
2.00	2.23		1.84
5.00	5.08		4.13
5.00	5.84		4.21
6.00	6.51		4.21

9-in. O. D. × 20-in. dingot analyses, wt. % Zr			
	At top	Half-height	At bottom
0.78	0.60	0.64	0.62

Derby composition, wt. % Zr	Ingot top crop, %	Ingot analyses, wt. % Zr		
		Top*	Half-height	bottom
2.0	0	5.8		
	7 1/2	6.2		
	15	5.1		
	22 1/2	3.1		
	30	1.9		
2.0	10	2.38	1.34	1.45
2.2	25	1.96	1.77	1.89
2.3	25	2.16	2.22	2.42

*Top of section remaining after cropping.

In other work larger scale efforts involving 300-lb derbies have attempted a coreduction of Nb_2O_5 with magnesium in the usual UF_4 charge. This technique has met with somewhat indifferent results as shown in Table 5, both as to alloy uniformity and niobium recovery. A careful study of the reaction indicates that the amount of heat generated and the quantity of MgO produced are unfavorable for a successful metal-slag separation. The effect of this is shown in Fig. 7, giving a view of a cross section of a derby from a bomb reaction using 6 1/4 per cent each of metallic niobium and Nb_2O_5 (equivalent metal basis) reacted with UF_4 and magnesium and aimed at 10 wt. % niobium alloy. It is concluded that the compound used in the Ames experiments is the preferred additive, but, so far, no trials have been made in large size or with magnesium instead of calcium.

3.7 Outlook for Alloying by Coreduction

A review of the experience presented for the six alloy types cited permits the following conclusions with regard to the degree of success that may be anticipated in preparing uranium alloys by a thermite coreduction.

1. The additive should be in a chemical form that will provide extra heat to the bomb reaction wherever possible.
2. The use of oxides in quantities to produce a product slag of more than 5 wt. % MgO should be avoided. This represents the approximate eutectic composition of the MgO-MgF_2

Table 5—RESULTS OF Nb-U COREDUCTIONS

Point, wt. % Nb	Excess Nb in charge, wt. %	Charge ratio (metal:oxide)*	Derby analyses, wt. % Nb		
			Top	Center	Bottom
4	0	0.0	3.4†		6.9†
4	0	0.0	4.3†		2.9
8	0	0.0	5.5		5.5
8	0	0.0	6.9†		5.5†
10	25	1.0	7.0	6.6	6.0
10	25	0.33			8.2
10	25	0.0	8.0		8.8
10	25	0.0		6.7	
10	1	0.0		6.4	
12	0	0.0	9.3		7.8
16	0	0.0	12.3		12.3
16	0	0.0	13.0†		11.8†

*Refers to ratio on equivalent metal basis.

†These data reported incorrectly in an earlier publication⁶ with top and bottom analyses transposed.

Fig. 7—Cross section of a 6½ wt. % niobium-uranium alloy derby. Lower portion is clean metal, but upper mass is an intimate mixture of slag and metal which froze before separation could become complete.

equilibrium system with a melting point about 40°C below that of pure MgF_2 . With larger fractions of MgO present, the liquidus for the system climbs exceedingly steeply, the rate at which MgO can be dissolved in the slag becomes very sluggish, and the viscosity of the mixture increases seriously. The result of these factors is a derby containing some fraction of a metal-slag mixture which has no opportunity to separate before the slag freezes. In circumstances, therefore, where the use of an oxide additive represents the only choice, the outlook for an appreciable alloy addition is not favorable for a clean metal product of the bomb reaction for direct use. This does not suggest, however, that the coreduction route may not be a fruitful path in preparing an alloy charge for a vacuum remelt. This applies particularly to additives such as niobium where the melting point of the additive is high, and the liquidus of the uranium alloy system climbs sharply as the quantity of the second element is increased. The coreduction in this case avoids the need for exceedingly high furnace temperatures in order to bring about solution of the niobium in the uranium if the crucible charge is completely metallic. Such high temperatures lead to a very high carbon content by reason of reaction with the graphite crucible. An alloy derby charge prepared by coreduction can be melted rapidly and poured promptly, avoiding a prolonged holding time at high temperature and the consequent carbon pickup.

3. Systems involving appreciable differences in specific gravity of the component elements (or of side reaction compounds of these elements) may encounter a serious lack of chemical homogeneity within the metal whether in the derby status or after recasting as an ingot. The presence of carbides and nitrides with a relatively low density will contribute to a serious segregation of the additive at the top region of the metal shape. This is particularly noticeable for zirconium, which in the ingot state will preferentially react with the carbon present rather than remain dissolved in the uranium.

A comparison of the homogeneity to be expected in derby metal vs. ingot metal must take into account two separate influences. The role played by carbon has already been cited. The presence of this element in the ingot at approximately 25 times the level pertaining to derby metal presents a difficult problem if the alloying addition has a high affinity for carbon, as has been described. The second influence is the pronounced difference in cooling rate experienced by the ingot as compared with that of the derby. A small 5-in.-O.D. 600-lb ingot, such as has been used frequently for production of experimental alloys, will solidify in approximately 50 sec after pouring; a 300-lb derby, on the other hand, will require 45 min for solidification. In circumstances where differences in density will tend to float the alloy addition to the top of the cooling metal, this effect will be slight in the ingot but will approach essential completion in the derby or dingot.

4 FORGING OF BOMB REGULI

Early investigations in the development of dingot bomb reductions revealed that shapes suitable for rolling should be of appreciable length to permit satisfactory handling in ordinary rolling mill equipment. Such shapes, however, proved to be unfavorable for optimum yields of metal from the bomb reaction. The preferred technique has therefore been to design the bomb shell to provide the dingot proportions that are most favorable for good metal yields and to resort to fabrication techniques other than rolling for initial hot working. A primary metal breakdown in a forging press has proved to be acceptable for this purpose.^{12,15}

4.1 Surface Preparation of the Dingot

Chemical analyses of cross sections obtained from dingots and derbies have shown conclusively that the impurities present in the bomb regulus, namely magnesium and nitrogen, which most sensitively affect metal cleanliness are largely concentrated in the surface layers of the bomb product.^{5,6} The removal of this layer by a machining operation has been quite satisfactory in producing a large volume of high-purity metal that has no internal gradient either in density or in the traces of impurities that remain. This surface scalping has been per-

formed on a heavy-duty vertical lathe, removing up to $\frac{1}{2}$ in. of metal from the sides and bottom of the dingot and approximately a 1-in.-thick layer from the top, where the presence of firmly adherent slag is more common. The determination of the amount of metal to be removed in this machining has been the requirement that all traces of occluded slag particles be removed. This quality is demonstrated by a final test using a torch to tint the surface of the dingot and to reveal by sharp color contrast any remaining slag not yet machined away. The torch, mounted on the lathe tool post, does a complete traverse of the machined surface as the dingot revolves. The flame darkens the uranium surface, bringing any residual inclusion of MgF_2 into sharp color contrast. If slag is found, machining is continued, and the flame etch is repeated until the dingot passes inspection. This operation is shown in Fig. 8 as performed on the lathe after a tentative finishing cut. Comparisons made between acid etching and this heat-tinting technique (or flame etching) have demonstrated that exactly the same quantities and outlines of impurities are revealed by either procedure. The flame etch is therefore much to be preferred as a far simpler operation.

4.2 Preheat

The simplest method of heating the dingots to the forging temperature has been by immersion in a molten-salt bath. Figure 9 shows a dingot in a stainless-steel hanger that has been found to be a convenient means of handling the uranium into and out of the salt bath and to and from the forge press. The usual salt bath is a mixture of chlorides or of carbonates as preferred, usually selected to provide a melting point between 500 and 550°C. The control temperature should be adjusted to hold the metal in the high alpha-phase temperature range without undergoing risks of transformation to the beta phase at 662°C. The initial soak of a virgin dingot normally is at least 3 hr; as forging proceeds and reheating becomes necessary, this length of immersion can be diminished to approximately 45 min for a cross section of about 5 by 7 in.

The molten salt, in addition to providing for the transfer of heat, also protects the metal from surface oxidation. The film of molten salt retained on the dingot upon withdrawal from the salt bath continues to coat the metal during forging and minimizes the opportunity for release of uranium oxide to the air in the forging area. This affords a very complete protection for the health of the forging crew, and additional dust-arresting precautions in this working area have not been found necessary.

4.3 Forging to Rough Size

A 1000-ton oil-hydraulic direct pump-driven forge press (see Fig. 10) has been found adequate for the hot working of the full-sized dingot. A mechanical manipulator (Fig. 11) is quite essential in handling this massive piece of uranium weighing up to 3000 lb. The most important feature of the manipulator is the design of jaws to grip the dingot without permitting slippage. This is more of a problem with uranium than with ordinary forging assignments because of the very high density of this element.

The determination of the proper sequence of forging steps has been dictated by the influence of the original metallographic structure of the dingot. The as-cast dendrite pattern within this massive regulus is extremely coarse (average 19.02 g/cm³) and largely vertical as may be seen in Fig. 12. It is evident that the mass of hot slag above the dingot has made possible a progressive freezing within the bomb that has been nearly unidirectional. This very slow freezing creates an extremely coarse grain size that offers initial difficulties in the forging procedure. It has been found important to induce an early and appreciable surface flow of the metal, particularly in the flat ends of the machined dingot, if bursts or tears are to be avoided in this area during later stages in fabrication. The end faces then become two ultimate sides of the forged bar. This practice provides convex surfaces on the ends of the bar that are free of tears or fissures. The initial step in forging has therefore been to end-upset the dingot to destroy the as-cast grain structure in the end faces (see Fig. 13). The dingot is next turned on its side to forge a pair of flats on the cylindrical surface; hot forming then continues to

Fig. 8—Dingot undergoing flame etch.

Fig. 9—Dingot and hanger for handling during heat-treatment. The brackets at the bottom of the hanger hold the dingot off the bottom of the bath, allowing salt to circulate beneath for good temperature uniformity.

Fig. 10—Forge press. The platens between the columns measure 4 by 4 ft. The valve action is capable of about 10 strokes/min. The dies may be shifted sidwise to permit forging between the flats or in the closed contour as desired.

Fig. 11—Mechanical manipulator.

Fig. 12—Vertical cross section of full-sized dingot. The macrostructure reveals the effect of very slow cooling of the bomb contents after firing. The large mass of hot slag above the metal pool forms such an effective "hot top" that the dingot requires $2\frac{1}{2}$ hr to solidify.

Fig. 13—Dingot in position for initial end upsetting.

accomplish what has been termed "cross forging" to prepare a bar whose length is perpendicular to the original axis of the dingot cylinder. Figure 14 illustrates the dingot shape when this cross-forging operation is partially complete. Here the surfaces in contact with the dies are the original end faces of the dingot cylinder. The hanger partially visible at the right in Fig. 14 is in position on the roller table to receive the dingot for transfer to the salt bath for reheat. The rings of the hanger are spaced to pass down between the conveyor rolls and permit the manipulator to move the dingot to or from the dies without difficulty.

The amount of forming which can be accomplished in one forging sequence is a function of the rapidity of press valve action plus the skill of the operating crew. The effect of the forging strokes is to generate heat within the uranium while contact with the dies tends to withdraw heat; the salt film eliminates the heat contribution from surface oxidation that would otherwise be experienced with forging the metal in the bare condition. With a rapid-acting press, it is possible to maintain enough heat generation to hold a constant metal temperature and carry out the complete rough forging in a single cycle. Where the press controls are not of high speed, the metal will cool continuously, requiring interruption of the forging for reheating. It has been found desirable to return the dingot to the bath whenever the metal has cooled to about 575°C. Reheating may be done a number of times without detriment to the piece or to the fashion in which it responds to hot work. Very little time is lost in such a procedure if a salt bath of adequate capacity is available to permit a continuous interchange of pieces for forging.

The completion of rough forging is achieved when a smooth, rectangular shape of bar has been produced to the proper cross section. The control of final strokes of the press has normally been provided by the use of gauge blocks called "peggies" that are placed between the dies on either side of the bar being forged to limit the stroke of the press to an exact dimension. Where the ultimate fabrication of the bar is to be by rolling, the rough forging has normally been to a cross section of approximately 5 by 7 in. requiring four forging reductions, involving three reheats, for the operations conducted at the Mallinckrodt Chemical Works pilot plant. At the completion of the rough forging cycle, the bar is quenched in water to minimize oxidation during cooling and set aside to await final forging after a change of dies. Such a bar is illustrated in Fig. 15; at this stage the cross-section is approximately 5 by 7 in. The final treatment will provide curved edges to match the die cavity shown in Fig. 16. Note that the cross-forging procedure has yielded a well-bulged end contour (Fig. 15). This will undergo secondary rolling with no danger of splitting.

4.4 Procedures in Forging to Final Size

If rolling is to be undertaken as the final stage of fabrication, it is desirable to forge the bar to a contour within a closed die of a design such as that shown in Fig. 16. The contour is forced down on the bar until the dies close. The result is a flat-sided bar with curved edges, a shape that is selected for good behavior in entering the blooming mill rolls. For simplicity this contour has been machined near one end of a pair of dies used otherwise for forging between flats. It is brought into play by moving the dies sidewise until the cavity is centered under the ram axis. To minimize the total time devoted to this die change, a quantity of rough forged dingot bars is accumulated, and then the entire group is finish forged at one time. It is thus necessary to recharge the rough forged bars to the salt bath for reheat to the forging temperature. The final reduction in finish forging is relatively slight, and this stage is always completed within a single cycle.

In circumstances where the bar stock is intended for subsequent extrusion, the procedures are slightly different. If machining of the billet is an essential part of its preparation, it is simplest to prepare the stock as a rough round rather than to attempt a more accurate shape. This has normally been accomplished by cross forging to prepare a square bar that is then converted to an octagon in the late stages of rough forging. The final treatment continues this breakdown of the bar edges until a polygonal cross section is achieved as illustrated in Fig. 17. The machining of this rough round to final billet diameter admittedly sacrifices a small amount of extra metal beyond what would be involved in the forging of a true round. The forging proce-

Fig. 14—Dingot with cross forging partially complete.

Fig. 15—Dingot bar after rough forging.

Fig. 16—Die contour for final forging to rolling stock.

Fig. 17—Rough forged dingot round. This contour is produced by forging between flat dies.

Fig. 18—Vee type swage dies for forging rounds.

ture by this technique, however, is a faster operation than in the forging of a true round, and a gain in cost is obtained for this reason.

If secondary extrusion is to be done without intervening machining, it is desirable to forge to a finished round. This is carried out from the beginning in special die cavities, called Vee type swage dies (Fig. 18). Each cavity is formed by two 45-deg slopes terminating in an arc of a circle. Swaging begins with the bar making contact with the four 45-deg sloped faces. The final stage for each size involves pressure on the round from the Vee-bottom curvature only. Accurate positioning of the bar during forging produces a very smooth and straight cylinder. The forging procedure requires a large number of strokes with the piece rotated through a proper angle between each stroke. More than one pair of cavities within the die block is necessary if a large reduction from initial to final shape is involved.

The progression of forging strokes in this type of forming should always be from the ends toward the center. This means the reversal of the bar at the halfway point and a resumption of forging on the further end. This procedure eliminates the creation of bursts in the end face of the bar which will inevitably result if the forging proceeds as an uninterrupted sequence from one end to the other. In the final stages of forging, the bar is advanced through the die opening each time it is rotated. This ensures good uniformity of diameter and straightness.

The forging of slabs for the preparation of rolled sheet can also be achieved with a good quality of product. It is important in creating a thin shape of this sort that the original shape of the starting piece be large enough to permit a measurable reduction in both dimensions of the cross section. Without this advantage there will be considerable difficulty in preparing a slab having a good surface quality on the edges. The proper forging sequence corresponds closely to that described for the preparation of bar stock for rolling to rod. It differs mainly in that the change from a square to a rectangular cross section is brought about very much earlier in the forging sequence. In the finish forging of a slab it may be necessary to reduce the bite of each stroke so that the slab is advanced only a short distance through the dies between each contact. This advance may have to be as small as one-fifth the die width because of the greatly increased resistance to flow provided by rectangular sections where the thickness has been brought to one-sixth or one-seventh of the slab width. Without this reduced bite the maximum thrust of the press will be inadequate, and forging cannot proceed. The control of final dimensions is provided by the use of peggies to limit the forging stroke as previously described. The quality achievable in the forging of slabs is illustrated in Fig. 19.

Fig. 19—Forged dingot slabs cross forged from full-sized dingots. The cross section is approximately $1\frac{3}{4}$ in. thick by $10\frac{1}{2}$ in. wide. Finish forging encounters increasing resistance to flow as the slab thins, and shorter bites become necessary. These slabs were advanced only about 2 in. across the die face per stroke at this stage.

5 PRESS FORGING OF A SILICON-URANIUM ALLOY

An early attempt to roll a $1\frac{1}{2}$ at. % silicon-uranium alloy rod from a 5-in.-O.D. ingot was unsuccessful, indicating the as-cast structure to be too brittle for this type of forming. An attempt at forging a cored alloy was therefore undertaken to determine whether this lower carbon composition could be hot-worked in this fashion and whether this could provide a structure that later could be successfully rolled or extruded.

5.1 Forging in Preparation for Rolling

An assortment of alloy dingots of rectangular shape measuring approximately 5 by $5\frac{1}{2}$ by 17 in. long (an early experimental shape in the dingot program) was prepared for experimental forging. The reduction in rough forging was 33 per cent; final forging was done in a closed die contour similar to, but smaller than, that shown in Fig. 16. This work showed that the $1\frac{1}{2}$ at. % Si-U alloy could be forged if the strokes were shallower and the bites shorter than for pure uranium. There was, nevertheless, considerable cracking encountered in carrying out this deformation, and 60 per cent of the bars were eventually rejected as being unfit for further hot work. The behavior showed that forging between flats, although more successful than primary rolling, was difficult to accomplish without damage. The remainder (12 bars) was forwarded to the rolling mill, and an attempt was made to roll these to rod. This proved to be unsuccessful and indicated that, within the pass schedules employed in standard uranium rolling, this alloy does not possess the necessary ductility to undergo this deformation without tearing.

5.2 Forging in Preparation for Extrusion

For this program an assortment of $1\frac{1}{2}$ at. % silicon alloy cored dingots were prepared as 9-in.-O.D. by 20-in.-long cylinders (see Fig. 6). These were scalped to a nominal 8 in. O.D. by 18 in. long and were then forged to about $6\frac{1}{4}$ in. O.D. (a 38 per cent reduction) in Vee-type swage dies. The behavior here was very similar to that observed for standard dingot uranium except that more pressure had to be exerted by the ram, and it was also necessary to use shallower strokes and shorter bites. It was further determined that the metal temperature was very important and that damage resulted if the forging was continued after even a moderate drop in the billet temperature. The forming within the Vee dies was, however, very much more successful than the attempts between flat dies described above. These forgings were subsequently machined to extrusion billet size and successfully underwent extrusion, as described in the following section. It is to be concluded that a stress system that is completely compressive is a very advantageous condition for the hot working of brittle alloys.

6 EXTRUSION OF URANIUM AND URANIUM ALLOYS

Extrusion was one of the earliest hot-working techniques tried with uranium at the inception of the atomic energy program in the United States. It was attractive because of a number of advantages, notably a high productive capacity, and the ability to form metal to a wide variety of contours with a simple interchange of dies. There were certain discouraging problems, however, because of the reactivity of uranium and its tendency to attack and adhere to the steel components of the extrusion press. Because of these and other factors, extrusion was abandoned for a time in uranium fabrication. A number of active development programs have more recently been inaugurated to reexamine the potentialities of the extrusion process. These have been particularly concerned with the control of dimensional tolerances, the selection of appropriate tool compositions, and the development of a lubricant to eliminate metal-surface reactions with the uranium. The current outlook for the extrusion process will be reviewed in the following paragraphs.

6.1 Extrusion Tools

The general arrangement of a horizontal extrusion press is shown in Fig. 20, illustrating the cross section and the component parts of a typical commercial press of more than 1200 tons thrust capacity. The choice of press size for a specific extrusion of uranium is influenced by the interrelation of initial and final sizes with the properties of the metal, as expressed in the equation

$$P = K \ln \frac{A_L}{A_f}$$

where P = pressure (psi) on the butt of the billet

K = extrusion constant (psi) expressing the resistance of the metal to deformation

A_L = cross-sectional area of the liner cavity

A_f = area of cross section of the extruded shape

Fig. 20—Diagram of double-acting extrusion press. When used for the extrusion of solid rod, the inner ram may be actuated to augment the total available thrust.

For the extrusion of uranium in the high alpha-phase temperature range with a reduction ratio of approximately 25 to 1, the required thrust of the press must be at least 2200 tons if a 7-in.-O.D. billet is to be employed. Pressures of this magnitude, however, are quite unnecessary if the extrusion is to be accomplished in the gamma phase.

Figure 21 illustrates the cross section of a typical die design (including dummy block, liner, flow cone, and die supported by its adjuncts) for alpha extrusion of uranium rod. In alpha extrusions the use of a mild steel cone between the billet and the die has been found advantageous in attaining the proper surface quality on the extruded rod. This is not necessary for gamma-phase extrusions where the plasticity of the uranium is sufficiently high to make extrusion with a shear type die quite feasible. The entrant radius of the die opening may thus be diminished for gamma extrusion. The dies that have been most commonly employed have been fabricated from high-speed steel of the 18 per cent tungsten-4 per cent chromium-1 per cent vanadium variety.

The extrusion billet has, in general, been a simple cylinder with a length approximately twice the diameter and with a 45-deg bevel machined upon the corner of the nose. For the case of a 7-in.-O.D. billet, this bevel has varied from 1 to 2½ in. in length, depending upon personal preference, but on occasions a 1-in. radius has also been preferred.

Conventional steel dummy blocks have been used in alpha extrusions, but for the gamma-phase range the addition of a cutoff or follower block of graphite has been found advantageous. The action of the graphite has been to achieve essentially complete extrusion of the uranium at the end of the ram stroke, eliminating the need for shearing or sawing of the rod from the extrusion butt but creating a moderate-sized extrusion defect (Fig. 22). In Fig. 22 a graphite

Fig. 21—Extrusion die and flow cone contour. The reduction ratio represented is approximately 24 to 1.

Fig. 22—Extrusion defect from gamma extrusion with graphite cutoff.

cutoff (or follower) block placed between the billet and the dummy block has crushed near the end of the ram stroke and expelled the bar forward and completely free of the die. A small uranium remnant is left in the liner. This size and shape of defect represents far less crop loss than is frequently experienced in commercial extrusion.

6.2 Gamma Extrusion of Dingot Metal

The necessary preheat for extrusion¹⁶ can be accomplished by any conventional means if adequate protection of the surface from oxidation is provided. A molten-salt bath has the advantage that the residual salt film protects the billet during subsequent handling. A low-frequency induction coil offers a higher heating rate but requires a separate provision for billet-surface protection.

The preheat temperature should be high in order to avoid chilling any portion of the billet into the beta phase during the final stage of the extrusion stroke. Should such a transformation occur, the change in yield strength of the uranium will disrupt the pattern of flow and result in a section of rod that is worthless because of surface tears and abrupt discontinuities in diameter. To avoid this, the preheat temperature should be set in the range 950 to 1050°C.

The choice of lubricant for gamma extrusion is important mainly from the standpoint of die-surface protection. The use of oil-graphite mixtures has been found inadequate, with scoring of the die entrant radius occurring after one or two extrusions. The use of a low-melting glass has avoided this difficulty, and a satisfactory die life appears possible with this procedure. When a salt bath has been used for the preheat, the presence of the residual salt in combination with an applied layer of glass has not appeared to offer any difficulty.

The ram speeds for gamma extrusions should be relatively high in order to minimize heat loss from the billet to the liner and to reduce to a minimum the time of contact between the die and the uranium. In circumstances where the reduction ratio has been moderate and the resultant diameter and velocity of the emergent shape have offered no problem in handling, a ram speed of 200 in./min or more has been satisfactory. At high reduction ratios, however, the speed of the emerging rod may present serious problems in handling this on the run-out table, and a lower ram speed to overcome this situation may be essential.

The pressures necessary for gamma extrusion are an order of magnitude lower than those required for extrusion in the alpha range. Uranium at these temperatures is so soft that it is even something of a problem to measure the thrust on the billet butt with any great accuracy. The most recent data have been determined by electric resistance strain gauges attached to the main stem of the press, and these have indicated the value of the extrusion constant K to be less than 2000 psi. This value pertains to the high-purity metal of the dingot process, and a somewhat greater resistance to flow will be encountered if higher levels of the normal impurities such as carbon, silicon, aluminum, etc., are introduced.

The present interest in gamma extrusion for the fabrication of uranium is in the conversion of the massive dingot shape to bar stock that is satisfactory for a secondary forming operation in the alpha range either by rolling or by extrusion. For secondary rolling the ultimate preferred shape of extruded bar stock will be that already employed in final forging (Fig. 16). For secondary extrusion the round will, of course, be the desired contour. Figure 23 illustrates the surface characteristics and the cross section of dingot rod extruded in the gamma range with a reduction ratio of approximately 6 to 1. The external surface contains a number of longitudinal grooves that appear to result from the use of the glass lubricant. These are visible in silhouette in the perimeter of the cross section. Whether these will persist in secondary forming is not yet known, but the shallow nature of the grooves and the lack of any sharp re-entrant angle suggest that they should not be a source of difficulty. The grain structure of the cross section is typical for uranium hot-worked in the gamma range and is in interesting contrast with an alpha-worked structure (see Fig. 24). The moderate degree of shallow seaming in Fig. 24 is attributed to uranium-metal build-up on the die contour. The cross section

Fig. 23—Surface and cross section of gamma-extruded dingot bar. Top view, $\sim \frac{1}{3}$ size. Bottom view, magnification $\sim 1\times$.

Fig. 24—Surface and cross section of alpha-extruded ingot rod. Top, magnification $2\times$; bottom, $\sim 2\frac{1}{2}\times$.

shows a uniform macrostructure from surface to center. The as-extruded microstructure has been found to possess a fairly pronounced preferred orientation in the radial direction.

6.3 Alpha Extrusion of Uranium Rod

Billet preheating for extrusion in the alpha range¹⁷⁻²¹ has been accomplished in molten-salt baths in nearly all instances. The temperature of this preheat conforms to that used for forging and is held slightly below the temperature of the alpha-beta transformation at 662°C. Where 7-in.-O.D. billets have been handled, a soaking time of approximately $\frac{3}{4}$ hr has been found quite satisfactory for uniformity in internal temperature. Handling into and out of the bath and to the press has been with the aid of stainless-steel hangers of a design somewhat similar to that illustrated in Fig. 9. During the preheat, the hangers have been suspended from crossbars spanning the bath to ensure opportunity for adequate salt circulation beneath the billet as a desirable feature to promote temperature uniformity.

The lubricant for this type of extrusion has been dual in nature since a film of salt has always been present on the billet at the time of entry into the liner. The added lubrication has been in the form of an oil-graphite mixture applied to the liner, cone, and die with a swab immediately before bringing the billet into position. This combination has provided a satisfactory protection for the die, and, although erosion has been observed after a large number of pushes, the die life has been quite satisfactory.

Most of the experience with this type of extrusion has been with reduction ratios of the order of 24 to 1 using billets varying in diameter from 6 to 7 in. nominal size. The extrusion constant calculated for ingot uranium is approximately 35,000 psi for the peak thrust at the start of extrusion and 29,000 psi for the running pressure during the push. Dinged metal, however, with a very low carbon content shows a very different behavior. The extrusion constant for the condition of peak thrust is essentially 24,000 psi, and the corresponding value for the running pressure is slightly under 23,000 psi. The stiffening effect of carbon is therefore a very real factor in considering the necessary maximum thrust that the press should be capable of delivering. Experience indicates that with a 7.2-in.-I.D. liner and a 1.48 in.-I.D. die opening, a maximum press thrust of 2200 tons will from time to time be inadequate for the extrusion of the first billet of a day's campaign when the liner and die have not reached the full temperature usually attained after a number of extrusions.

A variety of ram speeds has been investigated with values ranging from 7 to 30 in./min. Experience suggests that the heat loss to the liner at the low end of this range may chill the billet to a lower temperature than is desirable for best behavior in extrusion. Ram speeds at or above the high value quoted tend to increase the generation of heat during the deformation, and, if used with high reduction ratios, may induce transformation to the beta phase in the outer surface layers of the rod. The general practice has been to extrude with an average ram speed of 15 in./min.

In a number of early experimental extrusions, a brass cutoff block was employed between the dummy block and the billet to achieve complete extrusion of the uranium, but this left a pronounced extrusion defect. Although the brass made the shearing of the butt easier, the long conical junction between the brass and the uranium was too well locked mechanically to permit any easy separation; therefore, to avoid a special chemical treatment, the use of the brass was abandoned. The alternate practice was to terminate the extrusion push when the dummy block came into contact with the flow cone. This left a cone-shaped butt which could be cut from the rod with the shears of the press and which represented a good quality of scrap for use in remelting.

The external appearance of an extruded rod and a macroetched cross section is illustrated in Fig. 24. Shallow seams may be observed in the extruded surface, but, as may be seen in the cross section, these have only a slight penetration. The grain size is too fine to be resolved at this magnification, the average diameter being less than 0.02 mm. The structure is uniform, indicating that the flow has been well balanced. Although X-ray examination will show a radial

symmetry of structure, there does exist in the as-extruded state a preferred orientation of the crystal structure in the radial direction.

6.4 Extrusion of Uranium Alloys

Rod extrusions of uranium alloys may be performed with essentially the same techniques as those described for the pure metal. The differences in behavior lie in the greater resistance to flow which the alloyed structures offer and the refinement of grain size created by the alloy addition. Table 6 presents a comparison of extrusion constants for three alloys, all

Table 6—EXTRUSION CHARACTERISTICS OF THREE URANIUM ALLOYS

Type of metal	Alloy content, at. %	Reduction ratio	Extrusion constants, psi	
			Peak	Run
Ingot	1.5 Si	17.8:1	44,000	37,200
Dingot	1.5 Si	18.0:1	31,400	30,200
Ingot	0.35 Cr	17.8:1	45,900	38,600
Ingot	0.50 Ti	17.8:1	36,300	31,200

pertinent to extrusions with essentially the same reduction ratio. These illustrate clearly the remarkable effect that a very moderate alloy addition may exert upon the yield strength of the uranium to which it is added. A similar effect is also shown in the comparison available between the dingot (20 ppm carbon) and ingot (500 ppm carbon) grades of the 1.5 at. % silicon-uranium alloy. Here the carbon difference between these two metals has had essentially the same influence as the silicon addition on the extrusion constant.

Figure 25 shows macroetched head and tail cross sections of a rod extruded from the 1.5 at. % silicon-uranium dingot stock. A fine-grained uniform structure plus a smooth ex-

Fig. 25—Cross sections of alpha-extruded 1½ at. % silicon-uranium cored alloy rod. (Magnification 1×.)

terior characterize the outcome of alpha extrusion for many uranium alloys. Although the individual grains are not resolved, examination at higher magnification has revealed a refinement in grain size beyond that found in the structure of Fig. 24. The effect of this is evident in the absence of detail in these macrostructures. A further influence of fine-grain size is inferred in evaluating the extruded surface of the alloy rod; this was notably smoother and freer of seams than the production-grade uranium.

7 SUMMARY

A process has been described whereby a thermite bomb reaction between UF_4 and magnesium may be controlled to create a $1\frac{1}{2}$ -ton cylinder of high-purity uranium metal. Similar procedures have been quoted for the coreduction of uranium alloys by the bomb technique. The limitations of the process require that (1) a suitable salt of the additive be available and (2) a favorable heat balance for the chemical reaction exist. Those reactions which produce compounds either of low density or of poor solubility in MgF_2 (creating a thick viscous slag) will yield derbies that are chemically inhomogeneous or physically contaminated with slag, or both. Techniques have been described for forging massive uranium dingots to shapes suitable for secondary rolling or extrusion to final size. Appropriate modifications of forging practice have been outlined for application to a coreduced silicon-uranium alloy. Extrusion of uranium has been discussed with a description of the differences in technique which are required for gamma-phase extrusion as compared with those for the alpha phase. The alpha-phase extrusion characteristics of three binary alloy systems have been briefly reviewed, with one example of the effect of alloy addition upon metal structure.

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Grain Refinement of Uranium by Heat-treatment and Alloying*

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ABSTRACT

Two basic methods of refining the grain structure of cast and fabricated uranium are described, and a review of applicable data is presented.

Practical refinement of grain structures in unalloyed uranium is based on rapid cooling through the beta-alpha phase transformation. Additional refinement of rapidly cooled uranium may be obtained by a recrystallization process during a short-time anneal in the high alpha phase.

Alloys of uranium containing up to several atomic per cent of additive that can be used for grain-size control are described. Chromium, silicon, and zirconium are among the most effective grain-refining elements. The neutron absorption cross section and the concentration required for each of these elements are sufficiently low to permit the use of natural uranium in thermal-neutron reactors.

1 INTRODUCTION

Grain refinement of metallic alpha-phase uranium has been generally accepted as a basic requirement for satisfactory reactor performance. It is a well-known fact that irradiation of large-grained alpha uranium will result in surface roughening,¹ the degree of which is proportional to total neutron exposure and grain size. Also established is the fact that stronger cladding will reduce the magnitude of the surface-roughening phenomenon and, if cladding of sufficient thickness and strength is used, surface roughening can for all practical purposes be eliminated.² To reduce surface roughening by means of cladding only, however, a high price in neutron economy must be paid. Another approach, such as grain refinement, is a more practical method of reducing the degree of surface roughening.

On the other hand, the attainment of fine-grained uranium is not sufficient in itself for making satisfactory fuel elements. If the uranium, although fine grained, has highly preferred orientation, a fuel element may exhibit dimensional changes¹ that may be more serious than the surface-roughening phenomenon. Although the mechanism of these dimensional changes has been the subject of much debate and has not been adequately resolved, the basic cause is some anisotropic property of the orthorhombic structure of alpha-phase uranium.

The attainment of a fine grain size accompanied by random orientation is therefore a major goal in the manufacture of fuel elements that will behave satisfactorily during irradiation. Grain refinement is also somewhat important in obtaining satisfactory surfaces of fuel ele-

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ments that are fabricated by extrusion.³ With large-grain-size uranium, extruded surfaces may be rough or striated, whereas fine grains result in a much smoother surface.

2 SUMMARY

The grain size of uranium metal normally encountered can vary all the way from approximately 5 to 3000 μ in diameter. Unalloyed cast uranium has a grain size that is normally in the range 2000 to 3000 μ . Fabrication or annealing in the gamma-phase region results in essentially no grain refinement.

The most effective grain-refinement methods for unalloyed uranium in either the cast or gamma heat-treated condition are (1) hot working in the alpha phase and (2) cold working followed by alpha annealing for recrystallization.

A still effective but not so drastic method of refinement for cast or gamma heat-treated uranium is to heat to, and water quench from, the beta-phase region one or more times. Quenching from the gamma phase is also effective but offers no advantages over quenching from the beta phase.

Further refinement of beta heat-treated and water-quenched uranium can be accomplished by a short-time high alpha temperature anneal. This is not effective for large-size castings.

Use of dilute alloys, up to 5 at. % of additive, can reduce as-cast, fabricated, and beta-treated grain size. Among the most satisfactory alloying elements are chromium, silicon, and zirconium.

The effectiveness of these methods for customary ingot sizes is summarized in Table 1.

Table 1 — GRAIN-REFINEMENT RESULTS
BY THE JEFFRIES METHOD⁴

Metallurgical condition	Grain size, μ
As-cast ingot	2000–3000
Gamma-annealed or gamma hot-worked	~1000
Cast, multiple beta treated	~300
Alpha hot-worked plus beta heat-treatment	150–300
Alpha-worked, beta-treated, alpha-annealed	80–120
Hot-worked (alpha phase)	15–60
Cold-worked and recrystallized	15–60
Very heavy cold-worked and recrystallized	~5 (not stable)
Alloyed:	
As-cast	5–1000
Alpha-worked	5–60
Beta-heated	5–200

3 HEAT-TREATMENT OF UNALLOYED URANIUM

Although this paper is concerned primarily with methods for grain refinement of uranium by heat-treatment and alloying, it seems appropriate first to discuss briefly the characteristics of both cast and hot-worked unalloyed uranium.

As-cast unalloyed uranium normally encountered may have a grain size of 2000 to 3000 μ . Grains are rarely equiaxed (Fig. 1) and are often columnar. Hot working in the gamma phase results in essentially no refinement, the grain size being very similar to cast metal. Both cast and gamma-worked metal are, for all practical purposes, randomly oriented, although in the cast metal there is normally oriented growth from the surface. As pointed out in Sec. 1, this unrefined structure causes surface roughening during irradiation.

Fig. 1—As-cast uranium (polarized light). (Magnification 100x.)

Fig. 2—Transverse section of hot-worked uranium (polarized light). (Magnification 100x.)

Working of uranium in the high alpha temperature range, on the other hand, whether it be by forging, rolling, or extrusion, generally refines the grain diameter to about 15 to 60 μ , a reduction of about 20 to 200 times. Grains are normally uniform in size and equiaxed (Fig. 2). Sometimes a banded structure can be observed under polarized-light examination as a result of the original large grains being elongated in the direction of working and the new grains formed from each large grain having similar orientation. Alpha working, however, imparts a preferred orientation to the metal which causes dimensional instability during irradiation; this is more serious than the surface-roughening phenomenon. Were it not for these phenomena, there would not be so much interest in grain refinement.

Unfortunately, the one method of eliminating the preferred orientation resulting from alpha hot working, i.e., heating the uranium into the beta phase, normally increases the grain size by a factor of 4 to 10. Efforts have therefore been directed toward minimizing this increase in grain size by varying the heat-treatment conditions and by alloying.

Fig. 3—Uranium cold rolled 92½ per cent and recrystallized at 475°C for 1½ hr (polarized light). (Magnification 500×.)

3.1 Recrystallization of Cold-worked Metal

If alpha hot-worked metal is cold reduced by rolling to moderate reductions, e.g., 20 to 60 per cent, and recrystallized, the recrystallized grain size is about the same as that of the original hot-worked metal. For light reductions from 4 to 10 per cent, the final grain size is usually somewhat larger. The smallest grain size in unalloyed wrought uranium observed by the writer for a completely recrystallized structure is about 5 μ for a heavily reduced specimen.⁵ Figure 3 shows the grain size of uranium that was cold reduced 92½ per cent in thickness and recrystallized at 475°C for 1½ hr. In order to satisfactorily resolve the grain size, a magnification of 500× was necessary. This extremely fine grain size, however, is not stable and will increase to the 15- to 30- μ range upon heating to higher temperatures within the alpha range. A banded structure can also be observed, the bands being parallel to the rolled surfaces of the specimen. Unfortunately, recrystallization does not eliminate preferred orientation.

When large-grained uranium is cold rolled and recrystallized, the final grain size is the same as that obtained with fine-grained cold-rolled metal. Figure 4 shows a typical structure of metal that has been annealed in the gamma phase and slow cooled. This specimen originally had been alpha-worked with the same grain size as that in Fig. 2. Figure 5 shows a specimen that had been lightly cold rolled (2 per cent) and heated to 550°C for 1½ hr. This reduction was not sufficient for complete recrystallization under these conditions but does show the drastic difference between the original and the recrystallized grain size. It has also been noted that the recrystallized grain size of adjacent areas may have diameters that vary by a factor of 2 or more, apparently the result of different amounts of cold work in the parent grains as a consequence of differing orientation. Another observation of the recrystallized structures of cold-rolled uranium that had been previously gamma annealed is the similarity of orientation of all the small grains resulting from the original parent grain. This suggests that fine-grained and randomly oriented metal with such a structure will probably behave under irradiation in the same way as a large-grained structure with respect to surface roughening.

L. R. Kelman of Argonne National Laboratory (ANL) has shown that a similar structure would exhibit surface roughening during thermal cycling experiments. Although it is recognized that thermal cycling experiments will not duplicate irradiation behavior, they do indicate the tendency of a fuel-element surface to roughen during irradiation. In Kelman's work large-grain-size uranium, when thermal cycled between 100 and 500°C for several hundred cycles, exhibited severe surface roughening in contrast to fine-grained uranium, which remained smooth. After cycling, however, the grain size of both types of specimen was the same (approximately that of the originally fine-grained specimen), the large-grained specimen having recrystallized as a result of the working and heating of the metal during the thermal cycles. When the originally large-grained but now fine-grained specimen was machined to a smooth surface and then recycled between 100 and 500°C, the surface continued to roughen in the manner characteristic of a large-grain structure.

These data on recrystallization show that fine-grained uranium can be obtained by cold working and annealing under the proper conditions. This applies to structures that were initially either fine or coarse grained. However, because preferred orientation effects are not removed during recrystallization, these structures are undesirable for irradiation.

3.2 Phase-transformation Heat-treatment of Uranium

The existence of phase transformations in uranium makes possible the development of appropriate heat-treatments that can be used as means of partial grain refinement of large-grain-size uranium and of removing preferred orientation of alpha hot-worked uranium. Although a phase-transformation heat-treatment of alpha hot-worked metal for the removal of preferred orientation normally increases grain size by a factor of 4 to 10, the ultimate grain size can be controlled to some degree by varying the cooling rate through the transformation and by employing a post-heat-treatment anneal.

(a) *Beta Heat-treatment of Cast and Gamma-fabricated Uranium.* Grain refinement of both gamma-fabricated uranium⁶ and cast uranium³ has been accomplished by multiple beta heat-treating and water quenching. In each case a single beta heat-treatment has been determined to be insufficient.

For ingot uranium fabricated into rod form, approximately 1 to 1½ in. in diameter, in the gamma temperature range, three cycles are necessary to obtain a structure that is comparable to that resulting from beta treating alpha-worked material. For dingot* uranium, also fabricated in the gamma range, S. M. Gill of Hanford (Hanford Atomic Products Operation, Rich-

*The term dingot is a contraction of the words direct ingot and means that it is formed directly from the bomb-reduction process without intermediate recasting. Dingot uranium is as pure as any metal produced in substantial quantities and has a total impurity content of approximately 150 ppm. Ingot uranium normally has a total impurity content of approximately 1000 ppm, carbon being the most significant impurity.

Fig. 4—Uranium annealed at 850°C and slow cooled (polarized light). (Magnification 100×.)

Fig. 5—Gamma-annealed uranium cold rolled 2 per cent and annealed at 550°C for $1\frac{1}{2}$ hr (polarized light). (Magnification 100×.)

land, Wash., operated by the General Electric Company) has reported that grain refinement in most samples is continuous up to six cycles. However, in some specimens there is no response to the heat-treatment, indicating that the higher purity of ingot uranium may make it more difficult to accomplish refinement.

Nuclear Metals, Inc., made a study on the effect of specimen size on the response to phase-transformation heat-treatment of cast uranium.³ For the specimen sizes used, it was observed that more refinement was accomplished in the smaller specimens. Two specimen sizes were used, both being cut from a long 3-in.-diameter casting. The smaller specimens consisted of 30-deg pie-shaped sectors of $\frac{1}{2}$ -in.-thick transverse slices cut from the ingot, and the larger specimens were 2-in.-thick slabs of the entire ingot cross section. Both types of specimen were heated for varying times and temperatures in the beta phase and then quenched in water (a range of 16 to 128 min for the small specimens; a constant time of 45 min for the large.) Neither time nor temperature within the beta-phase region had a significant effect on the final grain size.

Figure 6 shows the macrostructures of the ingot in the as-cast condition, after a single quench, and after four quenches from the beta temperature for the larger specimens. Figure 7 shows both the macro- and microstructures of the small specimens given single and multiple treatments.

Both figures show some refinement of the cast structure after a single quench and maximum refinement after four quenches. An incomplete rim of columnar grains which is noticeable in the structures of the specimens given a single quench is broken up during subsequent quenches.

(b) *Postannealing of Beta Heat-treated Uranium.* The typical structure of beta heat-treated uranium consists of very irregularly shaped grains of mixed size. Individual large grains also consist of colonies of small subgrains that may differ only slightly in orientation. These features are characteristic of all beta-heated uranium except that the faster the cooling rate the smaller and more irregular is the grain size, the more pronounced is the subgrain structure, and the greater is the amount of twinning. A. U. Seybolt of the Knolls Atomic Power Laboratory (KAPL) has reported that neither the time at temperature within the beta range nor the actual temperature itself has any significant effect on the final alpha grain structure. Only the quenching rate is important. These observations point to the conclusion that more strain energy is put into the structure with faster cooling rates. Confirmation of this has been made by measurements of the X-ray diffraction line widths for samples of uranium cooled at different rates than the beta temperature range. Slower cooling rates decreased the line widths.

When uranium that has been air cooled from the beta range is reheated in the alpha range, there is essentially no change in the microstructure except for some shortening of the ragged grain boundaries. H. R. Gardner of Hanford was the first to observe that with faster cooling rates, such as water quenching, the structures recrystallize upon annealing and uniform equiaxed grains are formed. This unusual phenomenon of a metal recrystallizing is possible because of the strains to which the individual grains are subjected by the volume change in transforming from the beta to alpha phase and the highly anisotropic thermal expansion characteristics of each grain.

This recrystallization may or may not result in a finer grain size. For small-sized specimens a grain refinement may occur, but for larger specimens the final recrystallized grain size is essentially the same as the beta-quenched structure.

Work at Du Pont's Savannah River Laboratory⁷ has shown that it is the quenching rate through the alpha-beta transformation rather than the quenching rate in the alpha phase that is important for obtaining grain refinement in this manner. In this work specimens approximately $\frac{1}{4}$ in. thick were beta transformed at 680, 700, and 760°C, quenched in water with moderate agitation after holding in air for times ranging from 1 to 30 sec, and then annealed for times of 3 to 15 min at temperatures of 600 to 650°C. For short holding times in air, grain refinement for the entire cross section was accomplished, the maximum permissible holding time increasing with higher beta-treating temperatures. For beta treatment at 760°C, the maximum delay time for complete refinement was 15 sec. Beyond 15 sec, a range of times was

As cast

Single water quench from 677°C

Four water quenches from 677°C

Fig. 6—Macrostructures of 3-in.-diameter uranium ingots (polarized light). (Magnification 1x.)

Fig. 7—Effect of repeated beta quench treatments at 677°C on small samples of cast uranium. Left, one beta quench. Right, four beta quenches.

found which resulted in only partial refinement. At still longer times no refinement was observed.

The partially refined specimens had some of the typical beta-transformed structure present on the surface. A probable explanation of the lack of refinement on the surface is that the surface of the specimen had cooled sufficiently to revert to the alpha phase prior to quenching and consequently could not be refined.

Typical structures of as-quenched and of quenched and annealed specimens are shown in Fig. 8. The grain refinement resulting from recrystallization can be most clearly seen in the interior structures of the $\frac{1}{4}$ -in.-thick specimens.

In order to determine more quantitatively the relation between cooling rate and the recrystallization kinetics of beta-quenched uranium, Gardner and Riches of Hanford⁸ studied the activation energy required for alpha-phase recrystallization of uranium samples cut from standard 1-in.-diameter Jominy end-quench specimens.⁹

To minimize the effect of chemistry variations, a single rod of dingot uranium was used. The rod was produced by rolling the dingot uranium from molten salt at a temperature of 630°C after it had been scalped and forged to suitable size.

During the quenching of the Jominy specimens, cooling curves were recorded by thermocouples attached at intervals along the surface of the specimens, and the reported rates were calculated on the basis of time required for cooling from 670 to 570°C.

At points corresponding to specific cooling rates, the Jominy specimens were cut transversely, and the 0.062-in.-thick wafers obtained were annealed for varying times and temperatures. Microstructures were examined, and the degree of recrystallization was measured.

Table 2 shows the results of metallographic examination for each cooling rate. As the cooling rate increases, not only the as-quenched grain size decreases, but the additional refinement during annealing becomes greater.

Curves for the determination of activation energy were determined by plotting the time required for 50 per cent recrystallization (at a given cooling rate) as a function of annealing temperature (Fig. 9). Activation energies for each cooling rate were then calculated from the Arrhenius rate equation: rate of reaction = $1/t = Ae^{-Q/RT}$, or

Surface, as water quenched

Surface, after recrystallization

Interior, as water quenched

Interior, after recrystallization

Fig. 8—Uranium heated to 720°C for 2 min, quenched in water after holding in air for <5 sec, and recrystallized at 600°C 18 min. Specimens are $\frac{1}{4}$ in. thick (polarized light). (Magnification 100x.)

GRAIN REFINEMENT OF URANIUM BY HEAT-TREATMENT AND ALLOYING

Table 2—COOLING RATE, ACTIVATION ENERGY, AND GRAIN SIZE CORRESPONDING TO DISTANCE FROM QUENCHED END OF JOMINY SPECIMENS

Distance from quenched end, in.	Cooling rate over 570–670°C range, °C/sec	Activation energy required for recrystallization, cal/mole	Average grain diameter, μ	
			As-heat-treated	Recrystallized
0.005	500 $\pm$ 100	30,000	200	80
0.060	200 $\pm$ 50	52,000	500	170
0.625	9.4 $\pm$ 2	88,000	550	400
1.125	4.4 $\pm$ 2	110,000	700	500

Fig. 9—Relation between time required for 50 per cent recrystallization and annealing temperature with cooling rate as a parameter.

$$\log \frac{t_2}{t_1} = \frac{Q}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where t_1 and t_2 are the times required for 50 per cent recrystallization at absolute temperatures T_1 and T_2 , Q is the activation energy in calories per mole, and R is the gas constant in calories per mole degree Kelvin.

Activation energies ranged from 110,000 cal/mole for a 4.4°C/sec cooling rate to 30,000 cal/mole for a 500°C/sec cooling rate. It was proposed by Gardner and Riches⁸ that the sharp decrease in activation energy for recrystallization with increasing cooling rate was due, at least in part, to greater amounts of lattice strain caused by the anisotropic nature of alpha-phase uranium. An observation that indicates a large amount of lattice strain for rapid cooling rates is that quench cracking occurred on the quenched end of the Jominy specimens. It was also concluded from this study that the nucleation and growth hypotheses for recrystallization in which the rate of crystal growth is equal for the x, y, and z crystallographic directions do not apply to the observed phenomenon.

In the work at the Savannah River Laboratory there was evidence that recrystallization proceeded not only by the nucleation and growth of new grains but also by the growth of small grains that were already present in the as-quenched structure.

(c) *Quenching from the Gamma Phase.* Concurrent with studies of grain refinement by quenching uranium from the beta phase followed by a high alpha anneal, some work was done at the Savannah River Laboratory⁷ and Nuclear Metals, Inc.,³ on the effects of quenching from the gamma phase using the same type of specimens described previously.

In both investigations results were reported which cannot be adequately explained at the present time.

For the Savannah River Laboratory specimens quenched from beta-phase temperatures, complete refinement was obtained as long as the surface of the specimen was above the beta-alpha transition temperature at the time of the quench. However, when heated to the gamma-phase temperature region, quenched after holding in air for increasing delay times, and then annealed at 600 to 650°C, samples showed complete refinement after very short delay times, then showed only partial refinement with somewhat longer delay times, and with still longer delay times again showed complete refinement. The partial refinement for the samples with the intermediate delay times occurred on the surface, whereas, for samples heated into the beta phase, it occurred in the center.

Since complete refinement was obtained only with either short- or long-delay intervals, it was assumed that both beta and gamma phases were present when only partial refinement occurred and that in order to obtain complete refinement the samples must be entirely in the beta phase or entirely in the gamma phase at the time of the quench. Data obtained from the cooling curve of a specimen during cooling from 800°C support this assumption.

Similar anomalous results were obtained on a 1-in.-diameter uranium specimen that was water quenched from the gamma phase after a very short delay time. Both the surface and the center of this specimen were completely refined after annealing, whereas only partial refinement was obtained in the annulus between these two zones.

The Nuclear Metals, Inc., investigation was not very extensive, the small specimens being held for only two times, 16 and 64 min, and at two temperatures within the gamma range, 788 and 899°C. Only for the combination of shorter time and lower temperature was there grain refinement. Subsequent quenching from 788°C did not cause further refinement.

When specimens were quenched from 788°C and then annealed at either 538 or 635°C, complete recrystallization occurred at the lower temperature, and only partial recrystallization occurred at the higher temperature. When these experiments were carefully rerun, the same results were obtained. Figure 10 compares the alpha-annealed with the as-quenched structure.

With 2-in.-thick 3-in.-diameter slabs, no refinement was obtained with either single or multiple quenching. Neither did any part of the quenched structures recrystallize upon alpha annealing.

As quenched

Annealed 2 hr at 538°C

Annealed 2 hr at 635°C

Fig. 10—Effect of alpha annealing on gamma-treated cast uranium (polarized light). (Magnification of each micro, 50X.)

(d) *Microstructural Characteristics of the Beta-to-Alpha Transformation.* As described previously, uranium cooled from the beta phase normally has a subgrain structure within most of the individual grains. Chiswik¹⁰ of ANL observed that these structures were not unlike veining in alpha iron that is obtained during the gamma-to-alpha transformation. Hultgren and Herrlander¹¹ in their studies on the alpha veining structures in iron concluded that, on the basis of its similarity to the structures obtained by hot deformation, the veining obtained during the gamma-to-alpha transformation is merely a special case of hot deformation occurring as a result of the volume changes in the transformation and that it may be absent when the cooling rate is very low. They interpreted the effect of reducing the cooling rate enough to be equivalent to a reduction in strain rate since, on hot deformation, decreased strain rates and higher temperatures tended to decrease the degree of veining.

To investigate whether the same or a similar mechanism is operative in uranium, Chiswik compared the structures of high-purity uranium cooled from the beta range (725°C) at 4°C/hr with those of air-cooled and water-quenched specimens. The specimen size was $\frac{1}{4}$ in. square by $\frac{1}{2}$ in. long. One large-grained specimen (alpha recrystallized after critical straining), $\frac{1}{8}$ in. in diameter by 1 in. long, was also hot deformed by 90-deg bending at 600°C.

Figure 11 shows the typical structure of specimens cooled at 4°C/hr. The majority of the grains showed no evidence of subgraining at any angle of rotation under polarized light (such as grains A and B). Some grains, such as D, had a definite subgrain structure. At other rotations grain D appeared homogeneous. Cooling at the same rate from the gamma range (800°C) or varying the holding time in the beta range from 1 hr to two weeks did not change the microstructure.

In the water-quenched specimen all grains were subgrained (Fig. 12). Also the subgrains appeared to be smaller and more regularly oriented with respect to the parent alpha grains than those in the slowly cooled specimens.

To study the degree of perfection of the microscopically homogeneous grains as compared with the grains containing the substructure, back reflection X-ray Laue photograms were taken of two of the grains shown in Fig. 11. The reflection spots from the grains were relatively sharp and distinct and of a single orientation. When compared with the reflections from an alpha recrystallized grain, however, they showed a slight tendency to be radially elongated, suggesting the presence of some strain in the lattice. The photogram from the microscopically inhomogeneous grain D in Fig. 11 is exactly what one would expect from a grain that had broken up into a large number of subgrains differing only slightly in orientation from each other and from the grain from which they were derived. It is significant to note that the individual reflections from the subgrains are sharp and distinct, with no evidence of the presence of strain in them.

Figure 13 shows a micrograph (taken on the tension side) of the large-grain alpha recrystallized specimen that was bent 90 deg at 600°C. The deformation is seen to have resulted predominantly in subgraining; on the compression side most of the grains deformed by twinning. The subgrain structure obtained on hot deformation is strikingly similar to that resulting from the beta-to-alpha transformation.

The phase-transformation heat-treatments described above are practical methods by which the grain size of uranium can be controlled. For section sizes up to 2 in. thick by 3 in. in diameter, multiple heating to and rapid cooling from beta-phase temperatures are effective in refining structures of cast or gamma-fabricated uranium to a grain size of about 300 μ . Such refinement may not be possible for appreciably larger sizes, except for the surface, since it may not be possible to attain sufficiently high cooling rates. For smaller specimens of alpha-fabricated uranium, a single beta heat-treatment followed by a water quench under the proper conditions can result in a grain size of 200 to 500 μ . A recrystallization anneal in the high alpha-phase temperature range can further refine the grain size to a range of 80 to 200 μ . All these structures should be randomly oriented.

Heat-treatments involving gamma-phase temperatures have so far not developed any advantages over the beta heat-treatments.

Fig. 11—High-purity uranium cooled from 725°C at a rate of 4°C/hr (polarized light). (Magnification 75 X.)

Fig. 12—High-purity uranium water quenched from 725°C (polarized light). (Magnification 75 X.)

Fig. 13—Microstructure of specimen (tension side) bent 90 deg at 600°C, showing deformation by subgraining (polarized light). (Magnification 75 $\times$.)

4 ALLOYING

Although unalloyed uranium can be made fine grained by appropriate heat-treatments, as described earlier, the grain size can easily be coarsened by heating into either the beta or gamma phase. It would be desirable if some means could be found to prevent this grain growth when a fuel element is heated into the beta or gamma phase. The most logical approach is the use of alloying additions. It must be recognized, however, that for a natural uranium fuel element the choice and amount of alloying additions are limited by their neutron cross sections, particularly for thermal reactors.

For these reasons exploratory work in the United States has been concentrated on alloys containing zirconium, silicon, aluminum, niobium, molybdenum, chromium, vanadium, and titanium. Of these, zirconium, silicon, and chromium have been found to be the most effective from an over-all standpoint. Some investigations have also been made on the effect of varying carbon contents in unalloyed uranium. However, the major goal in this work was to minimize longitudinal dimensional changes in fuel elements rather than to eliminate surface roughening.

On paper, binary alloys containing bismuth, lead, or tin would be good from a neutron cross-section standpoint, but, because of either the extremely low melting point or relatively high volatility of these elements, preparation of these alloys is difficult and little attention has been given to them. Compounds of uranium with bismuth and lead also have a tendency to be pyrophoric.

Table 3 is included here to show the relative importance of the poison effect of each alloying addition. Each alloy listed contributes essentially the same poison content for the concentration shown. At these concentrations, zirconium, silicon, and chromium definitely result in grain refinement whereas the effect of aluminum is doubtful. Niobium, molybdenum, vanadium, and titanium have grain-refining effects, but generally only at higher concentration levels.

Before discussing specific alloys, it should be pointed out that data reported from different sites on grain sizes of different alloys and even of the same alloy may differ appreciably

Table 3—CONCENTRATIONS OF ALLOYING ELEMENTS THAT PRODUCE THE SAME THERMAL-NEUTRON POISON EFFECT

Alloying element	Composition	
	Wt. %	At. %
Zirconium	2.0	5.1
Silicon	0.87	7.0
Aluminum	0.46	4.0
Niobium	0.36	0.91
Molybdenum	0.15	0.36
Chromium	0.064	0.29
Vanadium	0.041	0.19
Titanium	0.031	0.15

since in most cases grain-size charts have not been developed. Differences of 50 or even 100 per cent should not, therefore, be taken as too significant, particularly if the comparison is between two alloys of quite different microstructural characteristics. The size of sample and purity of metal may have additional effects on the grain size. Grain size, however, may not be the only important factor affecting surface roughening of fuel elements during irradiation. Other factors, such as the physical and mechanical properties of the alloys, may be equally important, and these may differ considerably from those of unalloyed uranium. Differences in microstructural features may also contribute to the extent of irradiation instability.

One of the earliest surveys of a wide range of alloys was performed at the Battelle Memorial Institute (BMI) by H. A. Saller, J. R. Keeler, and N. S. Eddy. This survey included 38 different alloying elements and was not limited to the alloys that would be of interest to natural uranium fuel elements for thermal reactors. Alloys were melted in graphite crucibles (with either vacuum or argon atmosphere), cast into graphite molds $1\frac{5}{8}$ in. in diameter, and rolled to $\frac{7}{8}$ in. in diameter at 600°C. After rolling, samples were heated into the beta range for unalloyed uranium (700°C) and water-quenched, and the as-rolled and beta-treated grain sizes were compared with the unalloyed uranium. Grain structures were considered to be refined if in the heat-treated samples the grain size was about 60 μ or less, the normal grain size for unalloyed uranium fabricated in the high alpha temperature range.

Table 4 lists the alloys that showed promise of meeting this criterion with their respective grain sizes after heating for 5 and 15 min at 700°C and water quenching.

The structures of unalloyed uranium quenched from the beta phase had an average grain size of about 150 to 200 μ .

Chromium additions appeared to have the strongest grain-refining effect. Figure 14 shows the structures of four chromium alloys with increasing alloy content. At a level of 0.18 at. % chromium (0.04 wt. %), most of the refinement has taken place; only minor further improvement was obtained with higher chromium contents.

Other alloys that had a grain size of 65 μ or less after a 5-min soak at 700°C were 0.55 at. % boron, 1.7 at. % iron, 2.04 at. % gallium, 1.34 at. % manganese, 0.97 at. % molybdenum, 0.93 at. % silicon, 2.8 at. % titanium, and 0.63 at. % zirconium. After a 15-min soak at 700°C, only the boron, chromium, manganese, molybdenum, and silicon alloys retained a 65- μ grain size.

Table 5 lists other alloys that showed little, if any, refinement, compared with the unalloyed uranium samples, after quenching from the beta phase.

4.1 Uranium-Chromium Alloys

In the course of other alloy studies, it was observed that in uranium-chromium alloys the beta phase could be retained (in a metastable condition) at room temperature by quenching

Table 4—ALLOYS SHOWING GRAIN REFINEMENT AFTER A BETA QUENCH

Alloying element	Composition		Average grain diameter, μ	
	At. %	Wt. %	5 min at 700°C and quenched	15 min at 700°C and quenched
Unalloyed			150	150
Unalloyed			200	200
Boron	0.37	0.017	90	90
	0.55	0.025	65	65
Barium	0.87	0.50	90	150
Beryllium	0.53	0.02	90	200
Bismuth	0.006	0.005	65	120
Carbon	2.0	0.10	120	150
Chromium	0.18	0.039	65	65-90
	0.60	0.13	45	45
	0.73	0.16	65	45
	0.78	0.17	15	35
	1.24	0.27	35	65
Copper	0.19	0.051	90	120
Iron	0.09	0.02	90	150
	1.7	0.40	65	90
Gallium	2.04	0.61	65	65
Manganese	0.10	0.02	90	120
	1.34	0.31	65	45
Molybdenum	0.14	0.057	90	120
	0.97	0.39	65	65
Lead	0.003	0.003	90	150
Silicon	0.05	0.006	90	150
	0.21	0.025	90	120
	0.46	0.054	65-90	65
	0.93	0.11	65	65
	1.45	0.17	65-95	90
Strontium	0.13	0.048	90	120
Thorium	0.03	0.03	90	150
Titanium	2.8	0.58	65	90
Zirconium	0.05	0.019	90	120
	0.36	0.14	65-90	150
	0.55	0.21	65-90	120
	0.63	0.24	65	90

0.23 at. % chromium

0.18 at. % chromium

0.78 at. % chromium

1.24 at. % chromium

Fig. 14—The effect of chromium on the structure of beta-quenched uranium. (Magnification 75 $\times$.)

Table 5 — ALLOYING CONSTITUENTS
THAT PRODUCED LITTLE GRAIN REFINEMENT

Alloying element	Composition		Average grain diameter, μ^*
	At. %	Wt. %	
Unalloyed			150–200
Silver	<0.044	<0.020	120
Aluminum	3.53	0.412	150
Barium	0.087	0.050	90
Bismuth	0.012	0.011	150
Calcium	0.18	0.030	200
Cadmium	<0.001	<0.0005	150
Cerium	<0.017	<0.01	150
Cobalt	4.1	1.05	150–200
Germanium	0.695	0.214	120
Lithium	<0.033	<0.001	>200
Magnesium	0.15	0.015	200
Niobium	0.078	0.030	150
Palladium	1.23	0.56	120
Platinum	1.32	1.09	120
Antimony	0.39	0.20	120
Tin	0.32	0.16	150
Tantalum	0.344	0.262	120
Terbium	0.43	0.23	>200
Vanadium	0.61	0.13	120
Tungsten	0.70	0.54	120
Zinc	0.003	0.0008	120

*5 min at 700°C and quenched.

from the beta temperature region. This observation pointed to the possibility of developing suitable heat-treatments for this alloy system which would produce a desired and controllable grain size in the alpha phase. With this purpose, White¹² of KAPL investigated the isothermal transformation kinetics of a series of alloys.

Four alloys were used: 0.3, 0.6, 1.8, and 4.0 at. % (0.066, 0.132, 0.40, and 0.90 wt. %) chromium. Three-quarter-inch-diameter ingots were swaged to $\frac{1}{4}$ in. at approximately 275°C, with annealing at 550°C after every 75 per cent reduction in area.

After heat-treatment to remove the effects of cold work, 4-in.-long specimens were heated at 715°C for 5 min and transferred quickly to a bath at some desired alpha-phase temperature and held there until the specimen was completely transformed, the degree of transformation being recorded by a dilatometer. After transformation, time-temperature-transformation (T-T-T) diagrams were obtained from the data and grain sizes were determined by metallographic examination.

For the two alloys of lower chromium content (0.3 and 0.6 at. %), the T-T-T diagrams exhibited both upper and lower C curves, whereas the higher concentration alloys (1.4 and 4.0 at. % chromium) had only the upper C curve.

At high transformation temperatures the final grain size was very sensitive to temperature, rapidly decreasing with decreasing temperature. At lower temperatures the effect is less, with the grain size decreasing to a minimum size and then increasing with successively lower transformation temperatures for those alloys having a lower C curve.

The grain sizes for the 0.6 at. % alloy specimens as a function of transformation temperature were as follows:

Isothermal transformation temp., °C	Position on T-T-T diagram	Average grain diameter, μ
624	Upper C, above nose	500
574	Upper C, at nose	100
515	Upper C, below nose	40
452	Upper C, below nose	35
396	Near transition	35
377	Lower C, above nose	75
265	Lower C, near nose	75
100	Lower C, below nose	70

The optimum grain size was obtained during isothermal transformation at a temperature as low as possible within the upper C. For practical use, however, the time required may have to be at a somewhat higher temperature, such as 525°C for the lower chromium alloys and 575°C for the higher percentage alloys, since at the temperature of maximum refinement the time required for complete transformation may be prohibitively long.

All microstructures were essentially the same as in Fig. 14, except for varying grain size, despite the fact that the two C curves indicate different mechanisms of transformation.

In subsequent work by H. A. Saller, F. A. Rough, and W. Chubb of BMI, similar grain sizes were obtained for a 0.35 at. % chromium alloy water quenched from the beta phase (15 min at 730°C). Annealing the water-quenched alloy at 600°C for 1 hr, however, increased the grain size from 70 to 200 μ , indicating that the chromium alloy after a standard beta quench is in a metallurgically unstable condition. Saller et al. also determined that for the 0.35 at. % chromium alloy neither the temperature within the beta phase from which the alloy was quenched nor the quenching rate itself had any significant effect on the grain size.

4.2 Uranium-Silicon Alloys

It has been pointed out above that silicon has a beneficial effect in maintaining a fine grain size in alpha-wrought beta-treated uranium. Silicon has also been evaluated by the National Lead Co. of Ohio as a grain-refining addition for centrifugally cast uranium slugs, a process described in another paper at this meeting. Attainment of fine as-cast grain size would probably eliminate the necessity for subsequent heat-treatment for this purpose.

The effect of three levels of silicon additions for centrifugally cast slugs is reported as follows:

Silicon content, ppm	Grain size, μ
880	390
1235	286
2190	192

Macrographs of each of these structures are shown in Fig. 15. Up to a level of about 800 ppm silicon, the as-cast grain size is normally about 1000 μ . A sharp decrease in grain size is obtained at this level, with additional refinement occurring more slowly with higher silicon contents. Although grain refinement to the size of normal hot-worked unalloyed uranium has not been attained, the structures are typical of normal beta heat-treated uranium. Uranium silicide apparently acts as a nucleating agent during the phase transformations upon cooling. The silicon content required for grain refinement of castings may be affected by both the method and size of casting.

880 ppm silicon

1235 ppm silicon

2190 ppm silicon

Fig. 15 — As-cast uranium-silicon alloys (polarized light). (Magnification 20 x.)

4.3 Uranium-Zirconium Alloys

Considerable attention has been given to uranium alloys of low zirconium content since they (1) can be made with fine grain size, (2) are among the most desirable alloys from the neutron poisoning standpoint, and (3) have good fabricating properties. Use of a 2 wt. % zirconium alloy in the coextrusion process is described in another paper at this meeting.

The microstructures of these zirconium-uranium alloys differ considerably from chromium, aluminum, or silicon alloys. Whereas the chromium alloys appear similar to normal beta-quenched structures and the aluminum and silicon alloys are characterized by the large amounts of second-phase precipitate that normally is uniformly distributed, low zirconium-uranium alloy structures are more acicular. Figure 16 shows typical structures of 2 wt. % zirconium-uranium alloy specimens as cast, slow cooled from the gamma phase, and water quenched from the gamma phase. The as-cast and gamma-heated slow-cooled structures are similar, consisting of platelets or needlelike units intimately interwoven. After water quenching the structure becomes more acicular and is more difficult to etch. Intermediate cooling rates produce microstructures of an intermediate character, with the etching characteristics becoming more difficult as the quenching rate is increased. If the quenched structures are tempered just below the eutectoid temperature of 610°C, the structure will spheroidize, although the rate of spheroidization is extremely slow.

It is difficult to state a definite grain size for these acicular microstructures. However, it could be said that the size of the platelets is 10 μ or less and that the apparent gamma grain size in the water-quenched specimens is of the order of 25 μ .

Similar acicular microstructures are obtained in low titanium alloys. Figure 17 shows a 0.95 wt. % titanium alloy,¹³ about the same atomic per cent of alloying additive as in a 2 wt. % zirconium alloy, that had the same basic heat-treatment as the zirconium alloy shown in the lower portion of Fig. 16, i.e., water quenched from 800°C. Except for grain size the structures are nearly indistinguishable.

4.4 Uranium-Aluminum Alloys

Uranium-aluminum alloys have not been investigated as thoroughly as the chromium, silicon, and zirconium alloys, but some interesting data have been obtained. Structures of alpha-fabricated alloys containing about 5 at. % aluminum contain large amounts of fine dispersed UAl_2 phase that is difficult to resolve satisfactorily. The grain size could not be determined by ordinary metallographic procedures. When such structures were heated into the beta temperature region, no basic change in the microstructure was observed, but areas were developed which had the shape of large grains and which polarized slightly.⁵

Back-reflection X-ray pictures of this alloy in both the alpha-extruded and beta heat-treated conditions, taken in order to compare the actual grain size of the uranium, indicate that the as-extruded structure may have been fine grained but that the samples that were heat-treated for 30 min in the beta phase definitely had large-grained characteristics. Thermal cycling of a similar alloy by Ziegler and Chiswick¹⁴ showed considerable surface roughening, although somewhat less than that for unalloyed uranium. Later work¹⁵ at BMI indicated that more dilute alloys with aluminum contents up to 2.9 at. % had only slight grain-refining effects.

Microstructures of a 2.6 at. % aluminum alloy that has been beta treated and annealed are shown in Fig. 18. Although in a 5 at. % aluminum alloy so much precipitate was present that the basic grain structure could not be seen under polarized light, it is easily visible at this level.

4.5 Other Alloys

In addition to the above alloys, dilute niobium, molybdenum, vanadium, and titanium alloys have been investigated by ANL using thermal cycling techniques. Most of the data has already been published¹⁴ and will not be repeated here. It was concluded from this study, however, that, compared with unalloyed uranium, alloying additions of 0.79 wt. % molybdenum, 0.07 wt. % sili-

As cast

Heated 800°C 15 min, slow cooled

Heated 800°C 15 min, water quenched

Fig. 16—Uranium—2 wt. % zirconium alloy (polarized light). (Magnification 500x.)

Fig. 17—Uranium—0.95 wt. % titanium alloy heated at 800°C 2 hr and water quenched (polarized light). (Magnification 200 $\times$.)

con, 0.56 wt. % aluminum, 0.035 wt. % titanium, and 0.33 wt. % vanadium decreased the surface roughening of specimens quenched from either the beta- or gamma-phase temperatures. In the case of molybdenum an addition of 2 wt. % was needed for complete elimination of surface roughening. The minimum amounts of other elements required to attain a similar improvement were not determined. For cast specimens 2 wt. % molybdenum and 0.6 wt. % niobium alloys showed no surface roughening on thermal cycling.

5 CONCLUSIONS

1. The maximum grain refinement of unalloyed uranium is accomplished either by hot working in the high alpha-phase temperature region or by cold working followed by recrystallization. These methods, however, promote undesirable preferred orientation that results in dimensional instability of fuel elements during irradiation.
2. Large-grained uranium, either cast or gamma annealed, can be refined to an average grain size of 300 μ diameter by multiple heating and rapid cooling through the beta-alpha transformation temperature. This refinement is more easily obtained in ingot uranium than in dingot uranium, probably because of the higher content of some of the various impurities.
3. Uranium that has been cooled through the beta-alpha transformation temperature at a sufficiently rapid rate will recrystallize upon annealing in the high alpha temperature range. This recrystallization will, under the proper conditions, produce an average grain size of 80 to 120 μ in small specimens. Complete refinement of the as-quenched structure is not obtained in large specimens since the maximum attainable cooling rate is too slow.
4. Heat-treating in the gamma phase followed by quenching does not have any apparent advantage over beta heat-treatments.
5. Uranium may be grain refined by the use of dilute alloying additions. Chromium, silicon, and zirconium are among the most effective alloying elements for this purpose.

6. Niobium, molybdenum, vanadium, and titanium are also effective in promoting grain refinement, but their neutron poisoning effect is higher than that of the chromium, silicon, and zirconium alloys.

Polarized light

Bright field

Fig. 18—Uranium—2.6 at. % aluminum alloy hot rolled at 620°C, heated 30 min at 730°C and water quenched, and reheated 1 hr at 600°C and furnace cooled. (Magnification 100×.)

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Techniques for Canning and Bonding Metallic Uranium with Aluminum

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ABSTRACT

This paper is primarily concerned with the technology of canning and bonding metallic uranium with aluminum for reactor service. The historical background leading up to the development of the now classical fuel element, a cylindrical uranium slug canned in aluminum, is traced. The technological factors associated with the design and manufacture of these reactor components are reviewed.

The use of an aluminum-silicon alloy layer to retard interaction between aluminum and uranium and to promote the transfer of heat across the interface is demonstrated. A metallurgical bond can be achieved by dipping aluminum and uranium in molten aluminum-silicon eutectic alloy; a thin adherent layer of the compound $U(Al, Si)_3$ is thus formed at the $AlSi/U$ interface which acts as an effective diffusion barrier up to a temperature of about $350^\circ C$. The importance of the closure problem is discussed.

A detailed description of the process developed and adopted for manufacturing $AlSi$ -bonded slugs for fueling the ORNL Graphite Reactor is given. Techniques for canning the fuel element for the Brookhaven National Laboratory reactor, as well as methods of testing, are briefly reviewed.

1 INTRODUCTION

Interest in the canning of uranium with aluminum dates back to the early days when the chain-reacting pile was first successfully demonstrated in 1942. The main task of the U. S. reactor program at that time was to exploit the newly found source of energy to produce and chemically separate plutonium for the war effort. It soon became evident, however, that the huge quantities of heat generated during the process of nuclear fission would have to be removed in order to permit operation at lower temperatures and thus prevent structural damage to the materials of construction. The original effort directed toward solving the heat removal or cooling problem led to the development of the now classical fuel element—a cylindrical uranium slug canned in aluminum.

This paper is written to acquaint potential fabricators with the status of technology on the canning and bonding of metallic uranium with aluminum. It deals mainly with the various techniques developed for manufacturing natural-uranium fuel elements protected with aluminum for reactor service. The use of diffusion barriers to arrest interaction between aluminum and uranium and bond aids to promote the transfer of heat across the interface is discussed. The performance of these fuel elements under irradiation is not included in the scope of this report; it is the topic of another paper presented at this conference.

2 BACKGROUND INFORMATION

Nuclear fission makes possible the generation of huge quantities of heat from a small quantity of matter. Theoretically there is essentially no limit on the rate at which heat is produced in a nuclear reactor, but in practice the amount of heat available is limited by the temperatures that the materials of construction can withstand.

An important factor in reactor design is the power density, in watts per cubic centimeter or British thermal units per cubic foot, at which the reactor operates. To produce any kind of a product (neutrons, plutonium, radioisotopes, heat, or electrical power) in large quantities efficiently, a high neutron flux, which means many millions of fissions per second, is required. Each fission liberates approximately 200 mev of heat energy that must be removed and wasted or converted into useful heat or electrical power. The basic engineering problem in the design of high-performance reactors, therefore, is one of efficient heat removal or cooling.

The fuel element is the central and most important single component in the heterogeneous reactor system and, as such, demands that the utmost attention be given its design and manufacture. It is the site where useful neutrons are born, and it is the source where the energy of fission is converted into useful heat. In manufacture a premium is placed on integrity or reliability because maintenance is impractical after the component is once placed in service. This usually means 100 per cent inspection of all components prior to service and the ultimate goal of no service-induced failures.

Uranium is reactive in the metallic state and must be protected for most service applications. It tarnishes on exposure to the ambient atmosphere and reacts readily to form compounds with carbon, oxygen, hydrogen, and nitrogen at elevated temperatures. The metal corrodes rapidly in boiling water and is subject to chemical attack by a large variety of inorganic and organic reagents.

When used as a source of nuclear fuel, containment of the uranium, as well as protection, is an important engineering consideration. Heat and fission products of a highly poisonous nature are created in sizable quantities during the process of fission. Heat removal is accomplished, of course, by the use of coolants. But, unfortunately, most of the suitable heat-transfer fluids which otherwise meet the rigorous demands for reactor service cannot be employed in direct contact with the active metal. In addition, measures must be taken to retain the by-products of fission in the fuel element and thereby prevent the needless spreading of radioactivity throughout the coolant system. In most reactor applications, therefore, it becomes necessary to sheath or jacket uranium in a suitable material to contain the products of fission as well as to afford the needed corrosion protection.

The main reasons why aluminum was selected as the fuel-canning and process tube material for construction of the first U. S. built reactors are quite well known. The scarcity of beryllium, the poor corrosion resistance of magnesium in air and water, and the unknown potential of zirconium at the time led to the obvious choice of aluminum. The metal is cheap, readily available, and amenable to most of the conventional fabrication operations. It has a low absorption cross section for thermal neutrons, good heat-transfer properties, and the necessary strength and ductility to withstand the thermal stresses and gradients encountered in natural-uranium reactors designed for plutonium production and research. Aluminum has excellent corrosion resistance in contact with air and water at the temperatures involved. It does not have serious poison-forming tendencies nor is it subject to structural damage under irradiation.

Many of the techniques widely employed by industry for the protection of metals are of little or no value in the manufacture of uranium fuel components. Coated metals prepared by hot dipping, spraying, etc., have a weak cast structure and are not structurally dependable. Likewise, impregnated metals such as are produced on steel by calorizing, as well as metals plated by electrodeposition, find no direct application. A rather wide application can be found in the nuclear field, however, for the use of clad or other wrought products.

Operation of the reactor at high power levels without the attendant impairment of structural materials can be achieved by proper design of the fuel element and cooling. It is common

practice to use extended-surface fuel elements to increase the heat-transfer surface available for each gram of fissionable fuel. Another expedient is to employ a metal-to-metal bond between the fuel and the container material in order to facilitate flow of heat across the interface. Only three fuel-element configurations are currently employed in the present-day reactor powered with natural uranium. These are solid cylindrical slugs or rods, tubular slugs or rods, and flat plates. The heat-transfer medium commonly used is either gas or water. It is impractical to consider a liquid-metal bond which is molten at the operating temperature because aluminum is attacked by most of the molten metals suitable for reactor application.

3 URANIUM-ALUMINUM DIFFUSION

In many respects the combination of uranium and aluminum is incompatible for solid-state bonding. Brittle compound layers readily form at the bond interface owing to the inherent nature of the phase equilibrium system which shows the existence of three intermetallic com-

Fig. 1—Surface appearance of an unbonded slug before and after 200-hr furnace test, showing blister formation.

pounds. Differences between the two metals in thermal-expansion and thermal-conductivity properties, as well as resistance to flow under deformation, lead to additional trouble. Because of the dissimilar nature of the metals, the problem of protecting or containing uranium with aluminum is a difficult task.

The original slugs for the ORNL Graphite Reactor were simply canned without bonding as a matter of expediency, and 50 of 160,000 failed during the initial stages of operation. Although this represents only 0.03 per cent, the nature of the failure caused serious trouble. The slugs swelled, stuck in the channels, and blocked the flow of air coolant, and, in cases where the can ruptured, the air became polluted. The failures were due to (1) air leaks in the welds, causing the formation of uranium oxide which has four times the specific volume of the initial metal from which it formed and (2) penetration of the aluminum-can wall because of interaction of uranium and aluminum at 250°C.

Tests on heating slugs in the furnace to 450°C reveal that uranium will diffuse through an aluminum can of 30 mils wall thickness in approximately four days.¹ Diffusion at this temperature sometimes results in the formation of conical-shaped blisters that contain gas. The surface appearance of an unbonded slug before and after a 200-hr furnace test at 450°C, showing blister formation, is illustrated in Fig. 1. Limited data from lower temperature tests gave inconclusive results.

The behavior of uranium and aluminum in carefully prepared diffusion couples has been studied² in the temperature range 200 to 390°C. Depending, of course, on the pressure and surface condition, interaction is observed to occur in a matter of hours at temperatures as low as 200°C. Figure 2 is a micrograph showing the appearance of the interface in an aluminum-uranium couple after heat-treating for 263 hr at 250°C. X-ray analysis shows that the structure of the compound layer formed is predominantly UAl_3 . Only minor amounts of UAl_2 and UAl_4 are sometimes observed. The line of demarcation is sharp at both the alpha-uranium and the aluminum phase boundary, indicating limited solid solubility that is due to the difference in crystal structure and atomic radii. The resulting intermetallic compound layer firmly bonds to the uranium but only poorly to aluminum. It is brittle, measuring approximately 500 DPH at room temperature, and can be easily fractured to interrupt contact between the two primary phases. Potential impairment of heat flow due to separation at the bond interface is another disadvantage of using aluminum in direct contact with uranium at elevated temperatures. This problem is naturally more acute in gas-cooled reactor systems because of the large temperature drop at the gas-metal interface.

4 USE OF DIFFUSION BARRIERS AND BOND AIDS

The desire to operate the reactor at higher power densities and thus achieve greater efficiency led early investigators to explore the possibilities of using diffusion barriers and bond aids in the make-up of natural-uranium fuel elements canned in aluminum. Barriers are of interest, of course, to inhibit the interdiffusion of uranium and aluminum at temperatures above 200°C, whereas bond aids are needed to enhance the flow of heat across the interface.

Unfortunately, most of the early techniques devised to arrest the uranium-aluminum reaction have a common disadvantage, i.e., impairment of heat flow. The refractory oxides of uranium possess good antidiffusional properties; however, the difficulty in maintaining a continuous adherent film on the uranium surface precludes their use. The British employ colloidal graphite as a diffusion barrier in the manufacture of uranium slugs for their British Experimental Pile O (BEPO) reactor. Interaction can be retarded also by the use of an anodized coating on the surface of the aluminum in contact with uranium; this is the basis of the process developed for preparing fuel elements for the Brookhaven National Laboratory (BNL) reactor.

Adequate bonding and impediment of the uranium-aluminum reaction can be achieved by the use of an aluminum-silicon alloy. A metal-to-metal bond is formed on dipping uranium and aluminum into a molten aluminum-silicon alloy of eutectic composition. The uranium reacts with molten $AlSi$ to form a thin, adherent layer of $U(Al, Si)_3$ at the $U/AlSi$ interface, which acts as a deterrent to diffusion in the 200 to 350°C temperature range. The alloying product $U(Al, Si)_3$ is rather brittle, measuring approximately 700 DPH at room temperature; hence care must be exercised during handling to prevent fracture of the compound.

In canning uranium slugs by this technique, measures must be taken to ensure that the uranium surface is properly wet and a continuous compound layer is formed; otherwise, diffusion

Fig. 2—Cross section of the diffusion zone of a uranium-aluminum couple annealed at 250°C for 263 hr at 5 tsi pressure. As polished. (Magnification 150 x.)

will ensue and blister formation may occur at elevated temperatures. Such objectional action can lead to penetration of the can wall and rapid oxidation of the uranium core. Figure 3 illustrates a ruptured can caused by a diffusion blister.

Fig. 3—Can rupture in bonded slug caused by diffusion blister at unwet area.

Green³ has measured the rate of diffusion in U/Al and U/AlSi couples in the temperature range of 200 to 390°C. The maximum penetration coefficient for the diffusion of uranium into aluminum and aluminum-silicon alloy is plotted as an inverse function of the absolute temperature in Fig. 4. This plot shows that AlSi offers essentially no advantage above 350°C but definitely impedes diffusion at lower temperatures. Figure 5 is a composite macrograph showing the diffusion products formed in couples annealed for 15 days at 200, 250, and 300°C.

The use of a thin layer of nickel to serve the dual purpose of a diffusion barrier and bond aid has been studied.⁴ During hot pressing, nickel reacts with both uranium and aluminum to form a host of intermetallic compounds. Yet, by careful control of the time, temperature, and pressure, a reasonably strong and adherent bond can be obtained.

5 IMPORTANCE OF THE CLOSURE PROBLEM

In jacketing uranium slugs with aluminum for reactor service, a sound closure is vital for the successful performance of the component. Shrinkage porosity, blow holes, cracks, foreign impurities, and other defects causing discontinuities in the closure must be avoided. The type of failure that can occur in unbonded slugs because of pinhole leaks in the weldments is illustrated in Fig. 6. Generally, failures of this nature can be avoided by employing reliable inspection and nondestructive test methods prior to placing the component in service.

Fusion welding by the argon-shielded tungsten-arc process is generally employed in the U. S. to obtain a sound joint between cap and can. It is the only process found suitable for welding aluminum without the aid of a welding flux. A steady arc is maintained by superimposing a high-frequency current on the welding circuit of standard a-c equipment.

A closure with a high degree of integrity can be obtained by this technique without the aid of filler wire. The resulting weldment is relatively free of discontinuities caused by oxide films, porosity, or lack of fusion. The weld structure is sound, uniform in strength, and smooth in appearance.

Uranium slugs prepared by the AlSi canning process offer greater insurance against failure due to faulty closure. The over-all closure is structurally sounder since there is double protection against air or water leakage by virtue of the presence of the AlSi layer between slug and can material.

Fig. 4—Maximum anticipated penetration coefficient, k_2 , for the diffusion of uranium into aluminum and aluminum-silicon alloy from the original U/Al or U/AlSi interface.

Fig 5—Effect of temperature on diffusion in U/AlSi couples annealed 15 days. A, 200°C. B, 250°C. C, 300°C, lightly oxidized after polishing. (Magnification 250 x.)

Fig. 6—Photograph showing early-stage failures resulting from faulty welds on slugs heated at 250°C.

6 MOLTEN-METAL CANNING

Experience has shown that aluminum-clad uranium fuel elements must possess the following general characteristics: (1) a barrier layer to prevent diffusion between the aluminum and the uranium, (2) a strong and continuous metallurgical bond between the uranium and the aluminum, and (3) a closure between the cap and can material with a high degree of integrity.

These requirements have been met by the development of a liquid metal or AlSi canning technique. The significant features of a slug canned by this technique are illustrated in the schematic drawing of Fig. 7. The presence of a thin layer of the intermetallic compound $U(Al, Si)_3$ at the U/AlSi interface retards interdiffusion of uranium and the aluminum-silicon braze layer. This layer is sufficiently thin (approximately 0.0005 in. thick) to adhere tightly to the uranium. The presence of an aluminum-silicon braze layer approximately 0.005 to 0.020 in. thick forms a thermal conducting bond between the aluminum can and the coated slug.

6.1 Flux-Alpha Canning Process

The ORNL Graphite Reactor is powered by natural-uranium fuel elements fabricated by the flux-alpha canning process. The process is so named because all the canning operations are carried out below the alpha-to-beta transformation temperature in uranium, and the use of molten-salt flux is an important feature of the process. The procedures and specifications for this process have been previously reported;⁵ therefore only the significant operations are discussed briefly below.

The component parts used in the manufacture of the ORNL Graphite Reactor fuel elements are illustrated in Fig. 8. The aluminum cans are deep drawn from commercially pure aluminum sheet stock, and caps are machined from wrought stock free of porosity. The uranium slugs are machined from alpha-rolled rods, degassed and beta heat-treated to provide a randomly orientated grain structure to reduce dimensional changes that occur during irradiation. Slugs are heat-treated by immersion for 90 sec in a carbonate salt bath held at 730°C and quenched

Fig. 7 — Schematic section of canned fuel slug.

Fig. 8—Exploded view of component parts for make-up of ORNL Graphite Reactor fuel slugs.

TECHNIQUES FOR CANNING AND BONDING METALLIC URANIUM WITH ALUMINUM

Fig. 9—Sequence of operation for canning ORNL Graphite Reactor slugs by the flux-alpha canning process.

into cold flowing water. Although not essential, slugs should preferably be heat-treated prior to final machining to avoid the slight pitting that develops on the uranium surface during heat-treatment.

A simplified flow diagram of the major operations in the process is given in Fig. 9. Prior to start of the canning operations, all component parts are thoroughly inspected for defects and checked for dimensional accuracy.

The mating surfaces of the component parts to be bonded must be properly cleaned in order to ensure that complete wetting and alloying will occur during processing.⁶ Uranium slugs are prepared by degreasing in stabilized tetrachloroethylene, etching in hot 50 per cent HNO_3 , rinsing in cold flowing water, and drying with a warm air blast. Similarly, the aluminum parts are prepared for canning by vapor degreasing, acid pickling in HNO_3 -HF acid solution, rinsing in flowing water, rinsing in methanol, and drying in a warm air blast. The storage time prior to canning is limited to approximately 2 and 4 hr, respectively, for the uranium and aluminum parts.

Steel sleeves are employed to hold the aluminum cans during the canning operation. The sleeves serve to protect the hot cans from mechanical damage and to protect the outside surfaces of the cans from attack by the aluminum-silicon alloy during immersion in the canning bath. Sleeves are machined from pipe or tubing and are closed by welding a plate on one end. They are blued by heating in air to produce a thin surface oxide film that is not wet by the aluminum-silicon alloy, and they are lapped to provide a smooth internal surface.

In the actual canning operation three molten-metal baths are used. The first bath, referred to as the aluminum-silicon coating bath, is illustrated schematically in Fig. 10. This bath oper-

Fig. 10—Schematic drawing of aluminum-silicon coating bath.

ates at a temperature of 590 to 615°C and consists of three layers: a lead layer on the bottom to preheat the slugs, an intermediate layer of 11.2 to 11.5 AlSi alloy, and a flux layer on top to provide a protective cover on the bath. The flux also serves the important function of the cutting oxide film to ensure uniform wetting of the slug and consists of a mixture of alkali metal halide salts. Slugs are held in basket type tongs, immersed in the lead layer, and held for a period

of 35 sec. On removal the slugs are agitated for 5 sec in the AlSi layer to wash off any adhering lead and to form the diffusion-resistant compound on the uranium surface.

The second molten bath contains only aluminum-silicon alloy that is maintained at a composition of 11.2 to 11.5 per cent silicon and held at a temperature of $595 \pm 5^\circ\text{C}$. It is simply a rinse bath in which the slug is agitated for 3 sec to minimize contamination of the AlSi canning bath.

The third molten bath is the aluminum-silicon alloy canning bath. It is also maintained at 11.2 to 11.5 per cent silicon and held at $593 \pm 3^\circ\text{C}$. The can and sleeve assembly, held in suitable fixtures, is preheated in this bath during the slug-dipping process by submersion to within $\frac{1}{2}$ in. of the top for 45 sec; it is then submerged to fill with AlSi and is held for 40 sec. Immediately prior to submersion the mouth of the can is flared slightly to facilitate insertion of the slug. Just prior to the arrival of the slug, the surface of the bath is skimmed back, and the slug is plunged beneath the surface and held for a maximum of 2 sec. The can and sleeve assembly is raised to the surface to permit the slug to be started into the can and then is lowered gently below the surface as the slug is inserted into the can. The cap is also preheated by submersion in the bath for 20 sec, removed to abrade the mating surface against a transite board, submerged again for 2 sec, and then inserted into the top of the can using pressure and a twisting motion to ensure good contact with the top of the uranium. The complete assembly is removed and shaken to remove excess AlSi from the can top and quenched in cold flowing water after all AlSi remaining at the top has solidified. After the assembly is cool to the touch, the slug is removed from the canning sleeve.

The excess length at the top of the slug is machined off, leaving a cap thickness of about 0.060 in. A weld bead is run around the exposed braze line at the top of the slug using an argon-shielded arc and no filler rod. After welding, the slug is quenched in cold flowing water. The joint of a slug canned by this method is illustrated in Fig. 11.

Fig. 11—Cross section of aluminum-silicon bonded slug showing closure at left. (Magnification $15\times$.)

The bond between the surfaces of the uranium slug and the can wall is illustrated in the photomicrograph of Fig. 12. The $\text{U}(\text{Al},\text{Si})_3$ compound layer is shown bonded to the uranium surface, and the AlSi braze layer has alloyed with the interior of the can wall. The contact between the $\text{U}(\text{Al},\text{Si})_3$ layer and the AlSi is masked by a shadow resulting from a difference in elevation

Fig. 12—Photomicrograph showing bond between uranium core and aluminum can as polished.
(Magnification 100 $\times$.)

between the uranium and the aluminum surfaces on the metallographic specimen. The photomicrograph shown in Fig. 13 was obtained using an incompletely polished specimen to minimize differences in elevation; the bond between the $U(Al,Si)_3$ compound and the AlSi braze layer is more nearly evident.

Fig. 13—Photomicrograph showing $U(Al,Si)_3$ compound layer at U/AlSi interface as polished. (Magnification 200 $\times$.)

After welding, various inspections or nondestructive tests may be applied to reject slugs with faulty bond layers, welds, insufficient cap thickness, and surface defects. For the slugs canned for the ORNL Graphite Reactor, this inspection is limited to visual inspection of the slug and spot checks to determine that the can-wall thickness is within specifications. Visual inspection is facilitated by etching the canned slug in hot 50 per cent HNO_3 solution which darkens any areas where AlSi has penetrated the can wall and brightens the aluminum surface so that defects in the can or in the weld are more easily detected.

Two other preoperational tests are used to ensure that faulty slugs are not charged into the ORNL Graphite Reactor. Slugs are heated in an autoclave in contact with hot steam at 90 to 135 psi pressure for 40 hr. Slugs that show any evidence of pitting or swelling are rejected. Following this they are heated in air at 400°C for 10 days and examined further for evidence of swelling or diffusion blisters.

6.2 Brookhaven Fuel Elements

Aluminum-jacketed fuel elements are used in the Brookhaven Graphite Reactor. Each fuel element consists of 33 4-in. uranium slugs canned in a finned aluminum tube about 11 ft long. A unique feature of these fuel elements is that a helium tube is connected to one end of each fuel element to allow a slight positive pressure of helium to be maintained within the fuel element. The pressure in each tube is monitored to enable the detection of any small leaks that develop during reactor operation.

The fabrication of these fuel elements has been described in detail⁷ and will be only briefly discussed here. The gamma-extruded uranium slugs are annealed in argon at 600°C, finish machined to close tolerances, vapor degreased, and again annealed at 400°C in purified argon. The extruded and drawn aluminum tubing is given an anodized coating about 0.001 in. thick on its interior surface to prevent diffusion and reaction with the uranium slugs. In the canning procedure the tube is closed off at one end by welding on a cap and is then heated under vacuum to remove water from the anodized layer.

The component is designed so that the clearance between the slug and the can is limited to 0.003 and 0.006 in., and a fine finish is required on the slug to avoid abrading the anodized layer. With all slugs in place the excess tube length is cut off, the end cap connecting to the helium tube is brazed to the end of the fuel tube, and the joint is leak tested. The aluminum tube is collapsed to fit tightly around the slugs by application of hydrostatic water pressure at 2500 psi. The helium tube connecting to the leak monitor system is brazed to the end cap, and the entire assembly is leak tested.

6.3 Testing and Inspection

Various methods have been developed for the inspection and testing of aluminum-clad uranium fuel elements. In recent years the rapid development of nondestructive testing methods based on use of ultrasonic, eddy-current, radiographic, and magnetic techniques has resulted in testing methods far superior to those used earlier.⁸ The later techniques can detect flaws in the bond layers and fuel-element closures, measure thickness of claddings, and detect uranium with faulty heat-treatment. The techniques and equipment used have recently been discussed in detail elsewhere^{9,10} and will not be included here.

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Aluminum Sheathing of Flat Uranium Plates by Extrusion Cladding*

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ABSTRACT

The aluminum sheathing of long flat uranium metal fuel elements by means of extrusion cladding has been developed to the point of trial production.

The process consists in using the uranium flat as a moving mandrel over which the sheath is extruded directly, thereby completely encasing the uranium with aluminum as it passes through the die.

Although the sheath may be extruded directly to size, for production reasons it is found to be preferable to extrude the sheath oversized (0.254 cm thick) and machine it to the required thickness (0.063 cm) as a second operation.

Bonding of the sheath to the core may be achieved in the course of extrusion. The bond is stronger and more uniform in the case of a uranium plate which has been nickel plated than in the case of bare uranium. However, in both cases the sheath is found to be in good sonic contact with the core.

Both nickel plated and bare uranium flat elements sheathed in aluminum by the extrusion cladding method have been successfully tested under irradiation. There was no evidence of poor thermal transmission through the uranium-aluminum interface under the test condition of 47 watts/cm².

The method has been developed for cladding all three sizes of flat plates used in making up the fuel rods for NRU. The sizes are as follows:

Uranium plate	Length, cm	Width, cm	Thickness, cm
Large	304.8	5.446	0.434
Medium	304.8	4.983	0.434
Small	304.8	3.109	0.450

1 INTRODUCTION

The NRU is Canada's large research and plutonium producing reactor which is in the process of being commissioned at the present time. It is a heavy-water moderated, heavy-water cooled, natural uranium reactor of 200 Mw rating. The high specific power of this reactor demands a fuel element of extended surface. The design of the fuel rod which was chosen is shown in Fig. 1. It consists of five flat plate uranium metal elements (308.4 cm long) clad in aluminum (99.5 per cent) and assembled in a circular aluminum flow tube.

Fabrication of the flat uranium plates presented no serious problems since the rolling and machining technology of uranium had been well worked out. On the other hand, the satisfactory sheathing of such long flat plates with a minimum of aluminum presented a new challenge.

*This paper may also be identified as Report CRL-46.

ALUMINUM SHEATHING OF FLAT URANIUM PLATES BY EXTRUSION CLADDING

Type 2A.

IS-Al cladding thickness = 0.063 cm

Size of U plate	Length, cm	Width, cm	Thickness, cm
Large	304.8	5.446	0.434
Medium	304.8	4.983	0.434
Small	304.8	3.109	0.450

Fig. 1—NRU fuel-element cross sections.

In the past, the cladding of uranium metal by aluminum has required the accurate mating of the uranium core to a preformed sheath of aluminum followed by some method such as drawing or pressing to bring the metals into good thermal contact. The cladding thickness in this case is limited by the ability of the manufacturer to produce aluminum sections within the required dimensional tolerances. In Canada, aluminum sheaths could not be produced to the required specifications in thicknesses less than 0.100 cm. In order to overcome the problem of accurately fabricating an aluminum sheath, a decision was taken to develop a process whereby aluminum could be extruded directly onto the uranium plate. As well as allowing a cladding thickness considerably less than 0.100 cm, such a process also offers the possibility of bonding the sheath to the core during the extrusion process. A further advantage is that the end straps may be extruded integral with the sheath.

The aim of the development program has been to produce a fuel element with high integrity sheathing (0.063 cm thick) which is sufficiently well bonded to the core to give good thermal transmission under reactor conditions.

Two approaches have been explored to meet these requirements: (1) The extrusion of the sheath directly to finished dimensions. (2) The extrusion of the sheath oversized followed by a machining operation to produce the required thin cladding.

This paper is concerned with the development of this novel method of cladding flat uranium plates and the problems which had to be overcome in order to make it a practical production process.

2 DESCRIPTION OF THE PROCESS

There are several possible methods of attacking the problem of extrusion cladding. The approach which is outlined in this paper was chosen principally to make use of relatively inexpensive equipment which was readily available.

The general conception of the process was settled at an early stage in the development. The principal features are the following:

1. In order to facilitate the flow of aluminum around the periphery of the plate, a double ram arrangement is used to simultaneously extrude two identical billets into the die cavity. To overcome the problem of having to synchronize the displacement of metal in the two streams, it was decided to use two parallel rams fixed to the moving crosshead of a 600-ton vertical hydraulic press. The die is designed to direct the flow of aluminum to the two sides of the plate by deflecting the flow of metal through two 90° angles.

A sketch of the equipment is shown in Fig. 2.

Fig. 2—Sketch of extrusion press.

2. Since three different sizes of plate require extrusion cladding, the die block is designed so that the inserts may be changed with comparative ease without having to use a different die block for each size of plate. Figure 3 shows how the inserts which define the shape of the die cavity are fitted into the die block. Note that the inserts are made up of two parts—the die proper which determines the shape of the extrusion and the core guide which centers the uranium core in the die chamber.

3. Each plate requires the simultaneous extrusion of two aluminum billets 8.57 cm in diameter by 15.25 cm long. As a continuous production operation, this means that each cycle must leave the billet chambers free to accept the billets for the succeeding extrusion.

Fig. 3—Die block showing how die and guide inserts are fitted.

4. Although it was not shown in the previous sketch, the uranium plate must be pushed through the die cavity by a force which is dependent on the design of the die.

5. The uranium core, for reasons which will be described later, cannot be fully heated to the temperature of the die block.

3 OPERATING CONDITIONS

A typical set of operating conditions for the extrusion cladding of 0.063 cm thick sheath is shown in Table 1.

Table 1—TYPICAL EXTRUSION CONDITIONS FOR 0.063-CM SHEATH

Aluminum billet temperature, °C	525 ± 5	
Die temperature, °C	525 ± 5	
Uranium core preheat, °C	200 ± 15	
	End straps	With U core
Ram pressure on billets, kg/cm ²		
Large flats	2180	3240
Medium flats	2150	2720
Small flats	2100	2450
Extrusion ratio		
Large flats	37	126
Medium flats	40	134
Small flats	56	148
Run-out speed, cm/min		
Large flats	330	270
Medium flats	320	265
Small flats	320	320

4 EQUIPMENT

Aside from the die, which will be described later, the only other major component of equipment which required development was the bar feed mechanism. This device serves a double function; it preheats the uranium core to the required temperature (200 to 300°C) and feeds it through the die during extrusion.

Depending on the design of the die, the bar feed mechanism is required to exert a thrust of anywhere from 0 to 2 tons.

The first unit designed for this service is essentially a large electric oven in which the bar feed mechanism is mounted. The feed or "pusher bar" as we call it is driven by a screw about 3 meters in length coupled to a hydraulic motor.

The following poor features have shown up in this design: (1) The feed screw which is unsupported over the 3-meter length develops an excessive whip in the range of operation which is of interest. (2) The method of heating requires all moving parts to operate at elevated temperatures. Lubrication is difficult at these temperatures and the components tend to foul with oxidation products. (3) Atmosphere control is very poor due to the bulky nature of the unit.

However, even with these limitations, the device has given good service during the development of the process.

A new bar feed mechanism has now been developed for production service. The design incorporates the following features: (1) The uranium core is resistance heated by passing a heavy electric current through the bar clamped between two copper electrodes. This has two advantages—not only may the core be heated to temperatures much more quickly (1 min versus 10 to 20 min for the first unit) but also the moving components of the mechanism may be operated at a lower temperature. (2) The bar is supported and propelled by two synchronized

chains driven from the front of the unit. This overcomes the whipping problem of a long drive screw. (3) The much reduced size and better seals allow much better atmosphere control.

Figure 4 shows a sketch of the new unit which has been commissioned recently.

5 PROCEDURE

The sequence of operation is as follows:

1. The pusher bar is brought up to a position in the die block just behind the extrusion chamber.
2. The preheated billets are loaded into the two cavities and the rams are brought down to extrude a short section of aluminum. This is done to equalize the amount of aluminum in the two billet cavities. With the pusher bar in this forward position, back extrusion is avoided during this operation.
3. The pusher bar is then pulled full back and a preheated uranium plate is dropped into position between the guides.
4. The extrusion of aluminum is started.
5. When aluminum is being extruded at the required rate, the pusher bar is engaged to move the core into the die block at a speed designed to match the speed of the extruding aluminum.
6. When the pusher bar has again reached its position in the die block just behind the extrusion chamber, the bar feed mechanism is stopped and the extrusion of a solid end strap of aluminum follows to clear the die of the uranium bar.
7. Two fresh billets of aluminum are loaded and the cycle is repeated.

6 DEVELOPMENT OF THE DIE

The major obstacle in proving the mechanical feasibility of the process was that of developing the proper shape of die cavity. There were four distinct objectives:

1. To achieve a high interfacial pressure between the extruding aluminum and the uranium plate.
2. To achieve a flow pattern of aluminum which would minimize the force required to push the core through the die.
3. To achieve the extrusion of the end straps integral with the sheath.
4. To achieve long die life.

In order to satisfy all of these requirements, a number of conflicting factors had to be compromised in designing the die. For example, the factors which favor high interfacial pressure usually require a higher thrust to push the uranium through the die because of the increased back pressure.

One of the first problems encountered was the jamming of the uranium plate in the guide insert. This resulted from the collapsing of the guide under the pressure required for extrusion of the uranium. The first die design is shown in Fig. 5. The pressure of aluminum required for extrusion was found to collapse the long snout of the guide insert so that the uranium was firmly locked in the die. When this happened, the uranium was heated in the die to the yield point and was ultimately pinched off as shown in Fig. 6.

This condition was relieved by a redesign of the die cavity so that the guide could be made stronger. Rollers were added to the top and bottom of the guide to prevent the uranium from binding at these points. Figure 7 shows a sketch of this revision. Dies designed on this principle can be made to work very well. However, the first extrusions indicated that there was a better flow of aluminum to the top of the die aperture than to the bottom, thus giving an extrusion which turned downward as it emerged from the die. This condition was corrected by incorporating flow deflectors as shown in Fig. 8. Samples of bars extruded from dies with and without flow deflectors are shown in Fig. 9.

Another important aspect of the die design concerns the angle of the guide and die faces to the extrusion direction. This angle is an extremely important factor in determining the

Fig. 4—Bar feed mechanism of advanced design.

Fig. 5—First design of die which resulted in jamming of the uranium plate in guide insert.

characteristics of the extrusion. Figure 10 shows the influence of changing the entrance angle of the aluminum.

Based on the foregoing principles, we have now succeeded in developing two sets of inserts—the one to extrude the sheath to finished dimensions (0.063 cm thick) and the other to extrude the sheath oversized (0.254 cm thick). A cross section of these two is shown in Fig. 11. A comparison shows that the 0.254 cm inserts have a longer bearing and wider gap between the die and the guide. This is necessary to retain a high interfacial pressure and good filling of the end straps.

It would, of course, be preferable to extrude the sheath to finished dimensions and avoid a subsequent machining operation to bring it to size. For this reason, the process of cladding to finished dimensions was carried through to trial production. Over 100 uranium elements have been extrusion clad by this method. However, it was found that the operation required too critical a control over the variables to offer a good basis for continuous production.

One of the most serious problems encountered was that of breakage of uranium. With so thin a cladding, in order to get good filling of the end straps, the die had to be designed to exert a considerable backward force. Thus the uranium required a push in the order of its yield strength to make progress through the die without pinching off. The breakage rate of uranium plates was about 12 per cent, a figure which could not be accepted on a production basis.

Although the uranium was well centered in these thin clad elements (to within ± 0.005 cm), the dimensional control of cladding thickness from one bar to the next was found to be poor.

Fig. 6—A core which has been pinched off in the extrusion chamber. (This happens when the core is jammed by the guide insert.)

Fig. 7—Die redesigned to prevent jamming of uranium in guide insert.

Fig. 8—Revision in die design to equalize flow of aluminum to the top and bottom of the die aperture.

Fig. 9—Comparison of fuel elements extruded from dies with (specimens at left) and without (specimens at right) flow deflectors. Note that there is no curvature of extrusions made with flow deflectors.

Fig. 10—Influence of guide and die angle on extrusion characteristics.

Fig. 11—Comparison of inserts for cladding 0.063-cm-thick sheath and 0.254-cm-thick sheath.

ALUMINUM SHEATHING OF FLAT URANIUM PLATES BY EXTRUSION CLADDING

Similarly, the quality of the end straps was found to vary considerably so that at times a good weld was achieved and at others, no weld at all (Fig. 12).

Fig. 12—Cross section of end straps showing variation in quality when extruded from the same die.

On the other hand, extruding the sheath oversized allows high interfacial pressures with consistently good filling of the end straps and, in addition, there is a strong forward component to the extrusion. In fact, the extrusions can be made self-propelled. Since the centering of the core is largely dependent on the alignment of the guide, there is no loss of accuracy in passing from thin to thick clad elements. Figure 13 shows sections of a plate clad with 0.254 cm of aluminum. Note the excellent centering of the core and the filling of the end strap. Note also the shape of the end of the uranium. In order to assure proper filling of aluminum in the end straps, it was found necessary to taper the ends of the uranium core for a length of about 1.2 cm.

Fig. 13—Sections of a plate clad with 0.254 cm of aluminum. Note the centering of the core and filling of the end strap.

In addition to the above obvious improvements in the process, a number of other advantages are offered by the oversized extrusion approach, as follows: (1) Rejections due to die scores and surface inclusions are eliminated because these defects can be machined away. (2) The die life can be greatly extended. To meet the tolerances required, an on-sized die would

have a life of about 300 extrusions. By extruding oversized, any change in dimension due to die wear can be taken up in the subsequent machining operation. A die life of up to 10,000 extrusions is expected by using the oversized extrusion approach. (3) The probability of surface contamination by uranium is much reduced because no uranium need be exposed in the area where the machining of the sheath is done.

The only disadvantage to extruding the sheath oversized is that a machining operation is required to bring the cladding to size. However, with a well centered core, the machining step is simple and inexpensive.

Table 2 shows a comparison of operation conditions with the thin and thick cladding.

As might be expected with the thicker cladding, the extrusion pressure shows much less variation in passing from the large flat to the small flat. Since the die for the large flat is also the weakest, the significant decrease in extrusion pressure for the thicker cladding is desirable.

Table 2—COMPARISON OF OPERATING CONDITIONS WITH THIN (0.063 CM)
AND THICK (0.254 CM) CLADDING

Die and billet temperature, °C	525 ± 5	
Core preheat, °C	200	
Cladding speed, cm/min	300 ± 40	
	0.063-cm cladding	0.254-cm cladding
Ram pressure on billets, kg/cm ²		
Large flat	3240	2760
Medium flat	2760	2760
Small flat	2450	2660
Thrust required to push uranium through die, kg	1300–1800	90–140 to start, thereafter self- propelled

The most important point brought out by this data is the marked decrease in thrust required to push the uranium through the die when the thick cladding die is used. This advantage has been gained at no loss in the high interfacial pressures required for bonding.

7 LONGITUDINAL AND TRANSVERSE WELDS

With dies which are designed to give high interfacial pressure, there is no difficulty in achieving a good longitudinal weld where the two streams of aluminum meet.

Similarly, no problems have been encountered with regard to the transverse welds which occur between succeeding billets. Simply as a precautionary measure, the billet size has been selected so that the die can be purged of the bulk of the interface before the core is introduced. It is, of course, impossible to completely eliminate the transverse weld since it stretches from one end of the extrusion to the other. However, the weld is so extended that excellent bonding is achieved between succeeding charges of aluminum.

8 BONDING

One of the basic criteria placed on the design of the dies is that bonding must be achieved during the course of the extrusion. The die development program which was discussed earlier has now led to die designs which will achieve bonding. Experiments have been done with both bare uranium and uranium which has been electroplated with a thin layer of nickel (0.0013 cm thick). The tests to date indicate that more uniform and stronger bonds may be achieved with

nickel plated uranium than with bare uranium. Bond strengths of $1,250 \pm 350 \text{ kg/cm}^2$ have been achieved with nickel plated flats, whereas the same dies used with bare uranium give bond strengths which scatter widely and vary all the way from no bond to $1,580 \text{ kg/cm}^2$. Ultrasonic nonbond testing equipment has been set up to give an indication of how tightly the cladding adheres to the core. Tests with this equipment indicate that there is no strong correlation between ultrasonic transmission and bond strength determined by destructive methods. With dies which give bonding on nickel plated cores, ultrasonic transmission indicates over-all bonding when bare uranium cores are put through the same extrusion die.

In general, if good atmosphere control can be kept in the bar feed mechanism, the higher the preheat of the core the better the bonding. Unfortunately, the poor atmosphere control offered by the first bar feed mechanism places a limit on the preheat temperature of the core because of oxidation of the surface. Thus bare uranium cannot be heated much above 200°C without giving rise to a flaky oxide coating. Using the same poor atmosphere control, nickel plated uranium can be taken to a preheat of 300 to 325°C before there is an appreciable discoloration of the surface through the development of an oxide coat. There appears to be no basic reason why excellent bonding should not be achieved with bare uranium provided an inert atmosphere can be maintained during the preheat period.

An interesting aspect of the bonding is that no diffusion zone can be detected in metallurgical sections under $500\times$ magnification.

9 SHEATH DEFECTS

During the course of the development, a number of defects in the form of two types of blisters were found in the sheathing. These had to be eliminated in order to make the process acceptable on a production scale. These defects have been given the names "interface blisters" and "aluminum blisters."

9.1 Interface Blisters

The early extrusions resulted in a high incidence of so called interface blisters. These are blisters that appear between the uranium and aluminum. This type of blister never breaks through the surface of the sheath but rather lifts the sheath away from the core. An example is shown in Fig. 14.

A number of these defects were drilled to sample the enclosed gas. However, in every case the blisters were found to be near perfect vacuums. This eliminated the possibility that air was trapped at the interface in the course of extrusion and suggested that the defects resulted from a contamination of the uranium surface with something that either condensed on cooling or reacted with uranium to give a nonvolatile product.

Subsequent experiments showed that the uranium surface must be kept very clean to avoid this problem. A single fingerprint on a clean bar is sufficient to give a blister.

The problem can be completely eliminated by taking the following precautions: (1) By specifying rigid cleaning and degreasing procedures coupled with strict supervision over the operation. (2) By handling the cores only with clean cotton gloves or clean tongs. In our case, once the uranium core has been cleaned and packaged in a sealed polythene bag, it is never touched again. (3) By taking care not to overlubricate the bar feed mechanism so that the core will not be splattered by contaminants.

It is interesting to note that the extrusion cladding process is an extremely sensitive inspection method for core surface contamination.

9.2 Aluminum Blisters

One of the serious problems that arose during the development of the process resulted from entrapment of air in the die block. Air pockets that are trapped in aluminum cause blisters in the sheath as the aluminum emerges from the die. Unlike the interface blisters,

these aluminum blisters almost invariably rupture at the surface of the extrusion. An example of such a blister is shown in Fig. 15.

Fig. 14—Interface blister.

Fig. 15—Aluminum blister (unruptured).

The most serious source of air entrapment is shown in the insert in Fig. 2. There is a 0.32-cm diametral loading clearance between the billet cavity in the die and the billet. When the billet is first upset, it assumes the shape of a barrel which can trap a skirt of air around the lower periphery of the barrel.

A second and less serious source of air entrapment is the irregular interface which can be left at the top of the last billet to be extruded because of the bonding of aluminum to the ram tips.

Three general approaches are available to overcome the problem of gas entrapment: (1) By designing conditions so that air is completely displaced as the billet is upset. (2) By purging the die cavity with a gas which will react with the aluminum to give an acceptable solid reaction product. (3) By evacuating the die before the billet is upset.

A few exploratory experiments were done with billets which were grooved to facilitate the escape of entrapped air but these gave unsatisfactory results. The use of billets machined to close tolerances and upset under a thermal gradient was also considered. However, calculations indicated that only 10 sec were available between the establishment of the thermal gradient and the upsetting of the billet. The facilities which were available precluded this approach.

A number of cursory tests was done in which the die cavity was flushed with oxygen. These showed some promise but did not give a positive assurance of success. The theory in this case is that if the oxygen was trapped in the hot flowing aluminum, the gas would react with the aluminum to give a small oxide inclusion which would be acceptable.

The most positive results were obtained by evacuating the die. To investigate the feasibility of the operation, a small press of 20-ton capacity was set up with a wire extrusion die designed to accept billets 2.54 cm by 5.08 cm and extrude wire 0.238 cm in diameter. A unique feature of this apparatus is that the billets may be upset in vacuum or in any chosen gas: 97 billets were upset in air; and 171 billets were upset in vacuum. The number of blisters in wire extruded from billets upset in air was 49 compared to 0 for wire extruded in vacuum.

The design of the evacuation sleeves for the full scale operation is shown in Fig. 16. The operation requires that a seal be used which can be quickly made or broken so that successive billets can be received by the die during a production run. Also, a moving vacuum seal is required on the twin rams.

The moving seal on the rams is made of a "V" type sliding rubber seal. To prevent the deterioration of the rubber seal rings, the rams are bored to accept a flow of cooling water. Similarly, the seal to the die block is water cooled to allow the use of a rubber "O" ring. Heat loss from the die is minimized by mounting the die block seal on a thin stainless-steel skirt welded in place.

Figure 17 is a photograph of the vacuum equipment taken at the time of loading the billets.

Although the scheme may be refined for convenient automatic operation, even in its present crude form it adds only 1 to 2 min to the time per cycle.

10 IRRADIATION EXPERIMENTS

Two irradiation experiments have been carried out on uranium plates which have been clad by the extrusion cladding process. The first experiment was done on an unplated speci-

Table 3—EXTRUSION CONDITIONS FOR IRRADIATED FLATS

	Nickel plated flat	Unplated flat
Die temperature, °C	525–530	525–530
Billet temperature, °C	525–535	525–535
Core preheat temperature, °C	300–315	200
Extrusion speed, cm/min	~250	~250
Sheath thickness, cm	Nominal 0.063 (not measured)	0.056 (measured by eddy current method)

men, whereas the second was done with uranium plated with 0.013 cm of nickel. The core material for both was prepared from uranium billets which were alpha rolled and beta heat-treated in a neutral salt bath. The extrusion conditions are shown in Table 3.

Fig. 16—Fittings for evacuating die blocks.

Fig. 17—Evacuation sleeves mounted on the rams of the press.

11 BONDING BEFORE IRRADIATION

Although the specimens themselves could not be destructively tested for bond strength, they were taken in each case from a series of extrusions done under similar conditions. Destructive tests on other samples of the series indicated that the nickel plated flats had bond strengths of $1,250 \text{ kg/cm}^2$, with a standard deviation of 350 kg . In the case of the bare uranium flats, the bond strength showed a wide scatter. In one specimen which was destructively tested, the bond strength varied from a maximum of $1,580 \text{ kg/cm}^2$ to a minimum of 180 kg/cm^2 , with an average of 960 kg/cm^2 . In a second bare uranium specimen, the bond strengths varied from a maximum of 740 kg/cm^2 to a minimum of 190 kg/cm^2 , with an average of 320 kg/cm^2 . These results indicated that the nickel-plated flat selected for irradiation probably had a more uniform and more strongly bonded sheath than the unplated flat. However, prior to irradiation, the unplated flat was inspected by ultrasonic transmission which showed that the sheath made sonic contact over the entire surface of the specimen. (See Table 4.)

Both irradiations were completed without incident or failure.

Table 4—IRRADIATION CONDITIONS

	Nickel plated flat	Unplated flat
Water flow, gal/min*	18.5	19.5
Water velocity over fuel, ft/sec	21	20
Heat output, kw	70	80
Max. heat flux, watts/cm ²	47	48
Max. sheath surface temp., °C	38	49
Average burnup, Mwd/ton	990	850
Maximum burnup, Mwd/ton	1550	1335

*International gallons per minute.

12 POSTIRRADIATION EXAMINATION

Both specimens showed a remarkable dimensional stability. Within the limits of accuracy of measurement (0.3 per cent) there was no change in the over-all length.

13 BONDING

The unplated flat was scanned by ultrasonic transmission following irradiation. As before, the cladding showed that the sheath was in sonic contact with the core over the entire surface of the fuel. It was found that the sheath could not be pulled off the uranium indicating a degree of bonding. However, in sections taken through both the plated and unplated flats, no diffusion zone could be detected under magnification of $90\times$.

It had hitherto been assumed that a strong metallurgical bond was required to give a fuel in which the thermal transmission through the uranium-aluminum interface was reproducibly acceptable. Thus the development of nickel bonded elements had previously received considerable attention. The results of the above experiments indicate that nickel plating may not be necessary in the case of the extrusion cladding method of fabrication in that the plated and unplated flats can be made to give comparable good performance.

Unfortunately, statistically significant results on fuel performance will not be available until there is an opportunity to irradiate comparatively large numbers of fuel rods. However, NRU is expected to be in full operation in the very near future, at which time a loading of fuel made by the extrusion cladding method will be inserted for irradiation. The program calls for the irradiation of fuel elements prepared from both bare uranium and nickel plated uranium.

If the irradiation of large numbers of fuel elements bear out the results of the two irradiations already described, there will be little incentive to retain the nickel plating step which is both expensive in itself and also undesirable from the point of view of neutron economy.

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Coextrusion Applied to the Fabrication of Solid or Disperse Fuel Elements

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1 ZIRCONIUM-CLAD URANIUM FUEL ELEMENTS PRODUCED BY COEXTRUSION

1.1 Introduction

(a) *Statement of the Problem.* The Atomic Energy Commission, Department of Metallurgy and Applied Chemistry, has been conducting studies on a fuel element for a pressurized-water-cooled reactor with high heat flux. Since the cladding metal for such a reactor had already been indicated to be zirconium, a fuel-cladding method was needed which would assure good thermal contact between fuel and clad.

(b) *Particular Difficulties.* The usual cladding methods (either mechanical, by drawing, or hydraulic, by liquid pressure) are not satisfactory.

In effect, by these two methods the clad is simply applied to the fuel by force. The thermal contact between fuel and clad may be insufficient for the high heat flux to be transmitted, with a low-temperature gradient between fuel and cooling liquid. In fact, the temperature of this coolant, pressurized water, would be raised.

1.2 Principle of Method

Accordingly, a more intimate contact between the two elements has been attempted by accomplishing a bond.

This presents, in addition, the advantage of limiting the area of contact between fuel and coolant in the case of accidental puncture of the clad.

The bond is obtained by a process called "coextrusion." It consists in simultaneously extruding the fuel and its clad.

This task has been entrusted to Mr. Sauve, engineer at the Center for Nuclear Study at Saclay.

Mr. Buffet, engineer at the Industrial Shop for Drawing and Sectioning Metals, has been put in charge of the work on extrusion by the Ugine-Sejournet Process.

1.3 Description of Operations

(a) *Preparation of the Composite Billet.* A description of one of the coextrusion experiments that we attempted follows.

A composite billet was made according to the following scheme (Fig. 1):

A billet of uranium-zirconium alloy is cast in a vacuum. The amount of zirconium is 1 to 2 per cent. This billet has a cylindrical shape, and the ends are hemispherical; it is introduced into a tightly fitting zirconium can of the same shape. In this way the entrapment of air which can oxidize the uranium is prevented.

Figure 1

The whole thing is then capped with a cylindrical cover pressed in copper. The purpose of this cover is to (1) protect the zirconium from pollution during the heating and drawing operations and (2) to prevent contact of the hot zirconium can with the cold container.

The uranium-zirconium alloy billet is extended by a cone, also made of uranium-zirconium alloy, that will prevent the copper from getting into the drawn element.

The cone is covered by a hard bronze piece on which the force of the press is exerted.

The tightness of the copper casing is secured at the end by a welded copper plate.

(b) *Fabrication of the Zirconium Can.* The most critical part of the element to fabricate is the zirconium can. Having been given the analogy of the problem, we addressed ourselves to a shell case manufacturer, the Luchaire Establishment.

Starting with zirconium billets 120 mm in diameter and 60 mm high, we carried out two extrusions by the Ugine-Sejournet Process. We obtained cans about 250 mm high, 92 mm O.D., and 4 to 4.5 mm thick (Fig. 2).

The first operation was done in an open die. The punch and the mold are fixed. The rammer of a 350-ton Morane press pushes the billet between the punch and the mold. The drawn product extends below the mold. It is then disengaged by the jack.

The zirconium billet has been previously heated to 750°C in a Holden salt-bath furnace.

The second operation is a lengthening pass done on an 800-ton Schuler mechanical press (Fig. 3).

Figure 2

COEXTRUSION APPLIED TO SOLID OR DISPERSE FUEL ELEMENTS

Figure 3

(c) *Coextrusion*. Before mounting, the billet of uranium-zirconium alloy and the zirconium can are carefully cleaned, polished, and treated in a vacuum furnace at 400°C.

The final welding of the copper end plate is done by an argon arc.

The composite billet thus obtained is heated to 620°C in a Holden salt-bath furnace and is then extruded by the Ugine-Sejournet method on a horizontal 1500-ton Morane press. The time for the drawing operation is from 1 to 3 sec.

The resistance to deformation of the metal appears to be, from the extrusion pressure, from 25 to 30 kg/mm². The coextruded product obtained is 28 mm in outside diameter; the zirconium clad is about 1 mm thick.

1.4 Results

(a) *Radiocrystallographic Analysis — Electron Microscopy*. The specimens of coextruded elements were entrusted to Mr. Winogradzki of the Center for Nuclear Studies at Saclay for radiocrystallographic and electron microscope studies.

From the mechanical point of view, the bonding between clad and rod is excellent.

Success in separating the clad from the rod was rarely experienced, and then only with difficulty (Fig. 4).

The optical micrographs show that the contact layer is very thin (Fig. 5).

The electronic micrographs show that the thickness of this contact layer is only about 1 μ ; the profile is irregular.

Some radiocrystallographic analyses have been run, particularly on those elements from which the cladding could not be removed.

The contact layer of the rods contains gamma-phase uranium-zirconium. Accordingly, there should be evidence of uranium-zirconium diffusion in the course of the coextrusion.

Previously, some diffusion experiments were carried out by contacting zirconium pellets and uranium-zirconium alloy heated to 600°C. The formation of the gamma phase of the uranium-zirconium system was verified.

(b) *Effects of Heat-treatment on the Contact Layer*. Several attempts were made at heat-treating the coextruded elements, at different temperatures and for different times, in order to study the effects of these treatments on the contact layer.

It was established that, after treatment at 600°C, the bond becomes more fragile. But, if the specimen is treated at 900°C, the fragility disappears. By virtue of this example, the treatment is cited at 900°C for 60 hr; an enormous increase was found in the thickness of the contact layer. The thickness attained was about 0.6 mm. However, several superposed layers of different aspect were noticed (Fig. 6).

The radiocrystallographic analysis has revealed that gamma-phase uranium-zirconium is always present, but the distribution in the diffusion layer is not uniform. There is a layer particularly rich in gamma phase, the thickness of which is about 0.2 mm.

(c) *Micrographic Analysis*. Madame Lanieste, engineer at the Center for Nuclear Studies at Saclay, has micrographically analyzed the cladding and the fuel.

The clad is recrystallized in fine grains between 2 and 10 μ thick (Fig. 7). The fuel is also recrystallized (Fig. 8). At the interface the grains are fine, about 3 μ in size. On the other hand, at the center the grains are larger, from 10 to 15 μ (Fig. 9).

In certain specimens (Fig. 10), the size of the grains reached 80 and even 600 μ . Then a grain orientation was postulated in the direction of extrusion. The wide variation in grain size could arise from some extruding conditions that, in the first experiments, could not be sufficiently explained.

(d) *Experiments with Thermal Cycling of the Extruded Elements*. Mr. Thomé, engineer at the Center for Nuclear Studies at Saclay, has subjected some as-extruded elements, 210 mm in length, to 2000 thermal cycles between 20 and 520°C. The cooling was done in a current of air. The elements were observed to contract from 6 to 11 per cent after this treatment. In the thermal cycling of fuel elements, it is uncommon to observe a contraction. The clad followed

Figure 4 (Magnification 150 $\times$.)

Figure 5

Figure 6 (Magnification 150 $\times$, polarized light.)

Figure 7 (Magnification 450 $\times$, polarized light.)

Figure 8 (Magnification 150 $\times$, polarized light.)

Figure 9 (Magnification 150 $\times$, polarized light.)

DRAWING DIRECTION

Figure 10 (Magnification 150 $\times$, polarized light.)

Figure 11

the deformation of the rod, which demonstrates the good mechanical contact between fuel and cladding.

A beta heat-treatment seems to be necessary for such fuel elements, owing to deformations established during the thermal cycling.

(e) *Experiments with Drawing.* Mr. Boudouresques, engineer at the Center for Nuclear Studies, carried out two drawing experiments on coextruded elements with a 25-ton press. The first one, done in the cold, did not result in a rupture, the press being too weak.

The second experiment was done at 400°C on an element 260 mm long. The breaking stress was about 37.2 kg/mm²; elongation at the rupture was about 19 per cent, and constriction at the rupture was 64 per cent. The crack resulting in the middle of the element showed no discontinuity between cladding and fuel (Fig. 11).

1.5 Conclusions

In conclusion it can be said that experiments continue, but this cladding process already appears to be of interest.

2 DISPERSED FUEL ELEMENTS

We have considered the fabrication of dispersed fuel elements made up of a uranium-aluminum alloy core clad internally and externally with aluminum. The use of uranium enriched to 20 per cent with a composition of 30 wt. % has been anticipated.

The results from the first series of elements prepared with natural uranium in order to determine the fabrication conditions and the properties other than nuclear properties are described as follows: The experiments were done in collaboration with the research center of the Antony Wire Drawing and Rolling Mill at Havre by virtue of a study contract.

For this first series of elements the following dimensions were set up:

Length of core, 300 mm
Exterior diameter of tube, 30 mm
Interior diameter of tube, 24 mm
Thickness of interior and exterior cladding, 0.4 mm

The structure desired is a homogeneous dispersion of round particles of UAl_4 in a matrix of aluminum (43.5 wt. % UAl_4).

The tubes obtained have been checked by radiography and micrography.

2.1 Preparation of the Alloy

The preparation of uranium-aluminum alloy by melting has been elusive up to the present time. It is very difficult to have homogeneity and a suitable structure at the same time.

Using powder metallurgy there are several possibilities: mixing of UAl_4 powder and aluminum powder, mixing of uranium powder and aluminum powder, or formation of UAl_4 before or during the extrusion. These three procedures have been followed.

The aluminum powder used is the lamellar 8- μ powder containing less than 4 per cent oxide. It was chosen for its satisfactory mechanical properties while hot and its low oxide content and because the thickness of the lamellae assures a certain capability for deformation.

The UAl_4 powder was prepared by vacuum melting of the compound and by vacuum diffusion in the solid state of a stoichiometric mixture of uranium and aluminum powders. The diffusion proceeds rapidly at 620°, with a very obvious exothermic reaction. Even with a slight excess of aluminum, we have never verified a stoppage at the compositions UAl_2 or UAl_3 during the diffusion. The compound obtained, although pyrophoric, is easily crushed and reduced.

Some other experiments were performed with solid-state diffusion in the final definitive mixture of compressed uranium and aluminum powders immediately before extrusion (or during). The granulometry of the UAl_4 particles formed, proportional to that of the uranium powder, is then quite easily controlled. This method is faster since it reduces the manipulation of powder to a minimum.

2.2 Fabrication of the Elements

The elements were obtained by fritting extrusion of powder mixtures inside a box of aluminum. All the experiments were done on a 150-ton vertical press. The fabrication of each element consisted in several operations.

1. Preparation of the "box" (diagram of arrangement, Fig. 12). The characteristic geometry was determined so as to obtain a clad with regular thickness and a tubular core presenting a slightly tapered end at the beginning of the drawing. The drawing ratio (S/s) must be sufficient to ensure a good bond between the particles, this determining the dimensions of the box.

Fig. 12—Drawing of the arrangement before extrusion.

2. Cold compressing of the powders in the box.
3. Placing the cap. The cap is made up of a cast aluminum disk set in the box under pressure. An interesting variation consists in replacing the aluminum disk with aluminum oxide powder. The choice of granulometry affects the discharge characteristics.
4. Extrusion. The closed box, preheated to 500°C, is drawn at the same temperature between a drawplate and a punch integral with the presser. The uniformity of the clad thickness depends on the profile of the drawplate and on the shape of the junction of the punch and the presser. Perfect centering of the punch and good lubrication are necessary to obtain smoothness at the end of the core when drawing begins (Fig. 13).

2.3 Results

The thickness of the clad obtained was 0.4 mm. To study variations in thickness, we measured, in a systematic manner, the periodicity and amplitude of irregularities at the core-clad contact for 25 bars. The measurements are in progress.

The shape of the core at the beginning of the drawing operation is very satisfactory, i.e., the well-rounded end protects the cladding obtained directly by extrusion, thus avoiding the welding of a cap (Fig. 14). At the other end it is easy to cut off at the desired length and weld on an aluminum plug in the shape of a cap (Fig. 15).

Nondestructive control of the tube geometry was accomplished by radiography; the thickness of the cladding was verified, and the shape of the core when drawing began was assured (Fig. 16).

Fig. 13—Sketch of coextruded tube.

The structure obtained is a dispersion of UAl_4 particles in aluminum. The first micrograph shows the structure obtained starting with 325 screened UAl_4 powder, $43\ \mu$ diameter (Fig. 17). The other two micrographs show the structure obtained by starting with uranium powder (Figs. 18 and 19). Uranium powder of $<43\ \mu$ diameter gives UAl_4 powder of $66\ \mu$ diameter.

In every case the porosity and percentage of oxide are very low. The core-clad contact is perfect (Fig. 20).

We have carried out several experiments on the tubes: (1) treatment for 100 hr at $500^\circ C$ does not influence the structure, (2) experiments with thermal cycling (20 to 520° , 1 cycle/hr) are in progress, and (3) experiments with mechanical drawing with heating and compressing from 20 to $500^\circ C$ are in progress.

2.4 Conclusions

These experiments have demonstrated that uranium-aluminum alloy tubes (30 wt. % uranium) clad internally and externally with aluminum can be fabricated by coextrusion. The use of powders permits precise control of the core structure and avoids machining operations. The method used is fast and permits tolerances that are altogether satisfactory.

For the first series of experiments the dimensions were fixed at 300 mm length, 30 mm exterior diameter, and 3 mm total thickness, including two clads of 0.4 mm. There is no limit to the length, diameter, or thickness except that imposed by the power of the press.

It is, of course, understood that this method is equally applicable to other uranium compositions, to other metals, to matrices, and to claddings.

Fig. 14 — Transversal section and longitudinal section showing the shape of the core at the beginning of drawing. (Diminished 2.5×.)

Fig. 15 — Weldment of aluminum cap. (Diminished 15×.)

Fig. 16 — Radiographic control of the beginning of drawing and thickness of cladding.

Fig. 17—Structure of UAl_4 + Al core, starting with UAl_4 powder less than $43\ \mu$. (An inclusion of UO_2 .) (Magnification $450\times$.)

Fig. 18—Structure of UAl_4 + Al core, starting with U powder. (Magnification $150\times$.)

Fig. 19a—Structure of $\text{UAl}_4 + \text{Al}$ core, starting with U powder. (Magnification $450\times$, ordinary light.)

Fig. 19b—Structure of $\text{UAl}_4 + \text{Al}$ core, showing recrystallization of the UAl_4 . Polarized light. (Magnification $450\times$.)

Fig. 20—Core-clad contact. (Magnification $150\times$.)

Zirconium Cladding of Uranium and Uranium Alloys by Coextrusion*

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ABSTRACT

The principles governing the techniques used in the coextrusion of two or more metals are discussed in general, and the application of these principles to the fabrication of zirconium-clad uranium fuel elements having integral zirconium end seals is discussed in detail. The extrusion billet consists of a uranium or uranium alloy core surrounded by a zirconium or Zircaloy-2 sleeve and end pieces (cladding); the core and cladding components are enclosed in an evacuated, sealed copper can and extruded. Special precautions to obtain good bonds between core and cladding, uniform cladding, and satisfactory interfaces between core and end seals are described. Specific techniques, component design, billet design, extrusion conditions, and a description of the resultant product obtained (clad rod or tube) are given for the zirconium or Zircaloy-2 cladding of unalloyed uranium, uranium-2 per cent zirconium, uranium-10 per cent molybdenum, uranium-4 per cent silicon, and uranium-5 per cent zirconium-1.5 per cent niobium.

1 INTRODUCTION

Zirconium is almost an ideal cladding material for metallic uranium fuel elements. It has a low absorption cross section for neutrons, excellent corrosion resistance to both water and sodium, and good mechanical properties. In addition, it has a high degree of metallurgical compatibility with uranium. Zirconium-uranium alloys in all proportions do not form any brittle compounds, and therefore the bond between core and clad has good strength. Interdiffusion of the two metals is relatively slow even at 1000°C. This makes it possible to heat them together for purposes of hot fabrication or heat-treatment. Of equal importance for the present work is the fact that the plasticity or stiffness of zirconium is reasonably similar to that of uranium at a temperature of about 600°C. This characteristic makes it possible to clad uranium by coextrusion in such a way that a complete fuel element is produced in one operation.

It is relatively easy to clad rods, flats, and tubes along their length and to achieve a good bond between the zirconium and uranium. It is much more difficult to simultaneously seal the ends of the uranium in a satisfactory manner. Techniques for accomplishing extrusion cladding have been under development for a number of years and have been applied to many materials other than those which form the subject of this paper. The knowledge which has been gained will be discussed in a general way in the following section in order that the reader may have a better understanding of the specific problem of cladding uranium with zirconium.

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2 PRINCIPLES OF COEXTRUSION

2.1 General

It is necessary to meet a number of conditions in order to accomplish extrusion cladding. Obviously the extrusion temperature must be high enough so that both metals can be made to flow at the required reduction ratio without exceeding the maximum pressure that the extrusion tools can stand. It is necessary that the metal flow be streamlined so that the clad will be on the surface of the extruded product and be of uniform thickness. The extrusion must be suitably lubricated or otherwise adjusted to ensure that the billet does not stick to the container and die walls. The stiffness of the two or more metals to be extruded must be approximately the same; otherwise one or the other will not flow uniformly, especially at the end closure. Finally, the flow shape over the cross section of the extrusion must be determined, and adjustments must be made at the ends of the core in the billet in order that a reasonably satisfactory shape is achieved at the ends of the core material in the extruded product.

2.2 Extrusion Pressure

The extrusion pressure P for a given set of operating conditions is a function of the reduction ratio as given by the equation

$$K = P/\ln R$$

where K is a constant for the prevailing conditions and R is the ratio of the initial and final cross-sectional areas. A more accurate expression would contain a term concerned with the effect of surface friction, but for the present purpose this may be ignored. The reader should realize that K values obtained on different machines with different sized billets and lubricants may be significantly different from those listed here. If R is less than about 4, the observed pressures will be substantially greater than the calculated values. K varies with temperature, and the rate of variation is different for each metal. Values of K for the materials of interest in this paper are given in Table 1. For practical work the pressures calculated from these values can be relied upon only to about ± 25 per cent since the conditions used in establishing the values of K may not be reproduced. Extrusion pressure does not depend markedly on die design, but it is influenced by the degree of lubrication. It is found also that small-diameter extrusion billets require substantially higher unit pressures than larger billets. The values of K in Table 1 were obtained on billets of 2 to 6 in. in diameter. In all cases the billets had an outer sheathing of copper, and the lubricant was graphite powder in oil.

The extrusion constant K is considered to be a good measure of stiffness. It is usually found that two metals having the same value of K at a given temperature may be coextruded satisfactorily. For composite billets the extrusion force is roughly equal to the sum of the forces that would be required to extrude each of the components at the given reduction ratio.

2.3 Flow Patterns

In commercial extrusion it is common practice for the die to have a flat face with some sort of radius leading to the orifice. It is difficult for metal on the surface of the billet to flow across this flat face, and, as a consequence, the metal will shear at an angle of 30 to 45 deg to the die face to form a cone. Surface metal will flow across this cone and drag with it some of the metal in the cone. The best way to avoid this situation in a clad extrusion is to provide a conical approach to the die opening. This may be done either with a conical die or with a separate cone of steel which can be heated to the same temperature as the extrusion billet. There is nothing critical about the cone angle, since streamlined flow is obtained with any angle between 30 and 60 deg. The flow of clad and core in the satisfactory coextrusion of a rod is shown schematically in Fig. 1. Tubing clad inside and outside can be made by extruding over a straight mandrel.

Table 1—EXTRUSION CONSTANTS OF SOME FUEL, CLADDING, AND CANNING MATERIALS

(K = $P/\ln R$, Where K = Extrusion Constant, P = Unit Pressure on Extrusion Billet, R = Reduction of Area Ratio)

Material	Temperature		K, tons/sq. in.
	°F	°C	
Uranium (alpha) (0.04% carbon)	1100	590	17
	1200	650	15
Uranium (gamma)	1600	870	3
Uranium-2% zirconium	1200	650	22
	1300	705	14
	1350	730	8
Uranium-5% zirconium-1.5% niobium	1200	650	17
	1300	705	13
	1400	760	10
Uranium-10% molybdenum	1600	870	30
Uranium-3.8% silicon	1400	760	28
	1560	850	23
Thorium	1100	590	17
	1200	650	16
	1300	705	15
	1400	760	14.5
Zirconium	1200	650	17
	1400	760	15
	1470	800	14.5
	1560	850	11.5
Zircaloy-2 (zirconium-1.5% tin-0.12% iron-0.10% chromium-0.05% nickel)	1200	650	25
	1400	760	20
	1600	870	16.5
Copper	1000	540	15.5
	1200	650	12.4
	1400	760	10
	1600	870	8
Copper-10% nickel	1000	540	27.5
	1200	650	24.6
	1400	760	17
	1600	870	15

An imaginary plane at right angles to the billet axis will not be plane in the extruded shape. For a round bar the final shape of such a plane is shown schematically in Fig. 2a. The length L of the flow shape is of particular interest in conjunction with the problem of extruded end closures. The flow shape can easily be several feet long unless steps are taken to reduce it. It is found that L for a given metal varies with reduction ratio, cone angle, extrusion temperature, lubrication, and position in the bar. In some studies carried out on naval brass by one of the authors (H. Sawyer, internal laboratory report), it was determined that L varied almost linearly with reduction ratio and that each of the other parameters (except position in the bar) could change L by a factor of 3 or 4. It is clear that the careful control of extrusion conditions is required to ensure that L may be consistently held to a value not greater than the bar diameter.

Fig. 1—Streamlined flow of cladding and core during coextrusion with conical approach die.

Fig. 2—Trace in extruded rod of surface which was originally plane and perpendicular to billet axis. (a) No shift (uniform lubrication). (b) With shift.

In an actual extrusion it is usually found that the flow shape is not axially symmetric. A typical shape as observed in a longitudinal section may be seen in Fig. 2b. The distance S by which the peripheral location of the original plane is displaced along the axis is known as "shift." It has been determined that shift is largely due to variability in the frictional force between the billet and the steel tools. In one case, for example, it was observed that a score mark on the wall of the container produced a noticeable local shift. It is possible to obtain an external indication of shift by examining surface markings on the bar which come from circumferential scratches on the surface of the billet. The same pattern of shift usually occurs along the entire length of an extrusion. In a clad extrusion any shift in the clad is transmitted to the core.

2.4 Matching of Stiffness

Good conditions for streamlined flow and uniform surface friction are not sufficient to ensure successful coextrusion. A substantial difference in stiffness of clad and core will lead to longitudinal fluctuations in their relative thickness which, in extreme cases, become actual breaks in the metal. The exact nature of the trouble will depend on the actual materials and on their relative thickness. A number of typical occurrences are shown schematically in Fig. 3. It is believed that, in addition to the difference in extrusion constant K , some other factor is important in determining the nature of the imperfections. Difficulties of the type shown do not usually arise if the values of K for the two metals do not differ by more than about 25 per cent.

The extrusion constant measures stiffness for a polycrystalline aggregate. Individual crystals, especially of uranium, beryllium, and zirconium, exhibit an anisotropic resistance to deformation, even at elevated temperature. This phenomenon can cause objectionable variations in clad thickness if either the clad or core is too coarse grained. The solution is to have a fine grain size in the starting materials. A quantitative correlation between grain size and roughness of interface between core and clad has not been determined. Examples of the effect for zirconium-clad uranium are discussed below.

2.5 End Closures

Extruded end closures are produced by entirely surrounding the core material with cladding and then extruding in the usual manner. The simplest arrangement is to place a disk of cladding (end seal) before and behind the core and surround these components with a sleeve of cladding as shown in Fig. 4. If the two materials are of comparable stiffness, the usual flow pattern (Fig. 2) will develop at the interface of core and end seals as shown in Fig. 5. For most fuel elements it is desirable to decrease the length of these naturally occurring end shapes to a value which is not more than two or three times the diameter of the element. This may be done by appropriate shaping of the interface between end seals and core in the starting billet. It is known that all elements of volume within a billet experience about the same elongation during extrusion. From this it follows that any distance l (Fig. 2a) in the end shape was originally a distance l/R in the billet, where R is the reduction ratio. If the interface between end seal and core in the billet is made to curve backward against the extrusion direction by the appropriate values of l/R as a function of billet radius, it might be expected that the final interface in the bar would be flat. It is impractical to achieve the exact prior shape needed for a flat interface, and such effort is not warranted since all the variables affecting end shape cannot be accurately controlled from one extrusion to the next. A reasonable compromise is to use a surface of constant radius for the initial shape. A billet prepared in this manner for a rod extrusion is shown in Fig. 6, with the resultant rod shown in Fig. 7. The radii used at each end need not necessarily be the same, especially if overcompensation is desired at the rear in order to have the final core end convex. There are other reasons, explained below, for not trying to achieve a flat interface.

If the clad and core have an appreciable difference in stiffness, a variety of undesirable effects can occur in the vicinity of the end closure, even though the clad along the length of the extrusion will be entirely satisfactory. All these lead to an undesirable thinning of the clad, and in extreme cases the core will reach the surface. The type of effect depends on the mag-

Fig. 3—Examples of imperfect coextrusions when core and cladding stiffness are significantly different. (a) Clad stiffer than core; core of low ductility. (b) Clad stiffer than core; core of higher ductility. (c) Core slightly stiffer than clad. (d) Core much stiffer than clad. (e) Core stiffer than clad; clad very soft.

Fig. 4—Simplified billet assembly for making a coextruded clad fuel element with integral end seals.

Fig. 5—Extruded rod resulting from extrusion of billet assembly shown in Fig. 4.

Fig. 6—Coextrusion billet assembly for clad fuel element with compensated end-seal shapes.

Fig. 7—Extruded rod resulting from extrusion of billet assembly shown in Fig. 6.

nitude of the difference in stiffness, and the phenomena are not the same at each end of the core. Furthermore, the clad thinning will depend on the degree of end-shape compensation that is attempted: thinning troubles are more severe with end shapes that are almost flat.

If the core is stiffer than the clad, it will be found that the core has an enlarged diameter at the front end as illustrated in Fig. 8. This always occurs at the front end but will not be found at the back end unless the preshape compensation was extensive. This end swelling is known as a "dogbone." In extreme cases the dogbone will penetrate entirely through the clad and, in addition, a void may appear on the axis immediately in front of the core. The best cure for this difficulty is to use an end-seal material of stiffness equal to that of the core. In this case there is no change of pressure as the core approaches the die, and all the billet components flow in a steady manner. A suitable end-seal material can usually be found by alloying of the clad.

If the core is softer than the clad and end seal, a phenomenon known as "whiskers" will appear at a rear end-seal interface which has been made relatively flat by compensation. An example is shown in Fig. 9. The whisker is caused by the normal tendency of metal on the axis to get ahead of metal on the surface as shown in Fig. 10. Penetration of the whisker through the clad is caused by dogboning of the rear end seal and, presumably, could be avoided by using a softer end-seal material. Unfortunately, it is not usually possible to obtain a softer form of the clad material, and it may be unsatisfactory to use an entirely different metal for the end seal. The best way of controlling whiskers is by drastic preshaping of the billet components at the rear interface so that the final end shape of the core is strongly convex. In this way the whiskers can be made shorter and farther from the surface and, in the limit, can be avoided entirely. The length of the convex rear end shape in the extrusion may need to be three or four times the core diameter to accomplish this.

Fig. 8—Dogbone configuration at front end interface when core is stiffer than end-seal cladding.

Fig. 9—Appearance of whisker when core is softer than end-seal cladding.

Fig. 10—Longitudinal section through partially extruded, copper-canned, clad rod showing metal flow during formation of whiskers.

The use of a long cone leading to the die opening tends to minimize end-shape troubles, including dogbones, whiskers, and excessive length of flow shape. An angle of as much as 60 deg between the die face and the side of the cone is considered practical.

The phenomenon of shift as defined above is encountered with integral end closures. Uniform resistance to flow at the billet surface is the most important control factor for shift. With the best techniques developed to date, it is usually possible to limit the length of shift to about one-half the diameter of the core.

For each application of integral end closures, it is necessary to determine by trial the best combination of preshape, cone angle, extrusion temperature, and end-seal material. The magnitude of this effort will depend on the degree of end-shape reproducibility demanded by the reactor engineer.

Fig. 11—Billet assembly for tandem extrusion of two rods of uranium clad with Zircaloy-2. Diameter of liner is 3.050 in.; extrusion ratio is 19.5 to 1.

3 ZIRCONIUM CLADDING OF URANIUM

3.1 General

An examination of Table 1 shows that the extrusion constants of zirconium and Zircaloy-2 are not exactly equal to the values for uranium and its various alloys. The differences are not great enough to prevent coextrusion but are sufficiently large to create special problems with integral end closures. Billet designs that have given satisfactory results are described in Sec. 3.2.

All billets are coextruded with an outer can of copper or iron. This outer can avoids galling of the zirconium on the die and provides an envelope that may be evacuated and sealed to prevent oxidation of the fuel-element components. The stiffness and the relative thickness of the outer can have an influence on clad thickness at the end seals, but in most cases this can be ignored. The use of copper-nickel alloys affords a method of adjusting can stiffness if this is necessary.

3.2 Unalloyed Uranium Cores

In coextruding pure uranium with zirconium, a temperature corresponding to the high alpha phase region of uranium is used since uranium is too soft in the gamma phase and too stiff in the beta phase. An extrusion temperature of about 640°C is satisfactory. A reduction ratio of about 10 times is required to bond uranium to zirconium at this temperature, but a reduction of 15 to 20 times is needed to bond zirconium to zirconium at the end seal.

A typical billet assembly for producing a 0.630-in.-diameter rod clad with Zircaloy-2 is shown in Fig. 11. With this configuration, end shapes such as those shown in Fig. 12 should be obtained. Details of the procedure are as follows:

(a) *Uranium.* The uranium must have a maximum grain diameter of about 0.5 mm in order to ensure a smooth interface between core and clad (care must be taken to ensure that large numbers of adjacent grains are not similarly oriented). Coarse-grained uranium will give an interface such as that shown in Fig. 13a, and the size mentioned (0.5 mm) will give an interface such as that shown in Fig. 13b. The grains of a cast ingot may be suitably refined by an extrusion at 10 times reduction or forging at two times reduction at 625°C. Another procedure is to heat into the beta phase at about 730°C and quench into water. This beta treatment should be repeated three times for best results. The quench may cause internal cracks in solid billets over about 4 in. in diameter, but this trouble is not encountered with heavy-walled hollow shells for producing tubular elements. The rough uranium billet is machined to the required size and shape. A clearance of as much as 0.010 in. between the uranium and the zirconium sleeve is satisfactory. The machined billet is cleaned in organic solvent and bright pickled in 50 per cent nitric acid-50 per cent water solution.

Fig. 12—Rod resulting from coextrusion billet shown in Fig. 11. Cladding is 0.030-in. Zircaloy-2; diameter of uranium core is 0.570 in.

Fig. 13—Interface between uranium and Zircaloy-2 resulting from extrusion of billet assembly shown in Fig. 11. (a) Coarse-grained uranium core. (b) Fine-grained uranium core. Magnification approximately 5x.

(b) *Zircaloy*. The Zircaloy sleeve and end seals should be made from hot-worked stock. Cast metal is too coarse grained and will lead to rough surfaces or interfaces. It is sometimes necessary to heat the Zircaloy into its beta phase in order to eliminate unsymmetrical crystal textures that are created during forging. The final parts are brought to size and shape by machining. Cleaning with organic solvent is followed by bright pickling in 48 per cent nitric acid-4 per cent hydrofluoric acid-48 per cent water solution.

(c) *Copper Can*. A copper thickness of about 0.035 in. is used for extrusion billets less than about 2 in. in diameter, and 0.065 in. of copper is used for billets greater than 2 in. in diameter. The forward end usually has the shape of the die cone, but in some cases a flat end has been found to be satisfactory. The flat back end is sealed by welding. The billet assembly is evacuated through a tube in the end plate, and pumping is continued while the billet is heated to about 400°C. The tube is sealed by crimping and shearing while hot. It is desirable to leak test the copper can before sealing it off.

(d) *Auxiliary Components*. The copper-nickel pieces at the front and back of the billet assembly shown in Fig. 11 are used to conserve Zircaloy. This alloy has the same K as Zircaloy at the temperature of extrusion. The end shape of the Zircaloy-uranium interface will be influenced by the stiffness of these auxiliary parts, especially if the Zircaloy end plugs are short.

(e) *Removal of Copper, and Other Considerations*. Pickling in 50 per cent nitric acid can be used to remove the copper clad. Under the conditions described, the zirconium will be contaminated with copper (about 0.01 to 0.02 per cent) to a depth of about 0.001 in. This contaminated layer can be removed by etching for about 2 to 5 min in 50 per cent nitric acid containing 2 to 4 per cent hydrofluoric acid.

Another billet assembly, which has been used to make three zirconium-clad uranium tubes in one extrusion, is shown in Fig. 14. The peculiar shaping of the core and end seals was necessary to avoid whiskers, especially at the inside on the back end. Further adjustment of these shapes would be required for Zircaloy cladding since it is appreciably stiffer than zirconium. A typical tube resulting from such an extrusion is shown in Fig. 15.

Zirconium or Zircaloy cladding of any desired thickness down to about 0.005 in. can be applied by the methods described above. As yet, no attempt has been made to produce integral end closures for clad thicknesses less than about 0.015 in. Variations in clad thickness have not been carefully studied, but in general it may be said that the variation can be held to about ± 20 per cent of the desired thickness, even at the end seals.

The bond strength between uranium and zirconium is at least as great as the strength of zirconium itself. This has been checked by welding a stud of zirconium to the clad with a stud-welding machine, removing the cladding outside the stud with a hollow end mill, and then pulling to destruction. The heat-affected zone does not reach to the bond line. In all cases the zirconium stud fails before the bond line separates. Bond strength between clad and end seal may be checked in a similar manner. Another procedure is to make a cut almost entirely through the element and then bend the remaining material to fracture. If the bond is good, there will be no separation between clad and core at the fracture. It has been found that it is easier to bond uranium to zirconium than zirconium to zirconium at the end seal. Therefore a destructive test for bond strength on the excess zirconium at the ends of a fuel element can be used to determine that the central part of the element is well bonded. With the fabrication procedure described above, a poor bond will occur only if the copper outer shell leaks or if some material inside this shell gives off gas during the heating for extrusion.

The all-zirconium integral end closures are usually longer than required. It is not practical to make these ends shorter than two or three times the diameter of the fuel element. The extremities of the uranium may be located fairly closely with a radiation meter, or precisely by radiography; the all-zirconium ends may then be cut off as desired.

3.3 Uranium-2 Per Cent Zirconium Cores

The stiffness of uranium-2 per cent zirconium is somewhat less than that of Zircaloy-2 at the usual extrusion temperature of 640°C. Accordingly, some care is required to prevent

Fig. 14—Billet assembly for tandem extrusion of three uranium tubes clad inside and outside with zirconium. Diameter of liner is 6.200 in.; extrusion ratio is 14.5 to 1.

thinning of the clad at the rear end-seal interface. The grain size of the 2 per cent zirconium alloy is sufficiently fine to give a smooth interface between core and clad even when the alloy is in the cast condition.* This characteristic makes it practical to produce cladding as thin as 0.005 in. by extrusion and 0.002 in. after cold working. A billet design that gives acceptable end shapes for a tube with 0.015 in. of clad inside and outside is shown in Fig. 16. Representative end shapes from such a billet are shown in Fig. 17. It is to be noted that there is no prior shaping at the front end of the core in the billet. The use of a relatively steep cone (60 deg measured from the die face) serves to limit the front end shape to about 2.5 in. in length. If the cone angle had been 45 deg, the end shape would have been about 6 in. long.

A billet design to produce Zircaloy cladding and end seals on a rod-shaped element with three extruded ribs is shown in Fig. 18. The ribs did not cause any unusual trouble at the end seals. The shape of core and clad at the ribs, after extrusion, is shown in Fig. 19. The penetration of uranium into the rib and the thinning of the clad at the base of the rib may be reduced by broadening the base of the rib as shown in Fig. 20.

Another technique for applying ribs is shown in the billet assembly described in Fig. 21. In this arrangement, strips of Zircaloy of appropriate size are placed along the outside length of the Zircaloy sleeve, and the spaces between the strips are filled with pieces of copper-10 per cent nickel, which matches the stiffness of Zircaloy. The assembly is canned in copper and extruded in the usual manner through a round die. After extrusion the copper clad and the filler metal are removed with acid. The ribs will be of uniform thickness and will not be penetrated by the uranium, as shown in Fig. 22. The technique will be less successful if the stiffness of the filler metal does not match that of Zircaloy.

3.4 Uranium-10 Per Cent Molybdenum Cores†

This alloy is stiffer than zirconium even at 900°C, when it is in the uranium gamma phase. In order to achieve a reduction high enough to ensure bonding without excessive extrusion pressure, it has been found necessary to extrude at 870°C. Because at this temperature copper

Fig. 15—Coextruded tube resulting from extrusion of billet shown in Fig. 14. Outside diameter is 2.370 in. over-all; inside diameter is 1.820 in. over-all; cladding is 0.030 in. thick.

* Extremely slow cooling during solidification of the casting will give a coarse grain size.

† Most of the work done by the authors and their colleagues on the uranium-10 per cent molybdenum pin elements has been sponsored by the Atomic Power Development Associates, Detroit, Mich.

Fig. 16—Billet assembly for coextrusion of the tube having uranium-2 per cent zirconium core and Zircaloy-2 cladding. (See facing page for materials list.)

ZIRCONIUM CLADDING OF URANIUM AND URANIUM ALLOYS BY COEXTRUSION

No.	Description	Material	Size
1	Die	Hot work steel, 45-50 Rockwell C	4.610 in. OD, 1.340 in. ID over $\frac{1}{8}$ in. land
2	Cone	Cold rolled steel	4.610 in. OD, 60° included angle, 1.600 in. opening
3	Mandrel	Hot work steel 45-50 Rockwell C	0.875 in. diameter, 15 in. long
4	Nose plug	OFHC copper	4.390 in. OD over $\frac{1}{4}$ in. flat, 1.005 in. OD
5	Inner can	Copper	1.000 OD, 0.900 ID, 9 in. length
6	Front end seal	Zircaloy-2	4.202 $\pm$ 0.000 in. OD 1.426 $\pm$ 0.003 in. ID $1\frac{1}{2}$ in. long
7	Outer can	Copper	4.525 in. OD, 4.394 in. ID, 6 in. long
8	Inner sleeve	Zircaloy-2	1.420 $\pm$ 0.000 in. OD 1.015 $\pm$ 0.003 in. ID 5.4 in. long
9	Core	U-2% Zr	4.202 $\pm$ 0.000 in. OD 1.426 $\pm$ 0.003 in. ID 2.800 $\pm$ 0.010 long over-all
10	Outer sleeve	Zircaloy-2	4.377 $\pm$ 0.000 in. OD 4.208 $\pm$ 0.003 in. ID $5\frac{1}{2}$ in. long
11	Rear end seal	Zircaloy-2	4.202 $\pm$ 0.000 in. OD 1.426 $\pm$ 0.003 in. ID $1\frac{1}{2}$ in. long over-all
12	End plug	Copper	4.385 in. OD, 1.010 in. ID, $\frac{1}{4}$ thick
13	Extrusion liner	Steel	4.625 in. ID $\times$ $24\frac{1}{2}$ in. long
14	Evacuation tube	Copper	$\frac{3}{8}$ in. diam. OD $\times$ 0.035 in. wall
15	Cut-off	Copper	4.525 in. OD, 0.900 in. ID, 2 in. long
16	Mandrel backer	Steel 40-45 Rockwell C	4.610 in. OD, 3 in. long, shrink fit with mandrel

Fig. 16—Materials list.

Fig. 17—End shapes resulting from extrusion of billet shown in Fig. 16 (discontinuities in sketches correspond to gradual taper from uniform core).
(a) Front end taper. (b) Rear end taper.

alloys readily with zirconium, it is necessary to use an iron (1020 steel) can, but even in this case it is desirable to oxidize the iron can at 760°C and to have a thin layer of Al_2O_3 between the zirconium and the iron. A billet arrangement for producing a 0.004-in. clad on rods of 0.158-in. diameter (after swaging) is shown in Fig. 23. If the core alloy has been previously extruded, its grain size is fine enough to make practical a clad of this thinness, which is constant within ± 0.0005 in. The element may be cold-worked by swaging without damage to the bond between clad and core.

No extensive attempt has been made to obtain extruded end closures with this alloy. Presumably this would be possible if a zirconium alloy of sufficient stiffness were used. An alloy of zirconium with either 5 wt. % silicon or 15 wt. % molybdenum might suffice.

3.5 Uranium-4 Per Cent Silicon Cores

This alloy exhibits appreciable ductility if it is properly heat-treated to form the epsilon phase.* In this condition it may be clad with Zircaloy at an extrusion temperature of 760°C and a reduction ratio of 25 times. About 15 per cent reduction by swaging has been carried out on the clad rod. Extruded end closures have not been attempted because of the stiffness of epsilon, but they probably could be achieved.

* A. Kaufmann, B. Cullity, and G. Bitsianes, *Uranium-Silicon Alloys*, *Journal of Metals*, 9: 23 (1957).

No.	Component	Material	Dimensions	+	-	Length	Remarks
1	Die	Hot work steel	3.615 OD 0.760 ID	0.002 0.001	0.002 0.001	2 ³ / ₄	Rockwell C, 45-50
2	Cone	Stainless steel	3.600 OD 0.990 ID	0.003 0.010	0.003 0.010	1 ⁵ / ₁₆ (ref.)	
3	Can	Copper	3.526 OD 3.446 ID			7 ¹ / ₂	Cut to fit assembled billet
4	Nose plug	Cu-10 wt. % Ni	3.436 diam	0.000	0.005	1.780 (ref.)	¹ / ₄ shoulder ³ / ₈ flat on nose
5	Front end seal	Zircaloy-2	3.174 diam	0.000	0.002	0.667	4.131 R. (convex)
6	Core	U-2 wt. % Zr	3.174 diam	0.000	0.002	1	4.131 R. (concave) 2.645 R. (convex)
7	Cladding	Zircaloy-2	3.436 OD 3.179 ID	0.000 0.002	0.002 0.000	3	
8	Rear end seal	Zircaloy-2	3.174 diam	0.000	0.002	1.333	2.645 R. (concave)
9	Cut-off	Cu-10 wt. % Ni	3.436 diam	0.000	0.005	2	
10	End plug	Copper	3.436 diam	0.000	0.005	³ / ₈	¹ / ₁₆ shoulder, ¹ / ₈ deep by ¹ / ₈ wide grooves
11	Evacuation tube	Copper	¹ / ₄ diam			15*	* Before sealing off

Fig. 18—Billet assembly for coextrusion of uranium-2 per cent zirconium core with ribbed Zircaloy-2 cladding by "ribbed-die" technique. Diameter of liner is 3.625 in.; extrusion ratio is 22 to 1.

3.6 Uranium-5 Per Cent Zirconium-1.5 Per Cent Niobium Cores

Cladding of this alloy with Zircaloy is relatively difficult. At temperatures below about 575°C, the extrusion pressures for a 25-time reduction become excessive. At 600°C the extrusion pressure is alternately high and low as the extrusion proceeds, and there are corresponding fluctuations in the thickness of core and clad with occasional breaks in the clad. It is believed that the difficulty in this case is caused by the core alloy periodically transforming to the gamma phase and then back into the alpha. Successful tube extrusions have been made at 680°C with the core entirely in the gamma phase. At this temperature the core is very soft compared with Zircaloy-2, and therefore satisfactory end closures are difficult to achieve. A billet design which gave good results is shown in Fig. 24; convex end shapes about 6 in. long at each end of the core of the extruded tube were necessary to avoid breaks due to whiskers at the end seals. A long conical approach to the die did give shorter end lengths in later work.

Fig. 19—Cross section through rod extruded from billet shown in Fig. 18. Note the variations in cladding thickness.

Fig. 20—Cross section through ribbed extrusion having broader base for ribs than shown in Fig. 19. Note the improvement in uniformity of Zircaloy-2 cladding thickness.

ZIRCONIUM CLADDING OF URANIUM AND URANIUM ALLOYS BY COEXTRUSION

Fig. 21 —Cross section of extrusion billet for making ribbed, Zircaloy-2 clad, uranium-2 per cent zirconium rod by "ribbed-billet" technique.

Fig. 22 —Section of ribbed rod extruded from billet shown in Fig. 21. Magnification 4x.

No.	Description	Material	Size
1	Die	18-4-1 Hi-speed steel, 45-50 Rockwell C	$1\frac{1}{16}$ in. OD, 0.250 in. ID over $\frac{1}{8}$ in. land, 1 in. long
2	Cone	Type 304 SS	$1\frac{1}{16}$ in. diam, 90° included angle, $\frac{5}{16}$ in. diam opening
3	Nose plug	Cu-17 wt. % Ni	0.920 in. diam for $\frac{1}{4}$ in. length, 45° taper to $\frac{1}{4}$ in. diam flat
4	Billet core	U-10 wt. % Mo	0.8705 ± 0.0005 in. diam, $2.312 \pm$ 0.005 in. long
5	Billet sleeve (cladding)	Zirconium	0.919 ± 0.001 in. OD, $0.8735 \pm$ 0.0005 in. ID, 2.312 ± 0.005 in. long
6	Oxidized can, spun nose	Mild steel	$1\frac{1}{16}$ in. OD $\times$ 0.065 in. wall
7	Cut-off	Cu-17 wt. % Ni	0.920 in. diam $\times$ 1 in. long
8	Extrusion liner	Steel	1.100 in. ID $\times$ 11 in. long
9	Evacuation tube	Mild steel	$\frac{1}{4}$ in. OD $\times$ $\frac{1}{16}$ in. wall
10	End plug	Mild steel	0.920 in. diam $\times$ $\frac{1}{4}$ in. thick

Fig. 23—Billet assembly for extruding rods of uranium-10 per cent molybdenum clad with zirconium. Extrusion ratio is 19.4 to 1.

3.7 Finishing Operations

(a) *General.* Extrusion-clad rods and tubes in general have a good surface finish after removal of the copper, provided that the starting materials are sufficiently fine grained. Quantitative measurements of the degree of roughness are not available. In several cases the users have been satisfied to irradiate specimens with the as-extruded finish; cold work may be used to obtain a smooth surface and to increase the dimensional accuracy. In addition to a slight dimensional variation found in as-extruded material, it is usually found that the end seals have a size slightly different from the clad core region.

(b) *Cold Work.* The bond between zirconium and uranium is not injured by cold work. Total reductions in area of 50 per cent can be obtained by swaging with properly designed dies

Fig. 24—Billet assembly for producing tubes of uranium-5 per cent zirconium-1.5 per cent niobium cores clad inside and outside with Zircaloy-2.

before annealing is required. An annealing temperature of 600°C is adequate for cores of uranium and uranium-2 per cent zirconium. Cold drawing may be performed provided that a suitable lubrication technique is employed for drawing of the Zircaloy itself. Wire as small as 0.051 in. in diameter with a clad thickness of 0.002 in. has been produced.

(c) *Heat-treatment.* The bond between clad and core is not damaged by heat-treatments into the beta or gamma phases of uranium. This makes it possible to carry out any such treatment that may be deemed desirable to get optimum radiation stability of the core. Drastic quenching from the high-temperature phases may be performed without damage to the fuel element. Repeated temperature changes including hundreds of thermal cycles from 100 to 500°C do not injure the bond.

The end seals of extrusion-clad uranium elements are usually slightly larger in diameter than the region over the core. Beta treatment of alpha-worked uranium will result in a small increase in diameter upon return to room temperature. This expansion makes the final diameter of the ends and the core region almost the same.

The region of interdiffusion between clad and core may not be so corrosion resistant to high-temperature water as the core itself. This effect is not observed, of course, if the core is pure uranium or a uranium-zirconium alloy. It does occur for the "corrosion-resistant" alloys, such as uranium-10 per cent molybdenum and uranium-4 per cent silicon, and presumably is caused by diffusion of the alloy addition into the zirconium clad. A heat-treatment after extrusion makes this situation worse.

(d) *Etching.* It is well known that surface contamination will decrease the corrosion resistance of zirconium in high-temperature water. It is standard practice to etch 0.001 or 0.002 in. from the zirconium surface before it is used. This same treatment should be applied to a zirconium-clad uranium element. A solution of 35 per cent concentrated nitric acid (1.42 sp. gr.) containing 5 per cent hydrofluoric acid (49.2 per cent assay) is suitable for this purpose. At a temperature of 40°C, about 2 min is required to remove 0.001 in. from the surface. The same amount of metal can be removed in about 20 sec by using 0.5 to 1 per cent hydrofluoric acid added to concentrated nitric acid (no water dilution) and heating to 86°C. Care must be exercised in etching zirconium alloys in nitric-hydrofluoric acids because the reaction is exothermic. If large quantities of metal are put in a small volume of etchant, the resultant temperature rise of the bath may be too great.

Any heat-treatment of the element should be carried out before the final etching. It is desirable to use an oxygen-free atmosphere for the heat-treatment. If the surface of Zircaloy develops a thin oxide film, the etching will cause pitting unless the oxide is first removed by vapor blasting.

4 ADVANTAGES AND DISADVANTAGES OF COEXTRUSION AND ZIRCONIUM CLADDING

The economic aspects of zirconium-clad uranium or uranium-rich alloys are not well understood. As yet there has not been any large-scale use of such material, especially for reactors designed to give economical power. In spite of this, it seems desirable to list some of the arguments for and against such fuel elements.

4.1 Advantages

1. Extrusion cladding avoids separate preparation of the core and clad in the final fuel-element sizes. The preparatory work is carried out on material of much larger dimensions. This should lead to savings of material and labor.

2. A separate bonding operation between core and clad is avoided.

3. If integral end closures are used, a separate operation to seal the ends is avoided. Also, it is believed that integral end seals can be made more reliable than other types of end closures.

4. With extrusion cladding it is possible to achieve a much thinner clad than would otherwise be feasible.

5. Heat-treatment for radiation stability can be carried out on the finished fuel element.

6. There is some evidence to indicate that zirconium cladding can be used to suppress dimensional changes of uranium during irradiation, at least at temperatures below about 200°C.

4.2 Disadvantages

1. Zirconium is expensive compared with aluminum and magnesium. This comparison has little meaning for use in high-temperature water but may be valid for other types of re-

actors. The fact that the zirconium clad can be made extremely thin, that it can be used to suppress growth, and that it makes possible a simple cladding technique needs to be considered before making a final judgment.

2. Removal of zirconium cladding in reprocessing after irradiation is considered by chemists to be a difficult question. A number of ways of overcoming this are conceivable, but these have not been evaluated.

3. Extruded end closures may lead to a greater production of scrap if the end shaping of the billet components is done by machining. Such end shapes might be achieved by a forging operation if large-scale production is required.

4. Extruded end closures are usually longer than required, and this leads to an excessive amount of zirconium scrap. This loss can be reduced by using thin end seals backed up with a suitable copper-nickel alloy as shown in some of the billet arrangements discussed in this paper. As the length of the fuel element decreases, excessive zirconium at the ends becomes a greater problem.

5 CONCLUSION

Coextrusion of metals to obtain cladding and end closures is a well-developed process. The cladding of uranium and uranium alloys with zirconium or Zircaloy-2 by this procedure has been successful, and the product has many attractions. Because extensive use of such fuel elements has not yet occurred, it is not possible at this time to evaluate them realistically from an economic standpoint.

Fabrication of the Fourth Set of Fuel Elements for the Experimental Pile EL2

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1 GENERAL DESCRIPTION

The reactor P2 or EL2 (Fig. 1 shows a vertical cross section of the reactor) is the second atomic reactor built in France. It is a laboratory reactor using heavy water and natural uranium. Its maximum power range is 2500 kw, and its flux is higher than 8×10^{12} neutrons/cm²/sec at 2000 kw. This reactor is used by physicists and chemists and for production of radioelements. Its cooling circuit operates with compressed CO₂ gas at a pressure of 8 kg/cm². For this reason it has been a world-wide prototype. The CO₂ temperature is 30°C at the entrance of the cooling system, 150°C at the exit, and the can temperature at the hottest point rises to about 350°C. The uranium mass of the reactor amounts to 3 metric tons and is distributed into 136 vertical channels.

A cell is schematically built as follows: The fuel element surrounded by its shield tube occupies the axial part of the cell. The whole is placed into another tube which is directly immersed in the heavy water. The cooling gas, when cold, goes down between the external plunger and the intermediate tube; then it goes up along the rod. During its downward travel, it cools the moderator, and, during its upward travel, it cools the uranium rod. During its upward travel, the gas temperature increases no more than 3°C because of the thermal shield.

The rods were originally one-piece rods, 2.15 meters long, aluminum canned with an underlying coating to avoid diffusion. Since there were some fears about the behavior of such long rods, cells were made which were composed of four uranium elements leaning on shelves borne by the shield tubes.

Since the start-up of the reactor, the set of rods has been renewed four times. The fourth set of rods has been running since May 1957. The subject of this paper is the manufacturing of this set. It was done at the C.E.A. in the research laboratories of the Technology Service. The purpose was to get 400 fuel elements, and it will be easily understood that the requirements for such rod making are not those of a large-scale factory. Therefore the methods used in some parts of the manufacturing process sometimes will seem obsolete. It must be kept in mind that the selected canning method has conditioned the rod making, and its originality will be emphasized all through this paper.

The same basic principles as those of the binding method given here will be used for the fuel elements of our future Marcoule reactors G2 and G3.

FABRICATION OF FUEL ELEMENTS FOR EL2

Fig. 1 — Vertical cross section of reactor EL2.

Air	Gas	Water
1, filter	11, heat exchanger	21, pool
2, bypass	12, principal exchanger	22, pump
3, fan	13, blowers	23, atmospheric cooler
4, chimney	14, auxiliary exchangers	
	15, venturi	

Fig. 2a—Cooling circuit diagram.

1, cold-gas entrance	4, thermal insulating tube
2, plunger	5, rod
3, D ₂ O	6, venturi
	7, warm-gas exit

Fig. 2b—Reactor cell detail.

2 BINDING PROBLEM

The binding problem has conditioned the uranium-rod design. Two canning modes are available: the free and the bound.

2.1 Free Can

The free can is one that comes off the uranium rod by differential expansion while running in the reactor. The pressure difference P between the internal and external pressures is applied to such a can, and the can must withstand this pressure difference.

If the can is empty, the internal pressure is equal to zero, and p is the absolute pressure of the cooling gas. The can is subjected to two stresses:

$$n_{\text{diametral}} = \Delta p D / 2e$$

$$n_{\text{longitudinal}} = \Delta p D / 4e$$

therefore

$$n_l = n_d / 2$$

If the can resists the diametral stress, it is certain that it will resist the longitudinal stress. The condition for withstanding the pressure difference is that the diametral stress should always remain lower than the value of a stress giving a negligible creep (0.4 per cent creep after 10,000 hr). Let $N = f(\theta)$ be that stress (see Fig. 3).

Figure 3

In the case $2f < \Delta p D / e < 4f$: $n_d > f$, f = diametral creep, and $n_l < f$. Under the action of Δp , there will be a diametral contraction without any longitudinal contraction, with an increase in the rod length, as in a rolling operation (see Fig. 4).

Fig. 4—Ineffective longitudinal creep.

When cooling down, the can has too small a diameter and will tend to coil the uranium rod. This coiling action will tend to prevent the rod from longitudinally shrinking, therefore again causing an increase of the rod length. The total increase of the rod length will be $l = a$, and after n cycles, $l = na$. A length increase of $l = 1.6$ mm for a 500-mm-long rod has been obtained with a smooth can, on the occasion of tests, after 36 cycles (vertical cycling was used).

In the case of reactor EL2: $\Delta P = 8 \text{ kg/cm}^2$, $D = 30 \text{ mm}$, $e = 1.5 \text{ mm}$, and $n_d = 80 \text{ g/mm}^2$. At 300°C the diametral stress of the can is superior at the negligible creep stress, $N = f(\theta)$.

By using a free can, a second process is available. The can is free, but an intermediate gas, which acts as a heat transmitter, is placed between the can and the uranium rod. Helium can be used, as in case G1 at Marcoule. In order to get good working conditions, a balance of the pressures is necessary:

$$P_{\text{internal He}} = P_{\text{external CO}_2} = 8 \text{ kg/cm}^2$$

The perfect balance of the pressures demands a very delicate filling under pressure and a well-defined and thoroughly constant working pressure (such conditions are far from actual working conditions).

Furthermore, the heat transmission is very poor owing to quite reduced contact with respect to the expected flux Φ ($\Phi = 20 \text{ watts/cm}^2$).

2.2 Bound Can

The second canning mode is bound canning, and it was selected for EL2. This canning mode, which provides good heat transfer, worked very satisfactorily while the first sets of rods were operating.

A bound can is designed never to come off the uranium rod. The differential uranium-can expansion, therefore, depends exclusively on the existence of stresses inside the can.

Extensive work has been done on stresses due to a uranium-can uniaxial binding action (see Fig. 5). Here the binding action is double: diametral and longitudinal. It may be assumed,

Fig. 5—Stresses on a bound magnesium can.

$$\left(\frac{\Delta e}{e}\right)_{\text{can}} = \left(\frac{\Delta e}{e}\right)_{\text{uranium}}$$

if no tests are made, that values of stresses are within the same range in each principal direction.

The bond, being responsible for the existence of stresses, must be able to resist those stresses. The traction stresses are absorbed by the uranium rod on which the can is stretched. The compression stresses lead to the fact that the can tends to come off the uranium rod. The basic problem consists in finding a mode of binding the can to the uranium rod which will resist the compression stresses. It is noticed that, once the first heating is completed (a stage of the manufacturing process which will not be discussed here because M. Gauthron details it in his paper), the cycling curves never drop, in the compression range, lower than $n = 0.5 \text{ kg/mm}^2$ with magnesium cans.

A fuel element functioning in a reactor may undergo the following cycles:

- (a) Cycle $\theta \rightleftharpoons 20^\circ\text{C}$ $\theta < 400^\circ\text{C}$
- (b) Cycle $\theta \rightleftharpoons 20^\circ\text{C}$ $200^\circ\text{C} < \theta < 400^\circ\text{C}$
- (c) Cycle $\theta \rightleftharpoons 20^\circ\text{C}$ $\theta < 200^\circ\text{C}$

Cases b and c are the only two possibilities for a fuel element in EL2 since the maximum can temperature is about 350°C .

When beginning to function in the reactor, the can is subjected to a traction prestress (point A in Fig. 5, $n = 10 \text{ kg/mm}^2$) due to the so-called "hot-canning" manufacturing operation. When doing the first heating in the reactor, we start with a can already subjected to tension (figurative point is A).

In case b ($\theta \rightleftharpoons 20^\circ\text{C}$; $200^\circ\text{C} < \theta < 400^\circ\text{C}$) (see Fig. 6), since there is a creep phenomenon which bends down the curves toward the zero-stress axis, we shall reach this axis for a tem-

Figure 6

perature value close to 200°C and turn into the compression range. We do not reach complete relaxation since the temperature does not rise to 400°C . We shall get a slow relaxation as long as the temperature remains constant and equal to θ_B . Running the reactor at a constant power leads, as far as the development of stresses inside the rod is concerned, to the relaxation straight-line segment BC. When stopping the reactor for the first time, we shall start again from point C, which still possesses a small compression. During the course of the cycles, point A will drop slightly until it reaches a stable position.

In case c ($\theta \rightleftharpoons 20^\circ\text{C}$; $20^\circ\text{C} < \theta < 200^\circ\text{C}$) (see Fig. 7), the curves for the successive cycles will drop step by step nearer to the negligible-creep-zone bounding curve and then become stable.

Figure 7

3 CONNECTION BETWEEN CAN AND ROD

Both external pressure and setting grooves help to bind the can, the connection being done (1) along the longitudinal direction by setting grooves and (2) along the diametral direction by the external pressure of the cooling gas.

If the can had to resist the external pressure, the stress developed inside the can would be $n' = PD/2e$. If this stress is larger than $n = 0.5 \text{ kg/mm}^2$, a stress that squeezes the can to the uranium rod is obtained and is larger than the stress necessary to maintain the connection. Keeping the connection tight depends on the inequality $PD/2e > 0.5 \text{ kg/mm}^2$.

Consider the EL2 case, where $P = 8 \text{ kg/mm}^2$, $D = 30 \text{ mm}$, $e = 1.5 \text{ mm}$, and $PD/2e = 0.8 \text{ kg/mm}^2$.

3.1 Diametral Connection

The diametral connection is secured by the CO_2 pressure inside the reactor.

3.2 Longitudinal Connection

It would be possible to secure the longitudinal connection only at both ends of the rod. However, some secondary phenomenon may take place, which makes more advisable a continuous intermediate longitudinal connection.

In fact, the hottest point A (see Fig. 8) while the can is heating is not necessarily the hottest point while it is cooling down.

Figure 8

While the temperature is rising, the can is subjected to compression. There is a squeeze due to the creep in A (hottest point). While the temperature is decreasing, the can is subjected to traction stresses, and the hottest point B will be stretched because of the creep phenomenon. At each thermal cycle, A will be squeezed and B will be stretched. This effect was experimentally observed by the fact that marks in the B zone move away at each cycle, the can length remaining the same. In order to avoid such a phenomenon, an additional connection was set up.

The longitudinal connection is secured by two systems of setting grooves, as shown in Fig. 9. The main connection is by four square grooves at both rod ends, and the intermediate continuous connection is by a square, 12-mm, threaded screw cutting. (In fact, grooves and screw cuttings are not strictly square, for some clearance is allowed for the cutting tool.)

The can is set into the setting grooves by the so-called hydraulic canning operation, which will be discussed later.

(a) *Depth of the Grooves.* With setting grooves, the hot-canning process goes on as follows: The can resists along the diametral direction but is longitudinally bound by the setting grooves. Once the can is squeezed in the diametral direction, the efficiency of longitudinal connection is perfect. When the can is entirely applied to the rod, the prestress effect begins.

The can tends to come off the uranium bar along the diametral direction, within a certain temperature range. The depth of the connection groove must be larger than the differential expansion looseness. The temperature rise is fast (the cold slug is introduced into the canning

FABRICATION OF FUEL ELEMENTS FOR EL2

DETAIL 2

Fig. 9—Two systems of setting grooves.

device, which has a temperature of 300°C), the creep is small, and it will be assumed, for more safety, that $\theta_1 = 300^\circ\text{C}$.

$$\text{Looseness} = \Delta r = (\alpha_G - \alpha_U) \frac{D}{2} \Delta \theta = 12 \times 10^{-6} \times \frac{26.3}{2} (300^\circ)$$

$$\Delta r = 0.05 \text{ mm}$$

In order to have the can teeth gripping the uranium rod along $h' = 0.15$, a groove depth of at least 0.2 mm has been designed. We have chosen, for the main groove, $h_1 = 0.3$ mm, and, for the intermediate screw cutting, $h_2 = 0.2$ mm.

(b) *Width of the Grooves.* The can resists being pressed into the grooves by the hydraulic pressure in two ways:

1. Flection on the groove edges. The pressure needed to squeeze the can into the grooves

under these conditions is p_1 . The uniformly distributed load, on a 1-mm-wide slice, is $Q = 1 \times l \times p_1$.

If we consider A and B as fitted in, the moment of flection is maximum at these points:

$$M = \frac{Ql}{12} = p_1 \frac{l^2}{12}$$

The moment of inertia of the considered slice is

$$\frac{I}{V} = \frac{1 \times (1.6)^2}{6}$$

The stress n is thus $n = 0.196p_1 l^2$. To squeeze the can into the grooves, the stress n has only to become equal to the load of rupture of magnesium, that is, $n = 12 \text{ kg/mm}^2$, and

$$p_1 = \frac{12}{0.196 l^2}$$

The can resists.

2. Compression along a cross section. The corresponding stress is

$$n = \frac{p_2 D}{2e} = p_2 \frac{29}{2 \times 1.6}$$

$$n = 9.05 p_2$$

In order to accomplish the pressing in of the can, it is sufficient that n be equal to 12 kg/mm² and

$$p_2 = \frac{12}{9.05}$$

The total pressure needed for driving the can into the grooves will be the sum of those two pressures, that is,

$$p = p_1 + p_2 = \frac{12}{0.196l^2} + \frac{12}{9.05}$$

If 1500 kg/cm² is chosen as canning pressure, then $l \sim 3$ mm. We shall take $l = 3 \pm 0.2$ mm.

The principle of the uranium-can connection, i.e., the principle of a prestressed bound can, for the EL2 reactor has been a very satisfactory prototype with respect to this aspect of the question. This binding mode has been chosen, for similar reasons, as a basic principle for the elements of the second and third Marcoule industrial reactors G2 and G3.

4 BASIC MATERIALS

4.1 Uranium

Uranium rods are obtained by extrusion while in the gamma phase. This extrusion technique has been developed by the "Compagnie Pechiney" laboratories at Chambéry, jointly with the C.E.A.

A paper by Stohr and Chevigny at the 1955 Geneva Conference was concerned with this method, and we shall not reconsider it. The four principal parts of the apparatus are the extrusion unit (Fig. 13), the heating furnace, the extrusion press (die diameter 28), and the receiving tube.

The billet heating furnace increases the billet temperature to 970°C. The extrusion press is a vertical one, of 70 tons maximum power. After extrusion of a 2.5-meter-long bar, the bar is straightened in a conventional planing machine, using two rollers having the same direction of rotation, of which one is cask shaped and the other is hyperboloid shaped.

The bar is heated (temperature = 200°C), protected from oxidation by a silicone-grease coating. After five or six such rolling passes, the bar is perfectly straightened. It is then cut into 600-mm-long pieces. This straightening operation has the drawback of giving rise to troublesome stresses. This process is the only one available for large-size bars, but it may be dropped for small-length bars. Actually, 500-mm-long rods are made by vacuum casting in a strictly straight shape. Since actual manufacturing opportunities allow us to use vacuum casting, the next set of rods will be obtained by this process.

The bars are machined after they have been straightened; tungsten carbide tools are used. Grooves and screw cuttings are not strictly square in order to manage the cutting-tool escape. Chamfers are machined at both ends of the bar ($\alpha = 30^\circ$; $h = 1.5$ mm). The reasons which led to these requirements no longer seem to be valid, and the latter may be removed in the next set of rods.

The rod sizes are (see Fig. 14) length $L = 527.5 \times \pm_{0.2}^0$ mm and diameter $\phi = 26.3 \times \pm_{0.4}^0$ mm. Afterward the rods are degreased and sanded in a sanding machine of the type "Vapor Blast," which throws out alumina grains in a water jet. Then the rods are degassed under vacuum. This last operation is started immediately after the degreasing and sanding. The pressure of the stove for all this treatment period must never get higher than 10^{-4} mm Hg. A 350°C temperature is kept constant for 2 hr, then the stove is allowed to cool, and it is opened only when its temperature reaches 40°C.

The total operation period amounts to 20 hr. Rods are kept under vacuum until they are used (Figs. 15 and 16).

Figure 11

Figure 12

FABRICATION OF FUEL ELEMENTS FOR EL2

Fig. 13—Gamma-phase-uranium extrusion device (billet, casing, die, and grain).

Fig. 14—Rod straightening.

Fig. 15—The "stove."

Figure 16

4.2 Cans

The cans are magnesium tubes of a nuclear grade delivered by "Tréfileries et Laminaires du Havre" (Antony). Hot extrusion of these cans is done in its Montreuil-Belfroy factory, using a 600 metric tons vertical press. Tubes leave the press, at an approximate speed of 3 meters/min, in 3-meter-long pieces. They are then cold-straightened on a roller machine, and afterward they are internally broached to take off the graphited grease and adjust the cans to the exact size. Their internal diameter is $\phi_i = 27 \pm 0.1$ mm, and their external diameter is $\phi_e = 30 \pm 0.1$ mm; their thickness is $e = 1.5 \pm 0.15$ mm. It is obvious that a can diameter of $\phi_i = 27$ mm is too large with respect to the uranium-rod diameter ($\phi = 26.3$ mm). Some clearance requirements, difficult to respect a few years ago, had led to the choice of such a diameter value. Since, during the manufacturing process, we force the can through a die, up to now we have not found it useful to decrease this diameter value.

Cans are scoured, polished to a shining surface, placed under a plastic cover with a small silica gel bar, and delivered in the shape of 600-mm-long pieces. When the cans are received, their surfaces and thicknesses are carefully checked.

A preliminary shaping of the can, using a hot-working roller without a mandrel bar, is done, which brings the external diameter of the can down to $\phi_e = 26$ mm. Then the grease is taken off the can according to the successive processes:

1. A soda bath at boiling temperature for 5 min and then ample rinsing with water.
2. A nitrate bath (300 cm³ of concentrated HNO₃ and 1000 cm³ of ethyl alcohol) at the ambient temperature for 1 min, rinsing with alcohol in a first bath, rinsing with alcohol in a second bath, and drying with lukewarm air (Figs. 18 and 19).

The cans are then immediately placed in a vacuum stove in order to degas them. The temperature is kept constant at 250°C for 2 hr at a maximum pressure of 10^{-4} mm Hg. This 10^{-4} mm Hg pressure is kept during the cooling period. Stove opening takes place only when the temperature does not exceed 60°C. When cans are not used immediately after the degassing operation, they are kept under vacuum up to the time they are used, i.e., forced through the dies.

As for the plugs, the rounds are delivered by the "Tréfileries et Laminaires du Havre." They are machined according to two different designs. A beryllium ball-and-socket joint is fitted into the top plug, and the bottom plug lies upon a fritted aluminum bed, through a beryllium cupel, which makes their shapes different (see Figs. 20 and 21). As soon as they are machined, the plugs, like the cans, are scoured and degassed.

The beryllium machining (see Fig. 22 for the ball-and-socket joint and Fig. 23 for the cupel) is done on special machines using a specially designed suction system. Powerful aspiration is obtained through large-cross-section muzzles placed very close to the active part of the cutting tool and between this tool and the operator. The suction system is equipped with filters (provided with safety devices) in order to throw back into the atmosphere only a negligible amount of fine dust. Scouring of the beryllium pieces is done in a ternary bath of the following composition: one-third pure ethyl alcohol (95%), one-third acetone, and one-third benzene.

No chemical troubles can arise with such a mixture, but its vapor may give ignition or explosion troubles, and its vapor is toxic.

4.3 Canning Operations and Welding

(a) *Canning Process Using a Die.* (See Figs. 24 to 27.) This operation attempts to apply the can to the uranium rod without locking air between the rod and the can after welding has been done. A canning cone that has been cleaned with ternary mixture is placed in the can, followed by the uranium rod; then the whole is forced through a die using a pushing rod. It is abundantly greased with lard oil, taking care not to put any oil inside the can. A die profile is chosen which gives the uranium rod the proper design. Afterward the whole is wiped with a rag soaked with ternary mixture. Once the canning by the die process is completed, the final rolling is done. An approach cut is made, and the canning cone is removed. The knurling tool is positioned with the positioning device (Figs. 28 and 29), and the stamping is done using a

(Text continues on page 208.)

Fig. 17a—"Striction" for the canning ("retreint"). Cutting distance = 600 ± 5 .

Fig. 17b—"Striction" of the can before canning ("retreint").

Figure 18

Figure 19

FABRICATION OF FUEL ELEMENTS FOR EL2

Fig. 20—Cupel plug. Material: magnesium.

Fig. 21—Plug for ball-and-socket joint. Material: magnesium.

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Fig. 22—Beryllium ball-and-socket joint.

Fig. 23—Beryllium cupel.

Fig. 24—Canning cone.

Fig. 25—Canning die. $A = (D + 2e) - s$, where D = uranium diameter = 26.3, e = average can thickness, and s = diameter decrease.

Fig. 26—Setting before die canning.

Figure 27

SETTING ON THE LATHE

Fig. 28—Stamping roller.

gas-air torch flame, which must never touch the knurling tool. The diameter is adjusted with a calibrating gauge (Fig. 30); then the can length is adjusted (can must go beyond the plugs by $\frac{1}{10}$ mm).

(b) *Welding of the Plugs.* Figure 31 shows the rod after the die canning operation, before it is welded. This figure gives the sizes of the pieces to be welded.

Arc welding under an argon atmosphere, with a nonfusible electrode (Fig. 32) is used. The argon flow rate is 6 to 7 liters/min. The electrode is of pure tungsten, $\phi = 2.5$ mm, operating under 60 amp of alternating current.

The torch remains fixed vertically while the bar is rotating. The rotation speed is 3.75 rotations/min for the first rotation and 10 rotations/min for the following rotations. As shown on the diagram, Ω rotations/min = f (time in seconds), and $I = f$ (time). The arc length is kept at a minimum by manual means.

The plug has a 1-mm-deep chamfer. At the beginning of the fusion, the edges of the V gorge melt down into the hot gorge. The bottom of the V gorge will be the limit of penetration. With a more open V gorge, the melting and dropping-down effect of the edges is decreased. With a less open gorge, the metal drop stays stationary between the two sides of the V and does not go down into the bottom of the V. The can is 1 mm above the plug, and this excess acts as filler metal. The large width of the plug allows more heating while welding, which improves the penetration (Figs. 33 to 36).

The welding process may be rendered automatic by using a rotation-speed programmer. This programmer is based on a single factor variation, namely, the rotation-speed factor, the current intensity keeping constant, at least for most of the welding operation time (a rheostat for the end of the welding process would permit the complete removal of the crater which occurs when the welding operation is stopped).

When the welds are completed, the rod ends are brushed on a drum provided with clean brushes. Then the second canning operation is performed.

(c) *Hydraulic Canning.* (See Figs. 37 to 39.) The can is compressed until it is driven into the rod grooves, under an oil pressure of 1500 kg/cm² (computed and radiographically checked). The fluid used in Houghton Society type 150.

The apparatus is a Basset canning machine which can reach a pressure of 5000 kg/cm² by using a compressor. A special tightness breech provides total safety and permits quick opening of the working chamber. This chamber is made in KNA (chromium, nickel, and aluminum) steel which, tempered and annealed, resists a 120 kg/mm² stress. The wall is 110 mm thick, and the useful diameter is 70 mm. The total duration of a canning operation is 5 min, of which the pressure rise takes 3 min if a 5 liter/min laboratory compressor is used.

Two bars previously placed in a basket are canned at the same time.

After the hydraulic canning, the plugs are scoured in soda, nitric acid, and alcohol baths. This scouring operation will be eliminated for manufacturing the next set of bars because the compressor oil circuit has been completely separated from the compression circuit itself by a diaphragm that is used to transmit the pressure. The hydrostatic compression is exerted by demineralized water, which has the great advantage of eliminating the scouring operation and making it possible to pass directly to the hot canning under pressure after a plain warm-air drying. This improvement will be used for manufacturing G2 fuel elements.

(d) *Hot Canning.* This operation must be done with maximum care. It is necessary to conform strictly to the following procedure:

1. Perfectly dry compressed air must be used.
2. The rods are quickly brought down into the apparatus, which is closed at once.
3. Pressure ($p \geq 15$ kg/cm²) is applied at once, and then the rod temperature is raised to $400 \pm 20^\circ\text{C}$ and kept constant at this value for 5 min. The rods are taken out of the furnace as soon as the pressure is released and are allowed to cool under a dry- and cold-air jet. Six elements are placed in the canning device at the same time. The total duration of an operation amounts to about 1 hr. The apparatus is externally heated by heating resistors set in such a way that there is a longitudinal temperature gradient as low as possible.

FABRICATION OF FUEL ELEMENTS FOR EL2

Fig. 29—Roller positioning device.

Fig. 30—Calibrating gauge for the stamping operation.

FABRICATION OF FUEL ELEMENTS FOR EL2

TUNGSTON-THORIUM ELECTRODE, $\phi 2.5$
 REFRACTORY PIPE, $\phi 11$
 ARGON FLOW RATE, 7 L/MIN.

Fig. 32—Placement of the electrode with respect to the plug.

Fig. 33—Argon welding unit.

Figure 34—Welding diagram.

Figure 35

Figure 36

FABRICATION OF FUEL ELEMENTS FOR EL2

Fig. 37—Basset hydraulic canning unit, 5000 kg/cm².

Figure 38

Figure 39

4. The rods are then polished to a shining surface, using 100 cm³ of concentrated HNO₃ and 1000 cm³ of pure ethyl alcohol at the ambient temperature for 3 min. The rods are set to drain and are rinsed with ethyl alcohol in two successive baths at the ambient temperature for 1 min; the rods are again set to drain and are dried with lukewarm, dry air.

(e) *Setting the Beryllium Pieces in Place.* The beryllium ball-and-socket joints are riveted on a lathe, the stops of which are made of aluminum. The operation is done by cold working according to Fig. 40 and is stopped when the ball-and-socket joint is locked.

In order to set the cupel into the bottom plug, the seat is drilled to the diameter $\phi = 21.5$ mm with clearance H₇; it is checked with a calibrating gauge, and the cupel is set in place using a mallet. Once this operation is completed, the fuel element is finished.

5 MANUFACTURING CONTROLS

5.1 Mechanical Controls

Some checks are made, during the manufacturing process, on the lengths, diameters, surfaces, and numbering of the uranium rods and of the cans.

5.2 Control of Tightness of Magnesium Cans

The can is surrounded by a helium atmosphere at a pressure of 2 kg/cm² (absolute pressure). The inside of the can is pumped to a pressure lower than 10⁻² mm Hg and is connected to a mass spectrograph. In order to take into account the passing of helium through the can, the possible appearance of the signal on the screen might require 10 min.

The tube holding the can is made with two end bridles which provide the tightness between the inside of the can under vacuum and the outside under pressure. The tube volume is pumped through a single-bodied paddle pump (2 m³/hr) down to a pressure lower than 2 mm Hg before introducing helium. The filling circuit sluice valves must secure enough tightness to the primary vacuum and must resist the 2 kg/cm² pressure.

The spectrograph connection circuit is pumped through a double-bodied pump (2 m³/hr). A safety valve set for 1.1 kg/cm² prevents an accidental extra pressure in the connection circuit to the spectrograph. The low-pressure sluice valves are of the conventional diaphragm type with a 10-mm channel. The tube connecting the can to the spectrograph is as short as possible (Figs. 41 and 42).

5.3 Size Control

Measurements of the length of the whole are made on the final plugs before and after the hot-canning operation. Fuel elements whose lengths have increased more than 0.2 mm are removed. This control, however, has been canceled for the fourth set of fuel elements. The controls used for the previous sets allowed us to state that the cans were never altered, provided that the uranium rods themselves were unaltered.

5.4 Control of Welds

A fuel element is from time to time taken off its can in order to examine the weld, check the penetration depth (Fig. 43), and check the micrographic appearance.

5.5 Radiographic Control

The fuel elements are radiographed when their manufacture is completed. The apparatus used is a constant-voltage X-ray generator called the Majorix 150, built by Philips. The X-ray tube is a short anode tube of which the radiating beam is included in a 40-deg cone. Its maximum power is 150 kv. Best results have been obtained with a 150-cm focus-to-film distance, an 80-kv voltage, a 4-ma intensity, and a 30-sec exposure time using a Kodak Definix film.

Manufacturing Diagram

Radiography allows us to check whether the canning is correct (that is, whether there is enough squeezing of the can into the connecting grooves) and to check whether the plugs have become unstuck during the hot-canning operation (Figs. 44 and 45).

6 MOUNTING IN THE REACTOR

The fuel elements are independent of each other. They rest on a fritted aluminum piece, inside of which is inserted the joint of the lower rod (see Figs. 46 and 47).

The mounting operations succeed each other in the following order:

1. The first fuel element (lower fuel element) is placed into the first element of the shield tube (magnesium tube with an internal aluminum can). The shield tube is threaded at its upper part, and a magnesium joint is screwed on there.
2. Inside this joint are placed first a magnesium ring, then a fritted aluminum star-shaped piece, and again a magnesium ring. Rings transmit the load on the shield tubes.
3. The second element of the shield tube is then screwed on the ring; the second rod is placed on the fritted aluminum star-shaped piece, and the mounting goes on in the same way for the third and fourth bars.
4. The ensemble thus obtained is placed down into a plunger tube, "brillalumag 3," of dimensions 57 by 60 mm.

FABRICATION OF FUEL ELEMENTS FOR EL2

Fig. 40—Riveting of the ball-and-socket joints.

LEGEND

- Ve-1-2-3 AIR INPUT VALVES
- V1-2-3-4 DIAPHRAGM VALVES
- R1-2-3 TAPS

Fig. 41—Apparatus for checking can tightness.

Fig. 42 — Apparatus for checking can tightness.

Fig. 43 — Micrography: welding of an EL2 plug.

Fig. 44—Radiography of the end of an EL2 fuel element.

Figure 45

Fig. 46—Mounting of ends.

Figure 47

SESSION III

Enriched-uranium Metallic Fuel Elements

Recent Developments in Dispersion Type Fuel Elements

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ABSTRACT

Considerable interest has centered around dispersion type fuel elements because they offer possibilities of performance not readily achievable in solid homogeneous fuels. Among these advantages are the possibilities of operation at high temperatures, high burn-ups, and the ability to withstand various corrosion conditions. This paper describes a wide variety of dispersant fuel materials as well as matrix materials to contain the fuel. The important factors governing the selection of both fuel and matrix are discussed.

Descriptions are given of the various techniques for preparing the fuel particles, including those for uranium oxide. In addition, descriptions are given of various combinations of fuel and matrix which have been studied and the results obtained therefrom.

Because of the wide variety of possible fuel materials, as well as matrices in which these fuels can be dispersed, it is suggested that there is hardly a solid reactor fuel whose requirements cannot be met by the use of the dispersant type fuel.

1 INTRODUCTION

The need for greater efficiency and lower cost in the production of nuclear power necessitates the development of fuel elements that will operate at higher temperatures and higher burn-ups than the conventional elements in use today. In addition, these elements should possess the greatest corrosion resistance possible. The dispersion type fuel element, in which the fissile material is uniformly dispersed in a continuous nonfissile matrix, is one of the more promising ways of meeting these requirements.

The proper selection of fissile and nonfissile materials to be used in a dispersion type fuel element involves the consideration of many factors. Of primary importance are compatibility of the fissile and nonfissile phases at both fabricating and operating temperatures, the neutron absorption cross section of both fuel and matrix, corrosion resistance of the nonfissile phase, weight percentage of the uranium in the fissile phase, and density of the uranium compound.

Powder metallurgy, far superior to melting and casting for the fabrication of dispersion type fuel elements, was the fabricating method utilized in all the work to be described in this paper.

2 OBJECTIVE

To meet the requirements of high-temperature strength, high burn-up, and good corrosion resistance, the fuel-element designer must develop a fuel system that

1. Utilizes a diluent of higher melting point than aluminum
2. Has a minimum thermal neutron absorption cross section
3. Has good corrosion resistance in its operating environment
4. Is subject to minimum radiation damage

Dispersion type fuel elements, which utilize UO_2 as the fissile phase and stainless steel as the nonfissile phase and which meet most of the outlined objectives, have already been developed and are operational. For the purposes of this discussion, however, we shall neglect this system since it has already been fully explored.

Dispersion type fuel elements in general meet all the outlined requirements. They offer higher burn-ups through localization of fission-product damage to the fissile phase or to the area immediately adjacent to it, leaving a fission-product-free region of matrix metal around the zone of damage. The continuous nonfissile matrix in this type of element offers increased corrosion resistance. A dispersion system also offers a wide choice of fuel-element materials and properties.

The ideal dispersion element incorporates the fissile material without any metallurgical reaction and consequently retains the desirable properties of the matrix material which provides the structural strength to the fuel element. Since uranium itself is a highly reactive element, the fissile addition is usually made of a relatively high-density chemically stable compound such as UO_2 . Indeed, since UO_2 is considered such a fine fissile addition in this type of fuel element, one normally only considers fissile dispersants with higher densities of uranium per unit volume as a replacement for it.

The particle size of the fissile addition is of extreme importance both from the standpoint of fission-product damage as well as from corrosion resistance. The use of relatively large particles ($200\ \mu$) results in confining the fission products largely to the dispersant, and, in addition, the use of large particles also permits, for any given fuel volume, a larger matrix area between particles, lending greater strength and corrosion protection to the mixture. The fissile particle should preferably be spherical since this is the shape that has the greatest volume to surface ratio. In some instances the volume of the matrix can be increased without decreasing the total fuel loading by the use of a uranium compound with a higher density than the one at first considered as the fissile phase. It is fairly obvious from all the foregoing statements that the dispersion of fissile particles in the matrix must be as uniform as possible to obtain to maintain the benefits as outlined.

From what has already been said, it is apparent that, to attain maximum endurance life, the volume fraction of the diluent metal should be large, the density of the uranium in the dispersed phase should be high, and the parasitic neutron absorption cross section of the fissile phase and matrix materials should be low.

3 FISSILE DISPERSANTS AND MATRICES

The required properties of the fissile dispersants and the matrix are fairly obvious. The fissioning material should contain a relatively high content of uranium, be relatively nonporous, and be sufficiently strong to maintain size and shape during fabrication. It should not interact with the matrix during fabrication or reactor operation.

The matrix should be strong, ductile, and insensitive to neutron damage at the operating temperature. It should be corrosion resistant to its environment and be able to retain any fission products if such a requirement is imposed upon it. Both phases, of course, should have low parasitic neutron absorption cross sections. Other matrix requirements such as high thermal conductivity, low coefficient of thermal expansion, and metallurgical and chemical compatibility with the fuel are, of course, desirable or necessary. Tables 1 and 2 on fissile dispersants and matrix materials show possible selections of materials.

RECENT DEVELOPMENTS IN DISPERSION TYPE FUEL ELEMENTS

Table 1 — FISSILE DISPERSANTS

Compound	Density, g/cm ³	Uranium volume ratio	Melting point, °C	Thermal reaction absorption cross section of second element, barns/atom
U	18.9	1.0	1120	
U ₆ Mn	17.8	0.91	726*	13.3
U ₆ Fe	17.7	0.91	815	2.53
U ₆ Co	17.7	0.90	830*	37.0
U ₆ Ni	17.6	0.89	790*	4.6
U ₃ Si	15.6	0.77	930	0.13
U ₂ Ti	15.22	0.73	890*	6.0
UN	14.3	0.71	2630	1.88
UC	13.6	0.69	2270	0.0032
U ₃ Si ₂	12.2	0.59	1665	0.13
UC ₂	11.7	0.56	2400	0.0032
UO ₂	10.96	0.53	2500	0.0002
U ₅ Sn ₄	13.0	0.49	1500	0.6
UFe ₂	13.21	0.48	1235	2.53
USi ₂ (beta)	9.25	0.40	1600	0.13
USi ₂ (alpha)	8.98	0.38	1600	0.13
UNi ₅	11.31	0.27	1300	4.6
UCu ₅	10.6	0.24	1052	3.69
UAl ₄	6.0	0.22	730	0.23
UBe ₁₃	4.37	0.15	2000	0.010
UAl ₂	8.9	0.35	1500	0.23
UAl ₃	6.7	0.26	1320	0.23
UFe ₂	13.2	0.48	1235	2.53
UPb	14.5	0.41	1280	

*Decomposition.

Table 2 — MATRIX MATERIALS

Matrix	Melting point, °C	Microscopic absorption cross section, barns/atom
Beryllium	1282	0.010
Iron	1539	2.4
Molybdenum	2625	2.4
Niobium	2415	1.1
Nickel	1455	4.5
Zirconium	1852	0.18
Graphite	3527	0.0048
Magnesium	651	0.059

4 METHODS OF PREPARATION OF DISPERSANTS FOR MATRIX TYPE FUEL ELEMENTS

4.1 Uranium Dioxide

Where the ultimate end use of uranium dioxide is in a matrix type fuel element, a coarse-grained material is usually desirable. The oxide particles should be dense and strong enough to resist breaking up during rolling or some other fabricating procedure. Particle size is also important in that the uranium dioxide must have a minimum of surface area to reduce the pos-

sible reaction with the matrix. Larger-size particles also reduce fission-product damage to the surrounding matrix. Coarse-grained uranium dioxide may be produced by several methods.

4.2 Geneva or Hydrothermal Oxide

In this process large crystals of UO_3 hydrates are grown hydrothermally in an autoclave. The bulk of the crystals is then heated to 1800°C under a hydrogen atmosphere and reduced to UO_2 . The large crystals that result may then be crushed and screened to give smaller particle sizes.

The process starts with either ammonia cake (ammonia diuranate) that is calcined at low temperature to form UO_3 -monohydrate or with peroxide cake (UO_4 -hydrate). To this material is added 10 to 20 wt. % uranium as a uranyl salt (usually uranyl nitrate hexahydrate crystals) or nitric acid. The mixture with some water added is then heated in a stainless-steel autoclave for 10 hr at 250°C . Rigid control of the autoclaving temperature is essential inasmuch as incomplete processing occurs at lower temperatures and different crystal forms may occur at higher temperatures. The size of the crystals may be controlled by the rate at which the salt goes into the solution and particularly by the concentration of the solution.

After autoclaving, the supernatant liquid is decanted, and the crystals are thoroughly washed to remove all the uranyl salt from their surfaces. Any remaining salt would cause agglomeration of the crystals.

The hydrate crystals are then heated under a hydrogen atmosphere at 1000°C to reduce them to UO_2 . The resulting product is not strong, but further heating to 1800°C results in a dense, hard material.

The final product is a dense UO_2 shape that has the same external form as the parent UO_3 -monohydrate but is about two-thirds the size. Needles, plates, rhombohedra, and bipyramids are observed, with the latter two being generally desired. Although the UO_2 particles are not single crystals, they are probably composites of UO_2 single crystals about 5 to $20\ \mu$ in size. Needles of UO_2 , 5 by $30\ \mu$ in size, have been observed and appear to be single crystals.

Of the crystals grown by this process, those that are 50 mesh and larger, and thus agglomerates, are unstable. Rough handling or decrepitation caused by sudden heating of the UO_3 will cause them to break into platelets; even without rough handling they will break down if allowed to remain at room temperature for moderately long periods of time. This defeats the intended purpose of the product since the platelets have one very small dimension that makes them useless for matrix fuel elements. A fairly small percentage of platelets in a batch of crystals will ruin the entire batch. Experiments are now being conducted to determine a useful method for separating the undesirable platelets from the remainder of the crystals.

One of the principal difficulties encountered with this method of uranium dioxide preparation is that the processing conditions for depleted, normal, and enriched cake are all different. This makes it difficult to translate results obtained using normal material, for example, into a finished product that might utilize enriched material.

Several other methods have been devised for the preparation of UO_2 . In the case of making dense oxide bulk shapes, a fine-grained powder commonly called "ceramic grade" is generally desirable. Where the ultimate use is in matrix type fuel elements, a coarser grain called "cermet grade" is desired.

Several of the more widely used processes are described very briefly. In the usual case each of these resultant oxides (except for the fused material) requires subsequent processing to produce a coarser, more stable product for use in matrix type fuel.

4.3 Peroxide Precipitation

UO_4 dehydrate is made by precipitation in a uranyl nitrate solution with hydrogen peroxide. The $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ is washed and dried, after which it is reduced to UO_2 at 900°C with hydrogen. The UO_2 is submicron in size, the particles often being about 0.05 to $0.1\ \mu$ in at least one direction.

4.4 Ammonium Precipitation

Ammonium diuranate is precipitated from a uranyl nitrate solution with aqueous ammonia. The precipitate is washed, dried, and calcined at 700°C in nitrogen for 2 hr. It is then ground and reduced to UO_2 in H_2 at 850°C for 4 hr, and then it is blended.

An extremely fine-grained UO_2 results which may be pyrophoric, burning to U_3O_8 . It rapidly takes up oxygen from the air in any case, generally stabilizing at about $\text{UO}_{2.15}$.

4.5 Steam Oxidation of Hydrided Uranium Chips

Uranium chips are converted to the hydride by heating in hydrogen at 250°C. Further heating in an inert atmosphere at 450°C decomposes the hydride to uranium powder, which is then steam oxidized as below. A stable UO_2 having particles about 1 to 5 μ in size results.

4.6 Steam Oxidation of Uranium Chips

Uranium chips are oxidized to UO_2 by passing 350°C steam over them. The product is heated in hydrogen at 900°C to stabilize it (increase grain size to prevent spontaneous oxidation). This UO_2 is about 1 μ in size.

4.7 Reduced U_3O_8

U_3O_8 is made by burning uranium chips. It is reduced to UO_2 in hydrogen at 900 to 1000°C.

4.8 Reduced UO_3 Hydrates

Uranyl nitrate is decomposed by heat to UO_3 hydrate.

This powder is then reduced in hydrogen at 800°C to UO_2 . A fine-grained oxide results which generally has particles less than 1 μ in size.

4.9 Spray-dried (Decomposed Nitrate) UO_3 Spheres

Uranyl nitrate is spray dried and decomposed in a heating chamber; spherical UO_3 particles result. These are reduced in hydrogen to UO_2 at temperatures of 1000 to 1800°C. An undesirable laminar shell effect results, making a very weak product. Spheres up to several hundred microns in diameter have been made.

4.10 Fused Oxide

UO_2 may be fused in a carbon arc process to very dense lumps. Pieces more than $\frac{1}{2}$ in. in size may be made and subsequently ground and screened to size. Sizable volatilization losses make this appear unattractive for enriched material.

4.11 Agglomerated UO_2

Fine uranium dioxide powders may be sintered at 1800 to 2000°C to a relatively loosely bonded mass. The resultant sintered mass may then be crushed, following which it is screened to remove the agglomerates of the desired particle size. These particles are then resintered at 2000°C to improve the bonding and to strengthen the particles. The best starting material to use for this procedure is uranium dioxide made by the reduction of calcined ammonium diuranate which is the common ceramic grade of material. The particles of this starting material are fairly fine, irregular, and active.

A slightly different approach to the sintering of UO_2 has been developed in which the UO_2 powders are bonded with an organic binder and crushed and screened to the desired size. These particles are then sintered into strong agglomerates. The effect of additives (ZrO_2 , MnO_2 , MoO_2 , TiO_2 , NiO , Al_2O_3 , CaO , etc.) has also been studied. Small additions of TiO_2 (0.5 to 1.0 per cent) or CaF_2 (3.0 per cent) increase sintering rates such that the UO_2 particles are made dense at 1500 to 1600°C. For example, peroxide type UO_2 sinters to 8.4 g/cm³ density

after 3 hr at 1500°C, but, with the addition of 1.0 per cent TiO_2 , the resultant density is 10.1 g/cm³. The addition of TiO_2 or CaF_2 also provides greater particle crushing strength. From the standpoint of neutron economy it would appear that the CaF_2 addition should give a superior material. Oxides prepared by the addition of such mineralizers seem less reactive and superior to Geneva oxide for cermet type elements.

A further approach is the use of U_3O_8 rather than UO_2 . U_3O_8 prepared by calcining UO_3 monohydrate seems perfectly stable after heat-treating Al- U_3O_8 plates for 600 hr at 600°C.

4.12 UBe_{13}

This compound is prepared by melting uranium and beryllium in a beryllia crucible at 1600°C. A 2 per cent excess of beryllium over the compound weight is added to compensate for the evaporation of the beryllium during the melting operation.

4.13 U_3Si

This compound is prepared by an induction-melting process. The material is held at the pouring temperature for 5 min, and, after pouring, it is slow cooled to prevent cracking. It is then heat-treated for one week at 700°C to obtain a homogeneous epsilon structure.

4.14 U_2Ti

U_2Ti has been prepared from high-purity uranium and sponge titanium. Stoichiometric ratios of the two metals were melted in an argon atmosphere in an arc furnace using a tungsten electrode. The resulting buttons were remelted three times to improve homogeneity.

4.15 UC

Two methods of preparing UC are by methane carburization of uranium and by arc melting. To produce UC by the arc-melting technique, a nonconsumable electrode using a water-cooled copper crucible is used. Helium is the protective atmosphere. A high-purity graphite water-cooled electrode held negative is employed. UC is a brittle compound the powder of which is extremely pyrophoric and must be handled in an inert atmosphere. Spectrographic grade electrode carbon (4.85 per cent) was needed to prepare the monocarbide containing 4.79 per cent carbon.

4.16 U_6Ni

The formation of U_6Ni takes place in a manner similar to that employed for U_2Ti . Stoichiometric ratios of the nickel and the uranium are arc melted under an argon atmosphere using a tungsten electrode. Subsequent remelts improve homogeneity.

5 FOR HIGH-TEMPERATURE USE

High temperatures are of interest for a power-producing breeder reactor because of the increased thermal efficiency of the power-plant cycle and because of the possibility of a relatively short doubling time.

5.1 Graphite Matrix

Graphite is one of the most attractive matrix materials being considered in the development of fuel elements which would permit higher operating temperatures in reactors. It has a high sublimation point, good high-temperature strength, and excellent resistance to thermal shock. It is also one of the better moderators. Graphite matrix fuel elements also feature relatively simple decontamination, easy recovery processes, and simplicity of fabrication.

Considerable data are available on the diffusion of fission fragments at elevated temperatures, and the indication is that for sufficiently high temperatures of operation a homogeneous

uranium-bearing graphite reactor would be self-decontaminating. For reactors operating at lower temperatures, it might be possible to remove the fuel elements periodically and to decontaminate them by heating.

The problem of the annealing of radiation damage is closely associated with that of decontamination. It is probable that any thermal treatment that would provide decontamination would also anneal the radiation damage and would thus eliminate the need for elements made by introducing uranium during the graphite fabrication process. This process is more complicated and hence less desirable than the impregnation technique.

With regard to both fabrication and fuel processing, it is expected that the uranium-graphite fuel element would have a definite economic advantage over the conventional metal type. The impregnation process involves only simple chemistry and thus eliminates the metallurgical processing required for metallic elements.

5.2 Fabrication of Fuel Elements

Uranium can be introduced into a graphite matrix by several methods such as (1) granules of a uranium compound such as the oxide or carbide can be mixed with powdered graphite and a suitable pitch and then baked. By using such methods, it is possible to obtain a wide selection of particle sizes and good control of the uranium distribution. It also permits fabrication of high-density bodies and (2) solid graphite can be impregnated with a uranium compound. Common artificial graphite has a pore size of 6 to 12 μ and has a pore volume of 25 per cent, thus lending itself to impregnation by a uranium-bearing solution. One of the problems associated with the impregnation of graphite is the nonuniformity in the uranium concentration.

5.3 Fission-product Damage

The effects of radiation damage to graphite are well known. Fast-neutron damage is not expected to be a problem in high-temperature reactors because of simultaneous annealing. Fission-product damage, on the other hand, persists at high temperatures.

5.4 Diffusion and Loss of Uranium

Other problems in the use of uranium-graphite fuel elements at high temperatures are the diffusion and loss by volatilization of uranium. Solid-phase diffusion of uranium through graphite is negligible at temperatures lower than 2700°F. The process of uranium transport which is referred to here as solid-phase diffusion is characterized by a steep gradient of uranium concentration and by a limited penetration of the graphite by uranium. At temperatures above 4000°F, a second mechanism contributes to permeation of graphite by uranium. This appears to involve the flow of uranium vapor through the open pores in the graphite. This type of transport produces low concentrations, a very small concentration gradient, and apparently unlimited penetration. This is known as pore diffusion.

The use of large UO_2 particles, e.g., between 100 and 1000 μ in diameter, may have three important advantages: (1) less fission damage to the graphite, (2) less diffusion and loss of uranium, and (3) better retention of fission products by the fuel element.

It would appear that a temperature of about 2600°F would be the maximum operable temperature to avoid loss of uranium by diffusion.

5.5 Retention of Fission Products

The question of whether fission products will be retained by a fuel element at high temperatures is a very important design consideration. In some reactors that have been proposed, the coolant system would be thoroughly shielded, and fission products would diffuse continuously through the fuel element into the coolant. It has been suggested that such a self-decontamination process would result in high neutron economy and would simplify reprocessing of the unspent fuel. In many cases extra shielding about the coolant system and facilities for decontaminating the coolant are prohibitively cumbersome. Most of the solid-fuel reactors that have been built have some provision for keeping fission products in the fuel element. The

Materials Testing Reactor, for example, depends upon aluminum cladding to prevent the fission products from entering the coolant.

It seems very likely that the use of large fuel particles will ease the problem of fission-product retention in a porous matrix material such as graphite. With large fuel particles above 500 μ , most of the fission products would be stopped in the fuel itself. Diffusion of the fission fragments through dense uranium oxide or carbide would be much slower than through porous graphite. Thus with larger fuel particles fission-fragment retention would depend primarily on the rates of diffusion through uranium oxide or carbide.

5.6 Ability To Discharge the Fission Heat

If the uranium oxide or carbide is incorporated in the graphite in relatively large particles, the fuel itself will reach a higher steady-state temperature, for the same specific power, than if it is dispersed homogeneously throughout the conducting matrix. Both the temperatures of the fuel and the internal thermal stresses in the graphite will increase with the size of the fuel particles.

The oxide can be converted to the carbide by heating to temperatures above 1900°C. One of the problems associated with the impregnation of graphite is the nonuniformity in the uranium concentration. Three methods of fabricating graphite are extrusion, cold molding, and hot molding. Diffusion of the UC_2 in graphite is primarily a volume phenomenon. Diffusion of the UC_2 fuel has practically no effect on the operation of a high-temperature reactor. The migration of UC_2 in a reactor operating at high temperatures is very limited, and this migration will not appreciably alter the lattice constants or the operating characteristics of the reactor.

5.7 Nichrome V - UO_2

Nichrome V is resistant to oxidation at high temperature, and its stress rupture strength as a function of time at 1800°F is better than that of 310 stainless steel. However, the macroscopic thermal-neutron cross section of Nichrome V is 0.37 cm^{-1} as compared to 0.25 cm^{-1} for stainless steel.

Nichrome- UO_2 composites have been successfully fabricated by cold pressing and sintering in a hydrogen atmosphere at 2150°F followed by hot-rolling using a picture-frame technique. Sintered density may be as high as 80 per cent of theoretical. After the composites are hot-worked, theoretical density is obtained, and the high-temperature rupture strength is approximately 90 per cent of that of commercial solid Nichrome V at the same size.

Strong UO_2 particles are needed to avoid particle breakup and stringing.

5.8 Nb- UO_2

Niobium has good high-temperature mechanical properties and a relatively low neutron cross section. Powder-metallurgy fabrication of these cores has been successfully accomplished by cold pressing and sintering over 2100°C in vacuum. Densities after sintering are over 85 per cent. One of the disadvantages of this method of core fabrication, however, is that the vapor pressure of UO_2 becomes appreciable above 1800°C, and consequently part of the UO_2 is lost through vaporization at the compact surface. At 2150°C the vapor pressure of UO_2 is 400 μ . This loss may be minimized by sintering compacts of larger volume to surface area ratios or by sintering at temperatures lower than 1800°C.

The clad Nb- UO_2 composite cores are cold-rolled with intermediate anneals at 1200 to 1400°C. UO_2 particles larger than 10 μ are desirable.

5.9 Mo- UO_2 , Mo - 10 Wt. % UC, and Mo - 10 Wt. % UBe_{13}

No reaction has been observed between molybdenum and UO_2 . Mo- UO_2 cermets sintered for several hours at temperatures ranging from 1750 to 2000°C yielded densifications of 90 to 95 per cent of theoretical density. Difficulties were encountered, however, in trying to roll composites with UO_2 concentrations greater than 20 wt. %. A dispersion of 10 wt. % UC in

molybdenum was sintered 1 hr at 1760°C. Larger additions of UC_2 were not attempted because of rolling troubles at 10 per cent. The carbide particles appear to be distinct and separate from the molybdenum matrix.

A Mo-10 wt. % UBe_{13} mixture was examined. Some melting occurs at 1820°C. It was sintered at 1705°C but could not be rolled. Volatilization of beryllium is a problem.

5.10 Be- UBe_{13} , Be- UO_2 , and Be- UC_2

The potential use of beryllium as a matrix has many advantages. It would fulfill a duty as a moderator while properly diluting the uranium with a good thermal conductor.

Uranium and beryllium tend to react at fairly low temperatures, but there is a compound UBe_{13} that has a melting point of about 2000°C and is stable in contact with beryllium at temperatures up to 1250°C. This proposed fuel-element system then would consist of a beryllium matrix surrounding islands of the stable uranium compound UBe_{13} .

Experiments were performed on this system as follows: beryllium and UBe_{13} powders were blended and cold pressed at 60 tsi, following which they were sintered for 3 hr at 1160°C *in vacuo*. The compacts were then warm pressed at 425°C and 60 tsi. This treatment was again followed by a vacuum sintering identical to the first.

High density values have been reported as a result of this procedure. For example, at 10 wt. % UBe_{13} , nearly 100 per cent of theoretical density was achieved, and, at 75 wt. % UBe_{13} , a density of better than 90 per cent of theoretical has been reported. Similar tests carried out with Be- UO_2 mixtures resulted in lower densities, presumably because of chemical reaction during sintering. Attempts to sinter Be- UC_2 composites containing 10, 30, and 50 wt. % UC_2 were not successful at 1090 to 1250°C. During sintering all compacts expanded, especially in the direction such as to relieve the compacting pressure. The formation of Be_2C was probably responsible for this behavior.

6 FOR GREATER CORROSION RESISTANCE

6.1 Zirconium Matrix

The use of zirconium as a matrix is linked with the need to develop a fuel element for service at moderate to high temperatures which will resist catastrophic failure because of corrosion resulting from a pinhole in the cladding. Zirconium also has an extremely favorable thermal-neutron cross section. Since this metal is also favored as a cladding material, manufacturing problems should be considerably eased owing to the compatibility between core and cladding. This compatibility should also ensure a good thermal bond.

In this type of fuel element discrete particles of fuel material are placed in a continuous matrix of corrosion-resistant material. Thus the corrosion resistance of the core is increased, and the radiation damage may be confined to local areas in the core. In addition, powder-metallurgy techniques allow close control of grain size and the use of fabrication temperatures low enough to prevent many reactions that would occur with normal fabrication procedures.

It is important in a fuel element that attempts to have increased corrosion resistance to ascertain that the following requirements are met:

1. The matrix must have a high degree of purity.
2. There should be a minimum of diffusion between the fissile dispersant and the matrix.
3. A large particle size that is uniformly dispersed.
4. Fully dense matrix.

6.2 Zr- UO_2

The reaction between zirconium and UO_2 at 1000°F is negligible. A measurable reaction takes place at 1300°F, whereas at 2000°F the reaction is very rapid. The UO_2 seems to be reduced to its elements, uranium and oxygen, which diffuse simultaneously but not with equal

speed into the zirconium. The diffusion of oxygen into the zirconium results in a hard zirconium-oxygen solid solution.

Reactants heated at 1300°F and slowly cooled to room temperature were found to have formed alpha zirconium and alpha uranium adjacent to the UO_2 . Deeper in the original zirconium region the epsilon uranium-zirconium intermetallic phase was found dispersed in a zirconium-oxygen solid solution. On the basis of limited data it has been estimated that penetration of oxygen through the 0.030-in.-thick zirconium jacket walls would cause their destructive embrittlement in about 300 days at 1300°F or $2\frac{1}{2}$ days at 2000°F.

In any event it appears reasonably safe to assume that very little, if any, reduction of the oxide will occur during normal reactor operation where temperatures below 1000°F would be used. However, the relatively low temperature of reaction eliminates or makes difficult some attractive methods for fabrication of the fuel elements. Billets are prepared for coextrusion by warm pressing or cold pressing and sintering at a low temperature (1000°C) $\text{ZrH}_2\text{-UO}_2$ or Zr-UO_2 mixtures. At this low temperature of sintering the billets will be porous but should be fully consolidated in the extrusion process. Any processing of Zr-UO_2 mixtures above 1200°C will result in the disappearance of any UO_2 in a matter of a few hours at these temperatures.

6.3 Zr-UC

The reaction between zirconium and UC proceeds rapidly at temperatures above 1000°C, and extensive diffusion between the carbide phase and the matrix has a deleterious effect upon corrosion resistance. In addition, the corrosion resistance is sensitive to composition, particle size of the dispersed phase, degree of dispersion, matrix porosity, and the extent of contamination during processing. Any intrinsic corrosion resistance of UC itself is negligible.

Uniformity of dispersion is one of the important factors that affect corrosion behavior. Nonuniformity can appear either as occasional particle segregation of the UC or as a gross separation of the UC and zirconium powders because of the density differential.

Zr-UC has been fabricated by hot pressing at 1000°C in graphite molds for 30 to 60 sec, cold pressing and vacuum sintering at pressures of 12 to 75 tsi and temperatures of 1200°C for 6 hr, extrusion at 800°C, and hot rolling at 800°C in a sheath. Of these four methods, only the latter two are amenable to producing a dense product at temperatures less than 1000°C and thus are the methods preferred to produce a corrosion-resistant product. The corrosion performance of Zr-UC cermet is strongly influenced by the distance separating UC particles in the zirconium matrix. For example, a cermet containing 30 wt. % having a mesh size greater than 100 mesh was corrosion resistant, whereas the same composition with UC particles of less than 100 mesh was not. Water under pressure at 680°F was the corrosion medium. It follows that for a given composition a larger average particle size results in larger separating distances between the dispersed UC particles, resulting in improved corrosion resistance.

Diffusion zones are attacked at almost the same rate as are the UC particles, indicating that corrosion performance would be improved if the diffusion zones could be reduced to a minimum. Diffusion zones have been minimized in cermets made by extrusion and hot rolling.

Several means of inhibiting diffusion between UC and zirconium have been explored. Nickel plating of the UC, tin coatings by wiping and dipping, vacuum fusion of tin and UC, and application of indium by wiping were tried. These elements are not carbide formers and hence might be expected to act as barriers between the UC and the Zircaloy matrix.

7 FOR GREATER LOADING PER UNIT VOLUME

In an effort to improve corrosion resistance and decrease radiation damage in any dispersion type fuel element with a fixed requirement in terms of uranium loading, the designer of fuel elements looks to uranium compounds that permit a higher fuel loading per unit volume than UO_2 . The use of UC in a zirconium matrix as discussed in a previous section is an example of this type of thinking. Some other compounds that accomplish the same purpose are U_2Ti , U_3Si , and U_6Ni . The matrix used in a discussion of this type of fuel element is of secondary importance except from the standpoint of compatibility. Roll-clad plate type elements of all

these compositions may be fabricated by powder-metallurgy methods in such manner that good core to cladding bonds and cores with uniform dispersions of discrete uranium compound particles are obtained.

7.1 Zr-U₂Ti

There is a partial reaction of U₂Ti with zirconium at a temperature of 1500°F. Since this temperature is the normal fabricating temperature in a hot-rolling operation, this increases the problems involved in fabricating a fuel element of this particular dispersion combination. Attempts to hot-roll this combination at lower temperatures (1300 to 1400°F) result in poor core to cladding bonds. In addition, the U₂Ti particles are relatively ductile at elevated temperatures and tend to elongate at fabrication temperatures as low as 1300°F.

7.2 U₃Si-Zr

A slight reaction takes place between U₃Si and zirconium at temperatures near 1500°F. The particles of U₃Si were also fairly ductile at temperatures as low as 1300°F, resulting in elongated particles that are objectionable from the standpoint of radiation damage. Good core to clad bonding was obtained.

7.3 U₆Ni-Zr

U₆Ni-Zr cores may also be fabricated by hot-rolling. However, U₆Ni decomposes at 1454°F, and there is a eutectic between U₆Ni and U₇Ni₃ at 1364°F; therefore reactions between zirconium and U₆Ni or nickel-rich U₆Ni are possible at quite low temperatures. There is evidence of a reaction in specimens roll clad at 1300°F. Good core to clad bonding was obtained.

8 SUMMARY AND CONCLUSIONS

The dispersion type fuel element offers two unique advantages over elements having a homogeneous fissile core: (1) increased operating life through localization of the fission-product damage in and immediately adjacent to the dispersed phase, thus minimizing damage to the structural matrix, and (2) increased choice of fuel-element systems to permit use of normally metallurgically incompatible fuel and diluent metals and attainment of physical and mechanical properties not attainable in homogeneous fuel systems.

The specific dispersed phase and matrix metal used depends upon the particular reactor design under consideration, with factors such as operating temperature, type of coolant, and neutron-energy spectrum limiting the materials choice.

Although radiation damage in a dispersion system may result from fast particle or neutron bombardment of the fissile phase, whether it be metallic, ionic, or molecular, the major effect will be due primarily to the high-energy recoiling fission products. This could be called the "dynamic" properties of the fission products. Another significant metallurgical effect will be introduced by the "static" properties of fission fragments as they come to rest in the lattice atoms of the fuel. The total damage is a combination of these static and dynamic effects, and it is clear that as higher concentrations of fission products are approached the static effect will predominate. Thus the object of a dispersion type element is to concentrate the damage in the dispersed phase and in a highly localized region surrounding the dispersed fissile particle leaving a fission-product-free region of metallic metal around the zone of damage.

Of course at high temperatures thermal diffusion of fission products into the undamaged matrix region may occur and thus may markedly change the properties of the fuel.

Fabrication of dispersion type elements involves one or more of the following fabrication techniques along with conventional hot- and cold-working processes.

1. A blending and cold pressing of the powders followed by sintering at elevated temperatures
2. A blending of the powders followed by pressing at slightly elevated temperatures

3. Blending of the powders followed by pressing in a die at markedly elevated temperatures
4. Blending of the powders followed by hot extrusion

It is obvious that dispersant type fuel elements offer a very wide choice of fabricating procedures, of dispersant materials, and of matrix materials. It is difficult to imagine any reactor employing solid fuel whereby a dispersant type fuel element could not be considered.

Fuel Dispersion in Stainless-steel Components for Power Reactors

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ABSTRACT

The development of cheap and reliable stainless-steel components containing highly enriched UO_2 has made possible the construction of power-producing reactors of compact-core design and high-operating-performance characteristics. This paper discusses the selection of the materials for this type of fuel component; the powder metallurgical processing required; methods that may be used to fabricate composite plates, wires, pins, and tubes; and the manufacturing characteristics of this fuel dispersion in stainless steel. Joining of the basic composite part is described briefly, with emphasis on brazing methods. Pertinent property data are also listed.

1 INTRODUCTION

The availability of enriched fuel in the United States makes possible the construction of power-producing reactors of compact-core design and high-operating-performance characteristics. In such applications the fuel must be dispersed in a suitable diluent in order to maximize the heat transfer from each gram of U^{235} . In addition it must be contained in a suitable material to retain the highly poisonous by-products of fission as well as to afford the needed corrosion protection. Stainless-steel base components containing a dispersion of enriched UO_2 and of various extended-surface designs have been developed specifically to meet these requirements. In general, these long-life components are cheap to produce, and their reactor performance to date in the environment of pressured water and organic mediums has been excellent. As a consequence the capital investment required for reactor construction is small, and the cost of operation is low.

It is the object of this paper to present methods that can be utilized to advantage in processing stainless-steel fuel components of various shapes; to describe the characteristics of the product; and to point out some of the limitations that may be encountered.

In general, alloys of uranium in stainless steel or any of its elemental constituents cannot be considered as fuel material because of the presence of low-melting eutectics and brittle intermetallic compounds.¹ Therefore development of stainless-steel fuel elements has centered on the selection of a uranium-bearing compound that is metallurgically compatible and chemically inert when dispersed with stainless steel and processed at the necessary elevated temperatures. The fissile compound is dispersed in stainless steel by using powder metallurgy procedures that usually involve blending component powders, pressing them into a green compact, sintering, and coining. Such processing offers the advantage of accurate accounting of the materials in each compact. The fuel material is contained in a wrought stainless-steel

protective cladding that prevents leakage of fission products, and the cladding is metallurgically bonded to the fuel compact to maximize heat transfer. Figure 1 is an example of a UO_2 dispersion in stainless-steel composite plate manufactured by a roll cladding process. Other processing, such as extrusion and swaging, can be utilized with similar results.

2 MATERIAL SELECTION

In the selection of materials for the basic composite component of the fuel element, it is necessary to consider the cladding, the fuel compound, and the fuel matrix.

2.1 Cladding Material

Compared to the ferritic variety, wrought austenitic stainless steel is more favorable as the cladding metal because of its superior corrosion resistance.² The corrosion resistance of austenitic stainless steel in pressurized water at 260 to 315°C is excellent.³ The majority of results have revealed that the corrosion rate is less than 0.10 mg/cm²/month compared to ferritic stainless steel with a corrosion rate of approximately 0.50 mg/cm²/month. At 425 and 540°C at 5000 psi, the corrosion resistance⁴ of austenitic stainless steel is of the same order of magnitude as that at 315°C. However, after 132 days at 730°C and 5000 psi, the corrosion rate increases to 0.19 mg/cm²/month. The 309 and 310 surfaces showed scattered black spots and slight pitting along with the formation of the dark tarnish film. Deep pitting was observed in type 347 specimens. Since the majority of applications considered to date are in the 260 to 315°C range, it is evident that austenitic stainless steel is more than satisfactory. Above 540°C, the corrosion resistance decreases but still may be adequate for specific designs. The corrosion resistance of austenitic stainless steel in organic mediums appears satisfactory.⁵ For example, the corrosion rate in diphenyl at 315°C is approximately the same as it is in pressurized water.

2.2 Fuel Material

Uranium mononitride, monocarbide, and dioxide have been examined as the fuel compounds for this type of fuel element.⁶ Brief investigations indicate that UN may be attractive, with the

Fig. 1—Longitudinal section of a composite stainless-steel plate containing a fuel core of 34 wt. % UO_2 and 0.19 wt. % B_4C in 302B stainless steel clad with 304L stainless steel. Etchant: HCl-HNO_3 -glycerine. (Magnification 100 $\times$.)

possible exceptions that its neutron absorption cross section is somewhat higher and that it is not readily available at the present time. UC is not compatible with stainless steel at fabrication temperatures above 1000°C. UO_2 , on the other hand, is chemically inert with stainless steel at temperatures as high as 1400°C, is relatively economical to manufacture, is moderately corrosion resistant in pressurized water, has a relatively high density, and contains a substantial percentage of uranium. Because of the high density of UO_2 , reactor designs utilizing highly enriched uranium have only required a dispersion of it in the limited range of 15 to 30 vol. %. There are several methods for manufacturing UO_2 , and each type has characteristics that are dependent upon its previous history. The oxide generally contains some porosity, which is still retained in the finished product. This condition is illustrated in Fig. 2, a highly magnified photograph of UO_2 particles in a fabricated composite fuel plate.

Pycnometer density values have revealed a density of 10.33 g/cm³ for the hydrothermal grade oxides⁷ in comparison to the 10.9 theoretical density⁸ for UO_2 . Other types of UO_2 have been reported with densities less than theoretical.^{9,10} Experience at the Oak Ridge National Laboratory (ORNL) in manufacturing 1800 composite plates containing highly enriched uranium has also revealed that the U_T to UO_2 ratio is 2.5 per cent less than theoretical. UO_2 is moderately corrosion resistant in 500 to 600°F pressurized water, with an average corrosion rate³ of 5 mg/cm²/month.

2.3 Matrix Material

Iron, prealloyed austenitic stainless steel, and stainless steel, produced from the elemental powders during sintering of fuel compacts, have been investigated as matrix materials for the fuel-bearing sections. Silicon (2 per cent) added to the prealloyed austenitic stainless steel produces a high percentage of irregularly shaped particles, which are advantageous in preparing compacts requiring high cold-pressed strengths. As shown in Fig. 3 these powders, like the UO_2 fuel compounds, are also porous. Values of 7.50 and 7.45 g/cm³ for the high-silicon 304 and 347 stainless steel were obtained from pycnometer measurements.⁷ Similar measurements of iron powders have revealed a density of 7.69 g/cm³ compared to the theoretical density of 8.87 g/cm³.

Fig. 2—Porosity in hydrothermal UO_2 particles (as polished) in austenitic stainless-steel composite plate fabricated at 1175°C. (Magnification 1000 ×.)

Fig. 3—Porosity in 347 stainless-steel powder (as polished). (Magnification 1000 $\times$.)

3 PROCESSING OF FUEL COMPACTS

In preparing a dispersion of UO_2 in the selected matrix material, the sequence involves

1. Sizing the powders
2. Weighing and blending the powders
3. Compacting the blended powder into suitable shape
4. Sintering the compacts
5. Coining the compacts

Because of the extremely fine sizes of the UO_2 particles and the relatively high alpha activity associated with U^{235} , weighing of the UO_2 powder and cold pressing of the blended powders must be accomplished within dry-box equipment to confine contamination. Figure 4 shows the dry box in which the UO_2 is weighed. Gloves, not shown in the photograph, are attached to the ports, and the atmosphere within the box is maintained at a slightly negative pressure. After the UO_2 is weighed, it is added to blending jars containing the required quantities of stainless steel, and the jars are tightly sealed. Blending operations can then be done outside the dry box. Figure 5 illustrates the manner in which the contamination is confined during pressing of the blended powders. Once the material is cold pressed to a densification greater than 75 per cent of theoretical, the resulting product, by careful handling, can be sintered in conventional equipment and subsequently handled without any serious health hazard.

3.1 Sizing

Sizing of particles greater than $44\ \mu$ is accomplished with mesh screens. Classification of subsieve-size particles is done in an air classifier. The size of the UO_2 particle selected is primarily based on irradiation-damage effects and is not always the most desirable from a fabrication standpoint. Since irradiation damage is discussed in detail in another paper at this

Fig. 4—Dry box containing equipment for weighing enriched UO_2 powder.

conference, it has been excluded from the scope of this paper. In general, stainless-steel powder sizes less than $44\ \mu$ have led to better uniformity of the dispersion than larger sizes. However, this selection is also dependent on the particle size and quantities of the fuel compound. For example, in manufacturing the fuel material for the Army Package Power Reactor (APPR), a dispersion of 26 wt. % UO_2 consisted of UO_2 particles in the 44- to 88- μ range and stainless-steel particles ranging from 10 to 149 μ , with the larger fraction in the 44- to 149- μ range.¹¹ Chemical composition and size fractions of iron, nickel, chromium, and stainless-steel powders considered for stainless-steel dispersion elements^{9,11,12} are listed in Tables 1 and 2. Typical average particle sizes of the elemental powders (iron, chromium, and nickel) screened through 325 mesh, are 10.2, 7.8, and 4.6 μ , respectively.⁹

3.2 Weighing and Blending

After being sized, the powders are weighed and blended together. Blending is accomplished in a tumbling apparatus such as an oblique blender, and generally 2 to 3 hr is sufficient time for homogeneous mixing. Teflon cubes or steel washers are often added to the blend to improve conditions. Small quantities of zinc stearate or dodecyl alcohol also have been added with improved results. Batch blending of quantities of material containing 500 g of UO_2 has been done successfully.¹³ This technique lends itself well to production but has the disadvantage that the quantity of uranium in each subsequent individual fuel section depends on homogeneity of the blend. On the other hand, weighing the contents of each fuel core separately and blending the quantities for each core in its own container offer reliable fuel accountability as well as accurate accounting of small quantities of additives which may be desired in the fuel core.

3.3 Compacting

After the material has been uniformly blended, the required quantity is poured into a suitable die and compacted under pressure. The dies are often lubricated with a thin film of stearic

Fig. 5—Dry-box arrangement utilized during pressing of powder blends containing enriched UO_2 powder.

acid. As shown in Table 3, increasing the pressure increases the densification of the compacts.⁹ However, the densification is less at higher UO_2 concentrations. This trend is also apparent in the densification values after sintering 16 hr at 1300°C in dry hydrogen and coining. In general, cold-pressed densification values of 75 to 80 per cent are desirable for handling compacts without spallation. Densification of less than 75 per cent of theoretical results in fragile compacts that are prone to damage. It has been shown that in a dispersion of 18 wt. % UO_2 in type 304 stainless steel, the modulus of rupture of a compact cold pressed at 33 Tsi to 74 per cent densification is 1250 Tsi; this value increases to 1825 Tsi when the compact is cold pressed under 50 Tsi to 82 per cent densification.¹⁴

3.4 Sintering

After the compact is pressed into shape, it is most often sintered at elevated temperatures to increase the density of the compact and coined at room temperature to correct for dimen-

Table 1—CHEMICAL ANALYSIS OF METAL POWDERS

Metal or alloy	Composition, wt. %								
	C	Fe	Cr	Ni	Si	Mn	Mo	Nb	Others
Electrolytic iron*	0.06	99.7							Si, Mn, S, P, Mo, Al, Cu, Mg, Si
Carbonyl nickel*	0.12	0.002–0.02		99.8	0.001–0.01				S, P
Electrolytic* chromium		0.06	99.9	0.005	0.007		0.001		S, P, Al, Cu, Mg, Ca
High silicon 347† stainless steel	0.05	64.98	18.62	11.44	2.35	1.56		0.97	S, P
High silicon 304† stainless steel	0.07	69.83	18.16	8.62	2.37	0.93			S, P
Type 302* stainless steel	0.09	70.80	18.58	8.86	1.05	0.59			S, P
Type 302B* stainless steel	0.10	70.96	17.43	8.14	2.53	0.81			S, P
Type 310‡ stainless steel	0.09	56.33	23.39	18.56	0.99	0.58			0.06 Co
Type 314‡ stainless steel	0.15	52.58	24.03	20.12	2.20	0.98			0.24 Co

*Data from BML.

†Data from ORNL.

‡Data from Sylvania Electric Products, Inc. (SEP).

Table 2—TYPICAL PARTICLE-SIZE ANALYSIS OF HIGH-SILICON 304 AND 347 STAINLESS-STEEL POWDER

Size, μ	Type 304	Type 347
> 149	1.9	0.1
105–149	23.9	20.6
74–105	26.1	37.7
44–74	17.0	14.6
< 44	31.1	27.0

sional changes due to shrinkage. Sintering is accomplished in a dry hydrogen atmosphere with a dew point better than -50°C . Acceptable cores have been obtained at sintering temperatures as low as 1175°C ¹¹ and as high as 1350°C .⁹ Compacts containing 30 wt. % UO_2 in stainless steel, previously compacted under 50 Tsi to 77 per cent densification, showed an increase to 90.4 per cent densification after sintering 4 hr at 1300°C . Increasing the time to 16 hr showed no appreciable increase. Decreasing the time to $\frac{1}{2}$ hr resulted in a densification as low as 83.6 per cent. Significantly the density of the material in roll-clad composites after 88 per cent reduction in thickness at 1300°C was nearly the same regardless of previous history of the compact. Densifications as high as 95 per cent have been observed at sintering temperatures of 1350°C . As shown in Table 4, niobium additions to stainless steel appear to increase densification values.⁹ With a dispersion of 26 wt. % UO_2 in high-silicon 304 or 347 stainless steel cold pressed under 33 Tsi and sintered at 1175°C for $1\frac{1}{4}$ hr and coined, densification values of 82.5 per cent have been observed.¹¹ Iron behaves like prealloyed stainless steel when substituted as the matrix material; however, whenever the matrix contains elemental iron, nickel, and chromium powders of the proper stainless-steel composition, negligible densification is obtained after 4 hr of sintering¹² at 1205°C . Increasing the temperature to 1325°C results in a sintered density approximately 85 per cent of theoretical.¹⁵

In general, it may be stated that it is possible to sinter compacts containing dispersion of 30 wt. % UO_2 to densifications that are slightly greater than 95 per cent of theoretical, but, in

Table 3—EFFECT OF COMPACTING PRESSURE ON COLD-PRESSED AND SINTERED DENSITIES OF UO_2 DISPERSIONS IN STAINLESS STEEL

Compacting pressure, Tsi	310 SS from elemental powders, wt. % UO_2				Prealloyed 310 SS, wt. % UO_2		
	10	20	30	0	10	20	30
Cold-pressed density, % of theoretical							
30	72.6	70.4	69.5	69.4	72.2	71.1	70.7
50	79.4	78.2	76.7	77.1	77.1	76.7	76.1
60	80.0	79.7	78.0	76.0	79.6	77.3	74.7
Coined density, % of theoretical*							
30	78.5	74.5	72.0	86.9	81.6	81.6	78.5
50	82.5	78.0	75.7	91.5	86.1	85.0	83.5
60	84.2	78.5	75.9	91.1	86.4	86.3	84.1

*After sintering 16 hr at 1300°C in dry hydrogen.

Table 4—EFFECT OF NIOBIUM ADDITIONS ON SINTERED DENSITY OF DISPERSIONS OF 30 WT. % UO_2 IN STAINLESS STEEL COLD COMPACTED UNDER 50 TSI

Type SS	Cold-pressed density, % of theoretical	Sintering temp., °C	Sintered density, % of theoretical
Prealloyed 310	75.0	1300	90.4
Prealloyed 310 + 1% Nb	78.2	1300	95.0
Elemental 310 + 1% Nb	76.4	1300	95.1
Prealloyed 310	75.7	1350	95.2
Prealloyed 310 + 1% Nb	76.7	1350	95.7
Elemental 310 + 1% Nb	77.2	1350	95.8

preparing compacts for subsequent cladding, sintered densities as low as 82 per cent are satisfactory. In fact, preliminary experiments have indicated that it may be possible to eliminate the sintering operation and simply fabricate the cold-pressed compact into the desired composite.¹⁴

Although the fuel-bearing material is protected by wrought stainless-steel cladding, the cladding is thin and defects are possible. It is important that in the event of a failure the core be at least moderately corrosion resistant. Dispersions of UO_2 , UC, and UN in iron and austenitic stainless steel have been tested for short periods in 300°C static pressurized water. In some cases the material has been exposed completely; in others the material has been clad and sheared to expose the edges, or deliberate defects have been made through the cladding to expose the fuel dispersion. Attack was observed in dispersions of 26 wt. % UO_2 in iron after 500 hr at 300°C and 1200 psi, but the reaction did not proceed catastrophically. In contrast the same concentration in austenitic stainless showed no attack, and the corrosion rate was quite similar to that of austenitic stainless steel.¹⁶ Dispersions (44 wt. %) of UN in austenitic stainless also appeared unattacked after 500 hr; however, severe blistering was observed in specimens containing 43 wt. % dispersion of UC in austenitic stainless under the same conditions.⁶

4 PROCESSING OF COMPOSITES

Dispersions of UO_2 in austenitic stainless steel in the range of 20 to 40 wt. % UO_2 can be readily fabricated in a variety of composite shapes including plates, wires, pins, and tubes.

4.1 Composite Plates

Development of composite plates has progressed rapidly. For example, more than 3000 plates, each consisting of a 20-mil-thick core, clad on both sides with 5 mils of austenitic stainless steel, have been fabricated at ORNL. The fuel core consisted of a 26 wt. % UO_2 dispersion in austenitic stainless steel, with 0.14 wt. % B_4C added as a burnable poison.¹¹ Although rolling temperatures ranging from 1080 to 1300°C have been successfully employed in obtaining sound metallurgical bonding in composites containing dispersions¹⁷ of UO_2 , the selection of temperature is dependent upon billet preparation, concentration of UO_2 , concentration of desired additives, and total reduction required. The roll-cladding process established in fabricating composites for the APPR specifies unevacuated billets, which are simply preheated in a hydrogen blanket at 1150°C and reduced 90 per cent in thickness with intermediate preheats between mill passes. After hot rolling, the thin hot-roll oxide film is removed by pickling in a 15 per cent HNO_3 –5 per cent HF aqueous solution, and the plates are easily cold reduced 25 per cent prior to subsequent annealing and brazing into fuel assemblies.¹¹ Homogeneity of the finished product as qualitatively determined radiographically is excellent. Quantitative analyses of a fabricated composite plate containing 25.8 wt. % UO_2 reveal that 1-in.-diameter samples taken at random locations in the plate will contain 25.8 ± 0.5 wt. % UO_2 . The total fuel content of the plate, 26.11 g U^{235} , can be predicted¹¹ within ± 0.016 g.

4.2 Composite Wires

Composite wires, 50 mils in diameter and containing 30 wt. % UO_2 in type 304 stainless steel, have been metallurgically bonded to a 4-mil-thick clad of wrought type 304 stainless steel by hot swaging.¹⁸ This process includes an 85 per cent reduction in area at 1250°C followed by cold reductions of 10 per cent with intermediate annealing at 1150°C. The total reduction in area achieved was 99 per cent. Swaging temperatures below 1200°C did not yield satisfactory bonding; temperatures higher than 1250°C led to areas of high porosity; and cold draws greater than 10 per cent reduction in area caused tension failures.¹⁹

4.3 Composite Pins

Composite fuel pins nominally 0.175 in. in diameter can be fabricated by coextrusion followed by cold drawing and by a cold binder process requiring hot swaging and a diffusion treatment.¹⁶ In the extrusion process,²⁰ sintered cores containing a 25 wt. % dispersion of UO_2 in elemental 18 wt. % chromium–12 wt. % nickel–70 wt. % iron are machined to 0.750 in. in diameter by 1.333 in. in length and assembled in a type 304 stainless-steel tube. The billet assembly consists of three cores separated from each other by stainless-steel spacers and sealed with end plugs. The assembly is sealed within a thick-walled mild steel can that is chamfered at the leading end. After preheating $1\frac{3}{4}$ hr at 1050°C followed by a quick descaling treatment and an additional 15-min heating, the composite billet is extruded from a container heated at 310°C through a 480°C preheated 45-deg bell-mouthed die at a speed of 3.5 ft/sec. Total hot reduction in area is 95.6 per cent. After extrusion the mild steel can is removed by pickling in a 50 per cent HNO_3 aqueous solution heated at 100°C. Sizing of the extruded composite is possible with one hot-swaging pass at 1000°C, effecting a 10 per cent reduction in area. Density of the final product is greater than 97 per cent of theoretical. The sizing operation generally corrects ovality of the rod but only partially corrects ovality of the core of the composite. The magnitude of the ovality and eccentricity²⁰ of the pin after the 10 per cent swaging pass at 1000°C is shown in Table 5.

An alternative method, identified as the cold-binder process,¹⁵ produces pins that appear more satisfactory. However, only a few parts were fabricated by this method, and a greater quantity is required for complete evaluation. Basically the process circumvented deleterious extrusion effects by a minimum reduction involving hot swaging followed by a diffusion treatment. Iron oxides and a binder lubricant of 14 per cent starch solution in water are added to the 25 wt. % UO_2 dispersion in elemental stainless steel. The blended material is cold extruded through a 0.310-in.-diameter die, dried at 50°C, and sintered in hydrogen at 1325°C. After

Table 5—EFFECT OF 10% SWAGING PASS AT 1000°C ON OVALITY AND ECCENTRICITY IN EXTRUDED PINS

Distance from nose end of pin, in.	Max. ovality, mils		Max. eccentricity, mils	
	As extruded	After swaging	As extruded	After swaging
0	2		9	
8	3	1	6	14
24	4	0	10	23
32	3	1	12	15

electroplating a thin coating of nickel to the surface of the compact as a bond aid, a wrought stainless-steel tube is drawn tightly around the compact. The composite is reduced in area 60 per cent in three passes by hot swaging at 1200°C and subsequently subjected to a diffusional treatment at 1200°C for 4 hr. The results available indicate that a sound metallurgical bond is present in the final product.

4.4 Composite Tubes

Bonding by diffusion has also been exploited in the fabrication of tubular shapes.¹³ In this process a dispersion containing 25 wt. % UO_2 and a small quantity of B_4C in prealloyed austenitic stainless steel is cold shaped through rolls into a 30-mil-thick strip that is sintered at 1175°C and cold reduced 33 per cent in two passes with an intermediate anneal at 1175°C. After precision shearing and machining to a size approximately $1\frac{1}{4}$ in. wide by 20 in. long, wrought type 347 stainless-steel pieces are resistance welded to the fuel sheet. The sheet is cold formed into a tube, cleaned, and inserted into a wrought type 347 stainless-steel tube. Cleaning procedures are critical and include treatments in aqueous solutions of HNO_3 , Oakite 90, and a sulfochromic dip with intermediate water rinsing. The composite tube is drawn tightly about the fuel core by cold drawing to a reduction in area of approximately 18 per cent. Metallurgical bonding is achieved by a diffusional treatment of approximately 1 hr at 1150°C in a dry hydrogen atmosphere.

5 FRAGMENTATION AND STRINGERING OF FUEL DISPERSIONS

Dispersions of UO_2 in iron and stainless steel are typified by their tendency to fragment and stringer during fabrication. In most applications that include dispersions in the 15 to 30 vol. % range, these effects do not appear to be serious. However, fragmentation and stringering in plates containing higher concentrations may lead to a badly laminated structure that is prone to irradiation damage. These characteristics are affected by interrelated variables, i.e., particle size of the component powders, concentration of UO_2 , matrix material of the fuel-bearing core, and the deformation process. Available data indicate that dispersions in iron or stainless steel prepared from the elemental constituents are less susceptible to stringering than UO_2 dispersed in austenitic prealloyed stainless-steel powder.¹² The ductility of iron may be the cause of the improvement of dispersions in iron. On the other hand, it is significant that the average sizes of the elemental powders (iron, nickel, and chromium) are appreciably less than the size of prealloyed austenitic powder, and this size consideration may be the more important factor in the effect of the matrix material on the uniformity of the UO_2 dispersion. The longitudinal cross section illustrated in Fig. 6 is a prime example of the uniformity of the UO_2 dispersion in an iron matrix. The dispersion consists of 58 wt. % UO_2 (average size less than $20\ \mu$) in iron powder (less than $10\ \mu$ in size). The composite stainless-steel clad plate was reduced 90 per cent in thickness by rolling at 1335°C. Figure 7 compares the distribution in a 58 wt. % UO_2 dispersion in prealloyed type 302 stainless steel limited to a size fraction less than $44\ \mu$ and in the same type stainless steel with 70 per cent of its particle size between 44 and

Fig. 6—Composite stainless-steel clad fuel plate containing a dispersion of 58 wt. % UO_2 in iron after a total thickness reduction of 90 per cent at 1335°C (as polished). (Magnification $175\times$.)

70 per cent of 302B powder greater than $44\ \mu$

302B powder less than $44\ \mu$

Fig. 7—Effect of particle size of prealloyed 302B stainless-steel powder on the distribution of UO_2 (less than $44\ \mu$) in composite stainless-steel clad plates containing 58 wt. % UO_2 hot reduced 90 per cent in thickness at 1335°C . As polished. (Magnification $175\times$.)

149 μ . The gross agglomeration and stringering of the UO_2 in the composite prepared with larger size stainless-steel powder are striking. When the UO_2 concentration is reduced, the size of the stainless-steel powder loses its significance. Figure 8 illustrates a 26 wt. % UO_2 dispersion (44 to 88 μ) in prealloyed type 347 stainless steel in which 70 per cent of the powder ranged between 44 and 149 μ . The dispersion is shown after a hot reduction in thickness of 90 per cent at 1150°C. As a generality, when the UO_2 composition exceeds 40 wt. %, finer stainless-steel powders are desirable in order to minimize stringering. The effect illustrated in Fig. 7 also favors the selection of finer-sized UO_2 to improve the distribution in highly concentrated dispersions.

In addition to these effects the agglomeration and stringering are also dependent upon rolling temperature. Figure 9 compares these effects in composite plates, containing 37 wt. % UO_2 dispersions in type 302 stainless steel, after a reduction in thickness of 90 per cent at 1335 and 1100°C, respectively. The distribution is noticeably improved in the plate fabricated at 1335°C. These results are tempered with the cooling effect on the plate during the period of removal from the furnace to insertion through the rolls, especially in the latter stages of reduction. Fabrication at temperatures above 1200°C, however, is hampered by excessive oxidation of the stainless-steel cladding even when reheated in a semiprotective blanket of an inert or hydrogen atmosphere.¹² Fragmentation and stringering become very marked when roll-clad composites are cold reduced. This effect is vividly illustrated in Fig. 10, showing a 34 wt. % UO_2 dispersion in type 302 stainless steel. As shown, a cold reduction in thickness as low as 2 per cent causes cracking of the UO_2 particles.

The stringering and fragmentation phenomena are also dependent upon the deformation process. Whereas plate fabrication shows a marked tendency to produce these effects, as illustrated in Fig. 11, single hot extrusion results in a definite improvement.²⁰ Figure 12 reveals that further refinement is possible with the cold binder process.¹⁵ Figures 13 and 14 show the excellent distribution obtained in the final product of the process previously described

Fig. 8—Longitudinal section of 26 wt. % UO_2 dispersion in 347 stainless steel in stainless-steel clad fuel plate hot reduced 90 per cent in thickness at 1150°C. As polished. (Magnification 200 $\times$.)

1335°C furnace temperature

1100°C furnace temperature

Fig. 9— Effect of hot-rolling temperatures on distribution of UO_2 in stainless-steel clad fuel plates containing a dispersion of 37 wt. % UO_2 (less than $44\ \mu$) in 302 stainless steel (less than $44\ \mu$). Longitudinal sections (as polished). (Magnification $175\times$.)

for manufacturing fuel tubes.¹³ Whenever a minimum stringering and fragmentation of UO_2 are desired, it is recommended that elemental or prealloyed stainless steel with less than $44\ \mu$ particle size be selected as the matrix material; highest possible fabrication temperatures be utilized; hot deformation be limited; and cold reductions be eliminated.

6 PROPERTIES

Mechanical property data reveal that UO_2 dispersions in iron or stainless steel are typified by low transverse ultimate tensile strengths. Table 6 lists average room-temperature transverse ultimate strength values as a function of UO_2 concentration and, in the case of the 30 wt. % dispersion, as a function of temperature.^{9,21,22} The decrease in strength with increasing UO_2 concentration and increasing temperature is obvious. Table 7 lists room-temperature longitudinal strength values of an extruded unclad dispersion and also longitudinal strengths of clad fuel sheets as a function of temperature.^{23,24} As might be anticipated, failure in the fuel dispersion of clad fuel sheets initiates at very low stress, followed by necking of the wrought stainless-steel clad and then complete failure. An evaluation of the room-temperature bend ductility of clad fuel sheets is shown in Table 8 as a function of UO_2 concentration and particle size and fuel matrix material.^{12,21} It is apparent that dispersions in an iron matrix have superior bend ductility, compared to similar dispersions in stainless steel, and that increasing the size of the UO_2 particle improves bend ductility. The bend ductility decreases with increasing UO_2 concentration.

As hot rolled at 1225°C

Cold reduced in thickness 2 per cent

Cold reduced in thickness 20 per cent

Fig. 10—Effect of cold reductions on fragmentation and stringering of UO_2 in stainless-steel composite plates containing 34 wt. % UO_2 in type 302 stainless steel. Longitudinal sections. Etchant: glyceria regia. (Magnification 100 $\times$.)

Fig. 11 — Transverse (top) and longitudinal (bottom) cross sections of composite pin containing dispersion of 25 wt. % UO_2 in austenitic stainless steel extrusion clad with austenitic stainless steel at 1050°C with a 96 per cent reduction in area. (Magnification $10\times$.) (Courtesy of KAPL, General Electric)

The creep rate of a dispersion of 30 wt. % UO_2 in austenitic stainless-steel clad fuel sheet at 700°C is shown in Table 9 as a function of stress.²⁴

Dispersions of UO_2 in iron and ferritic materials are susceptible to early failure under thermal cyclic conditions.¹² Results of such testing on fuel sheets containing 30 wt. % UO_2 in iron, ferritic stainless, and austenitic stainless are listed in Table 10. The superior resistance of the fuel sheet containing the stainless-steel matrix to the cyclic treatment between 260 and 810°C is striking.

Other properties that have been observed for 30 wt. % UO_2 dispersions are 100-hr stress rupture loads of 8700 and 7300 lb for iron- and austenitic-cored fuel sheets and an electrical resistivity value of $96.52 \mu\text{ohm-cm}$ for the 30 wt. % UO_2 dispersion in type 347 stainless steel.²⁴

7 JOINING INTO FUEL ELEMENTS

Both welding and brazing have been considered for joining the basic composite fuel piece into a fuel-element array. Since the composite is generally a thin section that is susceptible

Fig. 12—Transverse (top) and longitudinal (bottom) cross sections of composite stainless-steel pin containing a dispersion of 25 wt. % UO_2 in austenitic stainless steel clad with stainless steel by the cold binder process. (Magnification 10 $\times$.) (Courtesy of KAPL, General Electric)

Fig. 13—Transverse cross section of composite tube containing a dispersion of 25 wt. % UO_2 in austenitic stainless steel clad with austenitic stainless steel by cold drawing and diffusional heat-treatment. (Magnification 100 x.) (Courtesy of Glenn L. Martin Nuclear Laboratory)

Fig. 14—Longitudinal cross section of composite tube containing a dispersion of 25 wt. % UO_2 in austenitic stainless steel clad with austenitic stainless steel by cold drawing and diffusional heat-treatment. (Magnification 100 x.) (Courtesy of Glenn L. Martin Nuclear Laboratory)

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Table 6— TRANSVERSE TENSILE STRENGTH OF UO_2 -IRON BASE FUEL DISPERSION

UO_2 , wt. %	Fuel matrix	Ultimate tensile strength, psi			
		Room temperature	540°C	650°C	760°C
20*	Iron	33,500			
25*	Iron	28,500			
30†	Austenitic stainless	26,000	13,000	12,000	8,500
35*	Austenitic stainless	16,000			
37‡	Austenitic stainless	14,500			
40*	Austenitic stainless	11,000			
45*	Austenitic stainless	8,000			
50*	Austenitic stainless	4,000			

*Data from SEP.

†Data from BML.

‡Data from ORNL.

Table 7— MECHANICAL PROPERTIES OF UO_2 -IRON BASE DISPERSIONS TESTED IN LONGITUDINAL DIRECTION

Temp., °C	UO_2 , wt. %	Matrix material	Ultimate tensile strength, psi	Yield strength, psi	Elongation, %
Room	25*	SS	59,500	32,700	
	30†	SS	57,000	45,000	
	30†	Iron	58,500		10.0
540	30†	SS	36,800	24,300	5.0
	30†	Iron	32,000		11.0
700	30†	SS	23,800	14,000	9.0
	30†	Iron	20,000		13.0

*KAPL data on unclad extruded dispersions.

†BMI data on 6-8-6 mil clad fuel sheets.

to warpage, joining by welding has been confined to tack welding to minimize heating and cooling effects.⁵ Joining by furnace brazing offers the advantage of producing the completed fuel element within very close tolerances, thus minimizing subsequent machining. Figures 15 and 16 illustrate the brazed stationary fuel element for the APPR. The only machining required after brazing involves attachment of the end adapters. The nominal 133-mil spacing between the 18 thin composite plates is maintained within ± 8 mils, and the over-all dimensions, within ± 10 mils. These results are accomplished by jiggling the part in a U clamp type stainless-steel jig followed by brazing in a hydrogen atmosphere with a dew point better than -60°C and a thermal gradient of less than 10 at 1130°C . Table 11 lists the majority of brazing alloys that have been investigated for joining stainless-steel fuel components operating in pressurized water. Of these alloys, Coast Metals, Inc., N.P. and G.E. 81 have received the most prominent consideration for 260 to 295°C water applications because of excellent corrosion resistance,²⁵ acceptable neutron absorption cross section, low cost, brazability, and quality of the brazed joints. Other alloys, including 2, 7, 12, and 21, listed in Table 11 also appear to have good corrosion re-

Table 8—EVALUATION OF BEND DUCTILITY OF FUEL SHEETS CONTAINING UO_2 DISPERSED IN AN IRON-BASE MATRIX

UO_2 , wt. %	UO_2 particle size, * μ	Matrix material	Bend radius, in.	Remarks	Clad-core-clad thickness of fuel sheet, mils
20†	< 44	Iron	0.0156	No cracking	4-12-4
25†	< 44	Iron	0.0156	No cracking	4-12-4
30†	< 44	Iron	0.0156	Cracking	4-12-4
30†	< 44	Iron	0.0313	No cracking	4-12-4
40†	< 44	Iron	0.0156	Cracking	4-12-4
40†	< 44	Iron	0.0313	No cracking	4-12-4
20†	< 44	Stainless steel	0.0313 (min.)	No cracking	4-12-4
30†	< 44	Stainless steel	0.0313	Cracking	4-12-4
40†	< 44	Stainless steel	0.0938 (min.)	No cracking	4-12-4
60†	< 44	Stainless steel	0.1250	Cracking	4-12-4
37‡	74-82	Stainless steel	0.010	Cracking	6-8-6
37‡	74-82	Stainless steel	0.029	No cracking	6-8-6
37‡	44-53	Stainless steel	0.010	Cracking	6-8-6
37‡	44-53	Stainless steel	0.029	No cracking	6-8-6
37‡	< 44	Stainless steel	0.029	Cracking	6-8-6

*Original size prior to fabrication.

†BMI data.

‡ORNL data.

Table 9—CREEP RATE AT 700°C OF 4-12-4 MIL CLAD FUEL SHEETS CONTAINING 30 WT. % UO_2 IN STAINLESS STEEL

Stress, psi	Creep rate, %/hr
6,000	0.004
9,000	0.03
12,000	0.18
15,000	1.3
18,000	4.0

sistance but do not meet all the selection considerations as well as Coast Metals N.P. and G.E. 81. Copper, which is ordinarily the more conventional metal for brazing stainless steel, has questionable corrosion resistance. Figure 17 illustrates the corrosion observed on a copper-stainless-steel joint after 1000 hr in 295°C water at 1200 psi. The weight loss of the T joint specimen after this period was 0.21 mg/cm² compared to a loss of 0.04 mg/cm² on a joint brazed with Coast Metals N.P. tested under the same conditions.²⁶ Brazing alloys 8, 10, 11, 12, 14, 17, 19, and 20, listed in Table 11, were tested in supercritical water conditions of 750°C and 5000 psi. G.E. 75 appeared to be superior.⁵ All the acceptable brazing alloys are brittle,

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but the shear and tensile strengths of the brazed stainless-steel joints are generally greater than 25,000 psi. Typical cross sections of stainless-steel joints brazed with Coast Metals N.P. alloy are illustrated in Figs. 18 and 19.

Table 10—EFFECT OF THERMAL CYCLING ON CRACKING OF 4-12-4 MIL CLAD FUEL SHEETS CONTAINING 30 WT. % UO_2 IN IRON-BASE MATRIX

Matrix material	Cycling temp., °C	No. of cycles	Remarks
Iron	260–810	250	First visible cracking
Iron	260–810	1,000	Badly cracked with bond failure
Iron	260–700	1,000	First visible cracking
Iron + 18% Cr	260–810	1,000	First visible cracking
Austenitic stainless	260–810	17,160	No cracking

Table 11—BRAZING ALLOYS CONSIDERED FOR JOINING STAINLESS-STEEL FUEL ELEMENTS OPERATING IN PRESSURIZED-WATER REACTORS

Alloy No.	Alloy trade designation	Nominal composition, wt. %	Brazing temp., °C	Strength of brazed joint, psi	
				Shear	Tensile
1	Coast Metals 50	93Ni–4Si–3B	1150		
2	Microbraz 10	90Ni–10P	1000		
3		89Ni–11Si	1180		
4	Microbraz	80Ni–5Cr–5Si–5Fe–5B	1150		
5		80Ni–10Cr–10P	1050		
6		75Ni–25Ge	1160		
7	Microbraz L. M.	70Ni–15Cr–5Si–5Fe–5B	1050		
8	G.E. 81	71Ni–17Cr–10Si–2Mn	1200	25,850	
9		68Ni–32Sn	1150		
10		64Ni–25Cr–11Si	1215	25,850	
11		59Ni–30Cr–11Si	1215	27,200	
12	G.E. 75	57Ni–13Cr–30Ge	1180	29,100	74,000
13	Coast Metals N.P.	50Ni–26Fe–11Si–8Mo–4P–1Mn	1130	28,800	62,000
14		40Ni–30Pd–20Mn–10Cr	1230		41,400
15		100Cu	1100	23,750	58,100
16		92Cu–8Si	1000		
17		85Cu–15Mn	1040		83,800
18		80Cu–20Ni	1215		
19		80Cu–20Sn	1000		
20		60Pd–40Ni	1250		
21		60Pd–37Ni–3Si	1180		
22		50Pd–30Ni–20Mn	1230		32,000
23		50Pd–50Cu	1220		33,800
24		45Pd–45Cu–10Mn	1215		
25		75Ag–20Pd–5Mn	1200		
26		64Ag–33Pd–3Mn	1200

Fig. 16—Magnified front view of APPR stationary fuel unit illustrating fuel plate—side plate joints brazed with Coast Metals N.P. alloy.

8 SUMMARY

The general nature, characteristics, properties, and processing of the basic component containing a fuel compound dispersion in an iron-base material clad with stainless steel may be summarized as follows:

1. Powder metallurgy processing of fuel dispersions for stainless-steel fuel elements is required because of the potential difficulties in the fabrication required to clad iron- or nickel-base uranium alloys with stainless steel.
2. Although UN and UC have been investigated briefly as fuel compounds with stainless steel, UO_2 is a more favorable selection because of economics and compatibility considerations.
3. UO_2 is manufactured by several different methods. The product is generally somewhat porous, and the density is less than theoretical. The percentage of uranium in the compound is often less than theoretical.

Fig. 17—Stainless-steel joint brazed with copper after 1000 hr in 295°C static water at 1200 psi. As polished. (Magnification 100×.)

4. The prealloyed stainless-steel powders selected are generally typified by a 2 per cent silicon addition to obtain an irregular shape, which results in higher green strengths. The powders are porous, and the densities are less than theoretical. Iron powder exhibits similar porosity and lower density.

5. Fuel compacts are ordinarily prepared by blending component powders, cold pressing, and sintering in dry hydrogen. If the material is to be subsequently clad by an elevated temperature fabrication treatment, a cold-pressed densification of 75 per cent and a coined densification of 85 per cent after sintering are satisfactory.

6. Most applications utilizing highly enriched uranium require 15 to 30 vol. % UO_2 . Additional deleterious effects associated with fabrication and irradiation damage may be anticipated in dispersions containing more than 40 vol. % of the fuel compounds.

7. Composite parts, either plates, wires, pins, or tubes, are readily fabricated by conventional rolling, swaging, extrusion, or diffusional heat-treatments. Stringering and fragmentation of the UO_2 are characteristic of this type of dispersion. These effects may be improved by proper selection of particle sizes of the component materials, increased fabrication temperatures, and minimum deformation. Fragmentation of the oxide may be anticipated when cold reductions are required.

8. The room-temperature transverse ultimate tensile strength of the material is directly affected by the UO_2 concentration and decreases appreciably at elevated temperatures. The bend ductility of clad fuel sheets containing iron as the fuel matrix material is superior to those with austenitic stainless steel. UO_2 particles less than 44 μ in size have a deleterious effect on bend ductility.

9. The poor thermal cycling behavior of UO_2 dispersions in iron, the unsatisfactory corrosion resistance of iron in pressurized water, and the susceptibility of the combination to irradiation damage have generally eliminated the material from consideration in the dispersion type stainless-steel component.

10. Austenitic stainless steel has been the popular selection as the cladding material for the fuel-bearing powder metallurgical compact because of its superior corrosion resistance in pressurized-water systems.

Fig. 18 — Typical fuel plate—side plate joint in APPR fuel assembly brazed with Coast Metals N.P. alloy. As polished. (Magnification 50 ×.)

Fig. 19 — Stainless-steel joint brazed with Coast Metals N.P. brazing alloy. Etchant: 10 per cent oxalic acid. Vickers hardness numbers at 100-g load are: phase 1, 143; phase 2, 202; phase 3, 189; phase 4, 764; phase 5, 732; phase 6, 176; and phase 7, 146. (Magnification 250 ×.)

11. For specific reactor applications joining of the basic composite into a fuel-element array by tack welding may be satisfactory. However, considerable effort has been directed to the development of brazing techniques, with the establishment of corrosion-resistant brazing alloys and suitable methods for obtaining metallurgically sound joints.

Although some unexploited aspects remain in the development of dispersion type stainless-steel fuel components, the application of this kind of fuel element is now being practiced. Specifically the APPR has operated with plate type elements for more than six months; Atomics International's Organic Moderated Reactor, which uses similar fuel elements, went critical this past September, and Glenn L. Martin Co. is preparing to manufacture dispersion type stainless-steel fuel tubes for the Martin Power Reactor. It is apparent that low-cost austenitic stainless steel is a real contender in the selection of a fuel-element material for power reactors.

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Fuel Dispersions in Aluminum-base Elements for Research Reactors

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ABSTRACT

This paper is concerned with the utilization of 20 per cent enriched fuel in the manufacture of aluminum-base plate type fuel elements, designed for service in high-performance research reactors. The fabrication problems imposed by limiting the enrichment of fuel available for export to less than the 20 per cent level are fully described. Potential uranium-bearing compounds for incorporating the fuel, in the form of either an alloy or as a dispersion in aluminum powder, are tabulated, and some of the important factors to be considered in their evaluation are discussed.

Because of the large fraction of intermetallic compound present, uranium-aluminum alloys containing upward of 40 wt. % uranium are inherently brittle and difficult to fabricate. Alloying studies, however, reveal that the structure of these alloys can be modified by ternary additions of silicon, tin, germanium, zirconium, and titanium. A 3 wt. % silicon addition, for instance, is sufficient to completely suppress the formation of the equilibrium compound UAl_4 in a 48 wt. % uranium-aluminum alloy and permit the primary nucleating compound $U(Al-Si)_3$ to be retained as a stable phase at room temperature. The beneficial effect of the silicon addition on grain size, conventional tensile properties, and formability is demonstrated. Fabrication procedures for preparing fuel plates containing a high uranium investment are described.

Preliminary results of studies underway to determine the compatibility of uranium oxides and carbides in contact with aluminum at 600°C are reported.

1 INTRODUCTION

This article is concerned with the utilization of 20 per cent enriched fuel in the make-up of MTR type fuel components.¹ Such components are needed to power an ever-increasing number of research reactors — many of which are planned for construction abroad — on the basis of partially enriched fuel available under the Atoms-for-Peace Program.

It will be our general purpose to discuss various considerations and problems associated with potential methods for incorporating U^{235} fuel, enriched to the 20 per cent level, into plate type elements for service in high-performance research reactors. We shall report specifically on attempts to incorporate the fuel in the form of a modified uranium-aluminum alloy and as nonmetallic oxides and carbides dispersed in an aluminum-powder matrix.

2 PREVIOUS EXPERIENCE

The fabrication problems imposed by limiting the enrichment of fuel available for export to less than the 20 per cent level were encountered initially during the preparation of the fuel loading for the Geneva Conference Reactor in the spring of 1955. Prior to that time, pool type

reactors were powered with a highly enriched grade of fuel (containing upward of 90 per cent U^{235}) in the form of 10 to 20 wt. % uranium-aluminum alloys. Because of the urgency of time, the Geneva task demanded, in addition, that the fuel be incorporated in a manner which precluded the use of any helpful design alterations. Attainment of these objectives without upsetting the nuclear balance on excess reactivity necessitated the upgrading of the total-uranium content in the fuel-bearing or core section of the composite plate by a factor of approximately 5.

Previous experience with inhomogeneity and lack of ductility in high-concentration uranium-aluminum alloys led to the opinion at that time that such a task could best be accomplished by abandoning the alloy approach and resorting to the unproved, yet promising, technique of incorporating the fuel as a UO_2 dispersion in aluminum powder. Hope for a quick success by this expedient faded, however, when trouble occurred during fabrication of the al-clad $UO_2 + Al$ cermet fuel plates. The plates blistered and exhibited abnormal growth when subjected to the elevated-temperature treatment developed for processing the alloy fuel components. Many changes in procedure were required before an acceptable loading of oxide-bearing fuel components was prepared for the display reactor. The most notable of these was a change from steam-treated metal oxide to a new grade prepared by hydrogen reduction of $UO_3 \cdot H_2O$ crystals grown hydrothermally in an autoclave.

Although some enlightening information was obtained, it was difficult to explain the nature of the behavior observed. X-ray diffraction and metallographic examination of the defective fuel plates revealed that the UO_2 had reacted with the matrix aluminum. The reaction products were identified as UAl_3 , UAl_4 , and Al_2O_3 . Pressure, due to gas generated during the reaction, was, of course, suspected of playing a major role in the gross changes in volume observed, but it could not be proved. More recently studies have been initiated to gain a better understanding of the basic mechanism involved and to investigate other potential methods for incorporating 20 per cent enriched fuel into aluminum-base fuel elements.

3 GENERAL CONSIDERATIONS

The fuel element is the central and most important single component in the heterogeneous reactor system and, as such, demands the utmost attention to its design and manufacture. Not least among the many metallurgical factors to be considered in evaluating potential material combinations for incorporating 20 per cent fuel into aluminum-base fuel elements are concentration, homogeneity, chemical stability, fabricability, and cost. A general discussion follows on how each of these factors is influenced by the chemical species and the method selected for incorporating the fuel.

An initial requisite is that the uranium-bearing compound selected for dispersing the fuel must contain a moderately high concentration of fissionable fuel per unit volume. This is true because MTR type components are designed to operate at high specific power levels in order to provide neutron flux densities as high as possible for rapid and extensive testing of materials. Some of the physical characteristics of several uranium-bearing compounds of potential interest are listed in Table 1. All these compounds are rather brittle in nature, measuring in the range of 300 to 900 on the diamond pyramid hardness scale.

It is desirable to limit the amount of compound present in the fuel-bearing material to a value of less than 50 vol. %; otherwise, significant impairment of the structural and mechanical working characteristics of the material is likely to occur. The variation in U^{235} content as a function of volume per cent of compound present is illustrated in Fig. 1. The general range of interest lies between the concentration values of 0.30 and 0.60 g of U^{235}/cm^3 . These values correspond to a loading of 0.015 and 0.030 g/cm², respectively, in composite fuel plates having a thickness of 0.5 mm in the fuel-bearing section. Of the various combinations plotted, it is interesting to note that the materials requiring preparation by powder metallurgy techniques offer the best approach for achieving a high concentration of fissionable fuel per unit volume.

Another important factor to be considered is the chemical stability of the uranium-bearing compound in contact with aluminum and other environmental constituents at the elevated temperatures required for fabrication. Interaction between the matrix, aluminum, and the ura-

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Table 1—PHYSICAL CHARACTERISTICS OF SEVERAL URANIUM-BEARING COMPOUNDS

Compound	Crystal structure	Melting point, °C	Theoretical density, g/cm ³	Uranium content, g/cm ³	Macroscopic cross section,* cm ² /cm ³
UAl ₄	Orthorhombic	730	6.06	4.16	0.091
UAl ₃	Simple cubic	1350	6.8	5.08	0.109
UAl ₂	FCC	1590	8.14	6.64	0.138
U ₃ O ₈	Orthorhombic	Decomposes	8.39	7.11	0.140
UO ₂	FCC	2800	10.96	9.64	0.190
UC ₂	BCT	2400	11.68	10.61	0.209
U ₃ Si ₂	Tetragonal	1665	12.20	11.31	0.225
U ₂ C ₃	BCC	2350–2400	12.88	11.97	0.118
UC	FCC	2270	13.63	12.98	0.225
UN	FCC	2630	14.32	13.51	0.331
U ₃ Si	BCT	930	15.58	14.99	0.296
U ₆ Fe	BCT	815	17.7	17.03	0.353
U	Orthorhombic	1132	19.04	19.04	0.374

*Calculated on basis of natural uranium ($\sigma_a = 7.77$ barns).

Fig. 1—Variation in U^{235} content with volume per cent compound present for several fuel-bearing material combinations.

niun compound may be undesirable. The equilibrium compound UAl_4 is compatible in contact with aluminum up to the point of liquation. The compatibility of the carbides of uranium with aluminum is questionable at 600°C . The oxides of uranium will react with aluminum at 600°C . Special care is also required in the handling of uranium carbides; both UC and UC_2 show an affinity for water and are pyrophoric in the dry state.

The inhomogeneity problem becomes serious when the fuel is incorporated in the form of high-concentration uranium-aluminum alloys. The inherent nature of the uranium-aluminum alloy system is such that alloys tend to segregate more progressively as one proceeds from the eutectic composition to higher concentrations of uranium. Macrosegregation is not a serious problem when the fuel is incorporated by powder metallurgy techniques, provided proper precautions are taken to avoid classification during handling.

Binary alloys containing upward of 40 wt. % uranium are difficult to fabricate into composite fuel plates. Such alloys are inherently brittle owing to the high percentage of compound present and tend to crack excessively at the edges when hot-rolled bare in order to refine the grain structure. In addition, differences in plasticity between the clad and core material lead to nonhomogeneous deformation and result in defects which will be described later.

An evaluation of cost invariably favors the alloy rather than the powder metallurgy process for the manufacture of aluminum-base fuel components. Powdered fuel materials are more expensive; the cost of converting 20 per cent enriched UF_6 to metal is of the order of \$5/lb, whereas UO_2 powder, for instance, varies from \$15 to \$200/lb, depending on the method of preparation and the particle size desired. Higher costs are also incurred during fabrication because of the extra precaution that must be taken to safeguard personnel and property. Rejected fuel plates prepared by the powder technique must be returned for chemical recovery and cannot be recycled directly to the melting stage as is the case with the alloy.

4 40 TO 50 WT. PER CENT URANIUM-ALUMINUM ALLOYS

The constitutional diagram of the uranium-aluminum alloy system is shown in Fig. 2. The composition range between 40 and 50 wt. % uranium is of particular interest in the make-up of aluminum-base elements containing 20 per cent enriched fuel. The diagram shows that this range lies in a two-phase region, containing primary aluminum and UAl_4 compound. There are two principal inferences to be drawn from the phase diagram: (1) that high-uranium-content alloys (>25 wt. % uranium) are prone to segregation by virtue of the wide temperature and compositional gradients between solidus and liquidus curves, and (2) that such alloys are difficult to fabricate because of the large volume percentage of the brittle intermetallic compound UAl_4 present.

The lack of ductility in the high-uranium alloys can be ameliorated in part by the use of certain ternary additions to the fuel material. These additions suppress the peritectic reaction ($UAl_3 + Al \xrightarrow{750^\circ\text{C}} UAl_4$) and retain $U(Al,X)_3$ as the stable compound at lower temperatures. Silicon is an ideal UAl_4 suppressant; an 0.8 wt. % addition is sufficient to prevent the formation of UAl_4 in a 20 wt. % uranium-aluminum alloy,² whereas an addition of 3 wt. % is sufficient to completely suppress UAl_4 formation in a 48 wt. % uranium-aluminum alloy. Other ternary additions which have been found to suppress the formation UAl_4 are tin, germanium, zirconium, and titanium. The suppression of UAl_4 formation decreases the amount of compound present in a 45 wt. % uranium-aluminum alloy by 18 vol. %. This is a worthwhile gain when working with materials of marginal fabrication potential.

5 MELTING AND CASTING

The two main problems encountered in the preparation of uranium-aluminum alloy ingot are uranium segregation and gas porosity. The propensity for the uranium-rich phase to segregate increases with increasing uranium content and is due to the rapid divergence of the solidus and liquidus boundaries which result in severe gradients during solidification of the alloy. In addition, the alloys possess a marked tendency to absorb gas, particularly hydrogen,

in the molten state, and blow holes will occur if proper measures are not taken to expel the dissolved gas as the temperature drops. Hydrogen porosity poses a serious problem in the preparation of higher-uranium-content alloys in an air atmosphere because of the higher temperatures and longer freezing times encountered in the preparation of these melts.

Fig. 2—Aluminum-uranium phase diagram.

The type of segregation most frequently observed in the preparation of uranium-aluminum alloy melts is inverse in nature. Uranium-aluminum alloys are subject to high rates of shrinkage during solidification and usually show a uranium-rich region in the upper portion of the casting. The mode of segregation is by interdendritic flow of eutectic liquid downward through the channels created by the contraction of dendrites, leaving above a porous region undiluted by the low-uranium-content eutectic.

The variation in uranium content from top-to-bottom in a series of 1-in.-diameter by 6-in.-long cylindrical castings is shown in Table 2 (reference 3). The castings were prepared by

Table 2—URANIUM-CONTENT VARIATION BETWEEN TOP AND BOTTOM IN URANIUM-ALUMINUM ALLOY CASTINGS

Uranium Content, Weight Per Cent Analyzed		
Nominal	Top	Bottom
16	16.1	15.6
25	26.1	24.9
30	30.2	30.0
35	35.4	34.6
40	41.5	39.3
45	45.1	43.4

pouring the alloy into thin-walled graphite molds. Additional data on segregation, in 1-in.-thick slabs of unmodified and silicon-modified 48 wt. % uranium-aluminum alloys, are shown

in Fig. 3. The data presented in Table 2 and in Fig. 3 illustrate the inverse nature of segregation in uranium-aluminum alloys. It can be seen from Fig. 3, however, that segregation is confined largely to the feeding head of the casting. This portion of the casting is subsequently removed by cropping.

Fig. 3—Uranium distribution in unmodified and silicon-modified 48 wt. % uranium-aluminum alloys.

In evaluating the effect of uranium segregation in fuel-bearing materials, the isotopic enrichment factor should be considered. If, for example, the uranium is enriched 20 per cent in the U^{235} isotope, then variations in the distribution of fissionable material will be only about $\frac{1}{5}$ as great as in the case of the same alloy containing a highly enriched grade of uranium.

Melting and casting in vacuum is another method which can be employed to minimize porosity in highly concentrated uranium-aluminum alloys. The procedure established involves induction melting of the desired charge in zirconia crucibles in a dynamic vacuum of less than 2×10^{-3} mm Hg. Zirconia rather than graphite crucibles are employed to obtain greater inductive stirring.³

The practice currently employed in producing sound castings of 45 to 50 wt. % uranium-aluminum alloys by air induction melting involves presolidification of the alloy. In this technique the required charge is melted in a graphite crucible, heated to 1175 to 1225°C, and allowed to slowly cool to 600°C. The melt is then rapidly reheated to 1200°C and again allowed to cool. This cycle is repeated about 4 times to completely degas the melt. The progress of hydrogen removal can be visually followed by observing the surface of the melt during the cooling cycle. Melts containing appreciable quantities of gas will bleed as the eutectic temperature at 640°C is approached. This bleeding results from eutectic liquid being forced to the surface by gas precipitation. As the gas content of the melt is reduced, the "bleeding" will subside and eventually cease. Figures 4 and 5 indicate the effect of presolidification on ingot soundness. These illustrations show the appearance of the subsurface in 1-in.-thick slabs which were conditioned by taking a light machine cut. The casting in Fig. 4 was poured directly from the single-melted alloy, whereas the casting in Fig. 5 was allowed to presolidify in the crucible four times prior to final remelting and pouring. The improvement in soundness with presolidification is strikingly apparent.

The ingot quality of 40 to 50 wt. % uranium-aluminum alloys can be improved by alloying. Minor additions of silicon will alter the grain structure from a dendritic to a completely equiaxed form and eliminate hot tearing in slab type ingots. These effects are illustrated in Figs. 6 and 7.

Fig. 4—Appearance of subsurface porosity in a 48 wt. % uranium—aluminum alloy casting.

Fig. 5—Subsurface appearance of a 48 wt. % uranium—aluminum alloy poured from a properly degassed melt.

Fig. 6—Refinement of macroscopic grain size with silicon additions in cast 48 wt. % uranium-aluminum alloy. (a) 48 wt. % uranium-aluminum. (b) 48 wt. % uranium-3 wt. % silicon-aluminum.

Fig. 7—One-inch-thick slab castings of 55 wt. % uranium-aluminum alloy illustrating elimination of hot tearing with silicon additions. (a) 55 wt. % uranium-aluminum. (b) 55 wt. % uranium-2 wt. % silicon-aluminum.

6 FABRICATION PROCEDURES

Rolling and extrusion are the fabrication methods generally employed in the primary working of high uranium-aluminum alloy castings into wrought shapes for fuel-element applications. Alloys containing up to 48 wt. % uranium can be readily extruded into rods in the temperature range of 500 to 600°C. For example, 3-in.-diameter billets of a 48 wt. % uranium-aluminum alloy have been successfully extruded at 600°C into $\frac{3}{4}$ -in.-diameter rods through a 45° cone-shaped die. When Nicrolene is employed as a lubricant, a starting pressure of 81 tsi is required to effect this 94 per cent reduction in area. When a 3 wt. % silicon-modified alloy is substituted for the unmodified alloy, the starting pressure is reduced approximately 30 per cent.

Rolling of 1-in.-thick castings containing up to 25 wt. % uranium down to $\frac{1}{4}$ -in.-thick plate can be accomplished at 600°C with little difficulty. In the rolling alloys of higher uranium concentration, however, a containing jacket is required to minimize edge and surface cracking. The container may consist of a 6061 aluminum-alloy frame to surround the four lateral sides of the alloy slab and two 0.025-in.-thick cover sheets of 1100-grade aluminum which are tack welded in place prior to rolling. Some of the component parts for make-up of the assembly prior to rolling and the surface appearance of the alloy plate after rolling are illustrated in Fig. 8.

Rolling tests indicate that the silicon-modified alloys can be rolled without frames, whereas their unmodified counterparts virtually disintegrated when subjected to the same treatment. Figures 9 and 10 illustrate the results of rolling unframed billets of 48 wt. % uranium-aluminum and 48 wt. % uranium-3 wt. % silicon-aluminum alloys, respectively. Although the silicon-modified fuel material, shown in Fig. 10, did crack appreciably at the edges, a reasonable yield of material could nevertheless be realized.

The microstructures of samples taken from alloys reduced 75 per cent from the as-cast state by hot rolling are shown in Figs. 11a and b. The structure in Fig. 11a is typical of a 48 wt. % uranium-aluminum alloy and contains primary UAl_4 surrounded by a eutectic of $UAl_4 + Al$, whereas the structure in Fig. 11b is representative of a 48 wt. % uranium-3 wt. % silicon-aluminum alloy. In the modified alloy the microstructure consists of primary $U(Al, Si)_3$ in a eutectic matrix. The relative "cleanness" of this microstructure compared to that shown for the unmodified alloy serves to explain in part the improved fabricability realized with uranium-aluminum alloys modified with silicon.

The fabrication of clad fuel plates containing alloys of high-uranium content requires certain refinements in the techniques previously established for fabricating alloys containing 10 to 20 wt. % uranium. Since the established practice for 10 to 20 wt. % uranium-aluminum fuel plates has been thoroughly described, it will suffice to say that a fuel core 2.3 in. wide by 2 in. long is punched from the rolled $\frac{1}{4}$ -in.-thick alloy plate and inserted in an 1100-grade aluminum picture frame, covered with aluminum sheet and the entire composite rolled at 600°C to the desired thickness, generally 50 to 65 mils. In fabricating fuel plates with high-uranium-content alloys, marked differences in yield strengths exist between the fuel core and the containment materials. The yield strength differential creates deleterious effects at the ends of the core in the rolled fuel plate with the cladding in this region being considerably thinner than the nominal requirement. This localized clad thinning, aptly termed "dog-boning" because of its peculiar shape, is illustrated in Fig. 12, which presents the longitudinal cross section of a sample removed from the end of a fuel plate. An example of the magnitude of this defect is found in fuel plates containing 48 wt. % uranium-aluminum alloy cores which have a nominal cladding of 16 mils. Inspection of a large number of fuel plates reveals that in many cases the cladding is less than 5 mils thick in the defective area and that clad rupture will occur in a few instances.

To minimize these end effects, two approaches have been used with a combination of both schemes yielding the best results. One technique involves the substitution of higher strength aluminum alloys for the 1100-grade aluminum canning material. These aluminum alloys, in-

Fig. 8—Procedure for fabricating 40 to 50 wt. % uranium-aluminum alloy castings into plate. (a) Cast alloy slab (1 in. thick). (b) Cropped and machined alloy slab with aluminum picture frame. (c) Rolled alloy with picture frame removed ($\frac{1}{4}$ in. thick).

Fig. 9—Partially rolled 48 wt. % uranium-aluminum alloy billet showing virtual disintegration of alloy during initial mill passes.

Fig. 10—Hot-rolled slab of 48 wt. % uranium-3 wt. % silicon-aluminum alloy.

Fig. 11a—Microstructure of 48 wt. % uranium-aluminum alloy showing primary UA₁₄ dispersed in a eutectic matrix. Electrolytic polish etch. (Magnification 500 x.)

Fig. 11b—Microstructure of 48 wt. % uranium-3 wt. % silicon-aluminum alloy showing primary UA₁₃ dispersed in a eutectic matrix. Electrolytic polish etch. (Magnification 500 x.)

Fig. 12—End effect (dog-bone) in composite fuel plate containing 48 wt. % uranium—aluminum alloy core and aluminum cladding. Etchant: 2 per cent HF. (Magnification 300×.)

Table 3—CONVENTIONAL TENSILE PROPERTIES OF UNCLAD U-AI ALLOYS AT ROOM TEMPERATURE

Uranium content, wt. %	Yield strength (0.2% offset), psi	Tensile strength, psi	Elongation, %
44.4	14,500	21,600	<1
34.2	10,600	18,900	4
24.7	7,820	16,800	14

Table 4—CONVENTIONAL TENSILE PROPERTIES OF CLAD U-AI ALLOYS

Uranium content, wt. %	Yield strength (0.2% offset), psi	Tensile strength, psi	Elongation, %
42.5	8,170	13,500	3
33.5	7,270	15,400	9
24.0	5,710	14,300	21

cluding 6061 and 5050, have yield strengths which more closely approach the yield strength of the fuel alloy at the rolling temperature. The second alternative simply involves the replacement of the standard fuel alloy with a silicon-modified fuel alloy. In practice it was found that replacement of a 48 wt. % uranium-aluminum alloy core with a fuel core containing 3 per cent silicon reduces dog-boning with a given frame and cover plate combination by a factor of 2.

Unfortunately, it is more difficult to achieve bonding with the high-strength aluminum alloys than with the conventional 1100-grade material. This problem can be overcome by applying a thin sheet of 1100-grade aluminum to the high-strength aluminum alloy prior to roll bonding the composite.

7 PROPERTIES

The mechanical strength of nominal 25, 35, and 45 wt. % uranium-aluminum alloys are included in Table 3. Each value presented represents the average of four flat test specimens obtained from a sheet that was reduced 6 to 1 from the as-cast condition by hot rolling and annealed for 6 hr at 600°C prior to testing.

Similar data are presented in Table 4 for alloys clad with 1100-grade aluminum. Again each value presented represents the average of four flat test specimens, but in this case the specimens were composites consisting of a 48-mil core of uranium-aluminum alloy clad on both sides with 20 mils of 1100-grade aluminum. With the exception of an anomalous result for the tensile strength of the clad 24 wt. % uranium-aluminum alloy in Table 4, the expected trends of increasing strength and decreasing ductility with increasing uranium content are apparent in Tables 3 and 4.

The change in tensile strength of a 48 wt. % uranium-aluminum alloy as a function of silicon content in the 1 to 3 wt. % range is illustrated graphically in Fig. 13. The observed decrease in strength at a decreasing rate correlates closely with the extent of UAl_4 suppression

Fig. 13—Effect of silicon on the room-temperature tensile properties of 48 wt. % uranium-aluminum alloys.

at each silicon content evaluated. These data emphasize the advantage of using silicon-modified alloys to better match the yield strength of the core with the cladding material and, thus, reduce end defects in the composite fuel plates.

The corrosion of nominal 30, 35, 40, and 45 wt. % uranium-aluminum alloys has been evaluated in a deionized 150°C water environment in an autoclave for exposures of up to 30 days. Results of these tests are tabulated in Table 5. The data presented indicate that under the test conditions the magnitude of corrosion is essentially independent of uranium content and is approximately twice as great as the corrosion of 1100-grade aluminum. In every case, the tenacious oxide film formed on the specimen inhibits attack.

Table 5—CORROSION TEST RESULTS OF URANIUM-ALUMINUM ALLOYS IN 150°C WATER

Series	Uranium content (balance aluminum), wt. %	Melting procedure	Heat-treatment	Total weight gain, mg/ cm ² , in indicated time, days				
				1	5	10	20	30
1	30	Melted in ZrO ₂	None; as cast	0.36	0.23	0.38	0.46	0.39
	35	crucibles under		0.36	0.38	0.40	0.52	0.44
	40	vacuum and cast		0.34	0.34	0.41	0.58	0.53
	45	into copper molds		0.34	0.40	0.45	0.31	0.63
2	30	Melted in air and	None; as cast	0.30	0.33	0.36	0.49	0.49
	35	poured in graphite;		0.30	0.48	0.54	0.66	0.61
	40	remelted in vacuum		0.38	0.41	0.48	0.62	0.63
	45*	and poured in copper		0.45	0.65	0.92	1.42	1.82
3	30	Melted in ZrO ₂	Sealed in evac- uated vycor and heat-treated at 1022°F for 24 hr	0.35	0.27	0.38	0.49	0.41
	35	crucibles under		0.34	0.29	0.39	0.34	0.49
	40	vacuum and cast		0.43	0.48	0.52	0.72	0.67
	45	into copper molds		0.40	0.38	0.42	0.65	0.44
25 alu- minum					0.20	0.32	0.32	

*Sample very porous; therefore, not a good indication of the corrosion resistance of alloy.

8 DISPERSIONS OF UO₂ IN ALUMINUM

Uranium-dioxide is attractive for use as a fuel dispersant in solid fuel components because it is readily available and offers a high concentration of uranium per unit volume. This refractory compound has marginal value, however, for incorporating fuel into aluminum-base fuel elements that require elevated-temperature treatments during processing.

8.1 Chemical and Dimensional Stability

It has been well-established that UO₂ is not thermodynamically stable in intimate contact with aluminum at elevated temperatures.⁴ Reaction can occur in 1 hr at 600°C in as-pressed UO₂-Al powder metallurgy compacts. The reaction products have been identified as UAl₃, UAl₄, and Al₂O₃ (reference 5). The rate of reaction can be retarded by the use of coarse grained UO₂, such as -100 + 325 mesh, which diminishes the total surface area available for reaction. Hot and cold working accelerates the reaction rate owing to the improvement in contact and the fragmentation of UO₂ particles. The reaction rate in fabricated plates decreases as the heat-treat temperature is decreased below 600°C. The method employed in the preparation of the UO₂ significantly affects the reaction rate.

The use of certain additives in the preparation of the UO_2 appears to retard the kinetics of the solid state UO_2 -Al reaction.⁶ Compatibility experiments were performed incorporating UO_2 prepared by various methods in 54 wt. % UO_2 -Al compacts. Mallinckrodt granulated UO_2 , which contains 3 wt. % CaF_2 , was superior to Mallinckrodt high-fired UO_2 , which contains 0.5 wt. % TiO_2 . A compact made with -140 +325 mesh granulated UO_2 showed only slight reaction after 8 hr at 600°C. Compacts containing high-fired UO_2 react somewhat more rapidly. Similar tests on UO_2 prepared by the reduction of $\text{UO}_3 \cdot \text{H}_2\text{O}$, steam oxidation of uranium chips and calcination of uranyl nitrate showed reaction in less than 1 hr at 600°C.

No reaction was observed in fabricated fuel plates containing 70 wt. % -325 mesh Mallinckrodt high-fired UO_2 , which were heat-treated for 16 hr at 450, 500, and 550°C. Fabrication heat-treatment involved approximately 1 hr at 600°C. Figure 14 shows a section from the plate

Fig. 14—As-polished section of fuel plate containing 70 wt. % -325 mesh Mallinckrodt high-fired UO_2 which had been heat-treated for 1 hr at 600°C. No reaction occurred. (Magnification 500 $\times$.) (Courtesy of Sylvania-Corning Nuclear Corporation.)

which had been heated for 1 hr at 600°C. No reaction is seen to have occurred. Figure 15 shows a section from the plate which had been heated for 16 hr at 600°C. Severe reaction is seen to have occurred.

During studies to evaluate the compatibility of UO_2 in fabricated aluminum matrix fuel plates, it was observed that the UO_2 -Al reaction is invariably accompanied by a significant increase in the volume of the fuel plate. This phenomena has been termed "growth." The fuel plates containing 52.3 wt. % UO_2 -Al were hot rolled at 590°C, flux-annealed at 610°C, and cold rolled prior to heat-treatment at 600°C. Volume changes occurring during heat-treatment were measured by the displacement technique. The volume of fuel plates containing UO_2 prepared by the hydrogen reduction of $\text{UO}_3 \cdot \text{H}_2\text{O}$ increased markedly during heat-treatment at 600°C relative to plates containing steam-oxidized UO_2 , as shown in Fig. 16. As Fig. 17 shows, however, extensive reaction had already occurred in the fabricated plate prior to additional heat-treatment. The associated volume increase could not be measured. The heat-treat control plate containing UO_2 prepared by the hydrogen reduction of $\text{UO}_3 \cdot \text{H}_2\text{O}$, on the other hand, exhibited only slight peripheral reaction, as shown in Fig. 18. The growth curve for this UO_2 would, therefore, depict close to the true values associated with the reaction. The mechanism of this reaction and its relation to the observed volume increase is not presently understood. Figure 19 shows the volume changes which occur during heat-treatment at 600°C of plates containing fused UO_2 and UO_2 prepared from $\text{UO}_3 \cdot \text{H}_2\text{O}$ in a helium atmosphere. The curves are similar in shape to that of the UO_2 prepared by the hydrogen reduction of $\text{UO}_3 \cdot \text{H}_2\text{O}$, which is

Fig. 15—As-polished section of fuel plate containing 70 wt. %—325 mesh Mallinckrodt high-fired UO_2 which had been heat-treated for 16 hr at 600°C . Severe reaction occurred. (Magnification $500\times$.) (Courtesy of Sylvania-Corning Nuclear Corporation.)

Fig. 16—Growth characteristics of 52.3 wt. % UO_2 —balance aluminum fuel plates. ▲—100 mesh + 325-mesh steam-oxidized UO_2 . ●—325-mesh steam-oxidized UO_2 . ▼—100 + 325-mesh hydrogen-reduced UO_2 from $\text{UO}_3 \cdot \text{H}_2\text{O}$.

Fig. 17—As-polished longitudinal cross section of a 52.3 wt. % dispersion of steam-oxidized UO_2 in aluminum showing extensive reaction which occurred during hot rolling at 590°C and a 1-hr heat-treatment at 610°C . UO_2 particle size prior to reduction was $-100 + 325$ mesh size. (Magnification $500\times$.)

Fig. 18—As-polished longitudinal section of a 52.3 wt. % dispersion of hydrothermal type UO_2 of $-100 + 325$ mesh particle size in aluminum showing only slight peripheral reaction after hot rolling at 590°C and 1-hr heat-treatment at 610°C . (Magnification $500\times$.)

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Fig. 19—Growth characteristics of 52.3 wt. % UO₂ and 55.7 wt. % U₃O₈ aluminum fuel plates.

Fig. 20—Warpage occurring as a result of heating for 24 hr at 600 C. Type A, -325 mesh U₃O₈ prepared from UO₃·H₂O. Type B, -100 +325 mesh steam-oxidized UO₂. Type C, -100 +325 mesh UO₂ prepared in hydrogen from UO₃·H₂O. Type D, -100 +325 mesh UO₂ prepared in helium from UO₃·H₂O. (Magnification 1×.)

shown in Fig. 18. It is not known why the differences in volume levels exist between the three types. Pronounced warpage of the fuel plate accompanies the volume increase occurring during heat-treatment of the UO_2 -Al plates, as shown in Fig. 20.

It should be possible to minimize the UO_2 -Al reaction and consequent growth of the fuel plates by the reduction in the time at elevated temperature during fabrication. Such changes could permit successful fabrication of fuel components by alternate techniques.

8.2 Mechanical Properties

Table 6 summarizes the available information on the mechanical properties of UO_2 -Al cermet. ^{7,8}

Table 6—CONVENTIONAL TENSILE PROPERTIES OF UO_2 -Al CERMETS CONTAINING VARIOUS UO_2 INVESTMENTS AT ROOM TEMPERATURE*

Material composition	Specimens tested	Yield strength (0.2% offset), psi	Tensile strength, psi	Elongation, %
100% Al	3	4,720	13,600	34
5 wt. % UO_2	3	6,060	13,300	19
10 wt. % UO_2	3	6,300	12,000	14
20 wt. % UO_2	4	6,025	11,500	6.5
30 wt. % UO_2	3	6,710	10,800	7
40 wt. % UO_2	1	5,830	7,430	1
50 wt. % UO_2	1	5,950	6,170	0.5
60 wt. % UO_2	1	5,210	5,520	0.5

*Cores sintered for $1\frac{1}{2}$ hr at 580°C in vacuum; -140 +325 mesh hydrothermal type UO_2 .

8.3 Composite Tube Fabrication

A process has been recently developed for the fabrication of aluminum-base fuel elements of tubular cross section.⁹ The process entails the bonding of a fuel-bearing section of tubular cross section with two concentric aluminum tubes to form the composite product which is shown in Fig. 21. The inner and outer cladding is 1100-grade aluminum, and the core is a dispersion of UO_2 in an aluminum powder matrix. In cores where a high uranium investment is required, a mixture of 95 wt. % aluminum and 5 wt. % aluminum-silicon alloy of eutectic composition is employed to gain additional densification.

In the initial preparation of the fuel-bearing core, two different techniques have been developed. In one method, the core mixture is cold compacted at 3.8 tsi into a thin billet, hot-rolled at 620°C into a dense sheet, trimmed to size, and formed into tubing by cold swaging on a mandrel. Tubular-shaped cores containing 30 to 50 wt. % UO_2 and of 0.010 to 0.015-in. wall thickness have been successfully prepared in this manner. The other technique involves cold-pressing cylindrical bushings $\frac{1}{2}$ -in. high at 42 tsi and sintering in hydrogen for 15 min at 620°C for added densification. Bushings containing 65 to 75 wt. % UO_2 and of 0.015- to 0.025-in.-wall thickness have been successfully prepared by this method.

Fuel-bearing cores prepared by either method follow essentially the same procedure in the make-up of the composite fuel tubes. The wrought aluminum cladding is chemically cleaned and activated for bonding. The core is assembled between the inner and outer cladding, and the assembly slipped over a steel mandrel. The fuel assembly is given an elevated temperature-vacuum degassing treatment of 45-min at 630°C to attain a vacuum of less than 5μ . This step is followed by a 35 per cent reduction in cross-sectional area by cold drawing under dynamic vacuum to effect contact between the component parts and achieve the desired dimensions. The mandrel is removed and a metallurgical bond attained by a final diffusion annealing operation of 30 min at 630°C . The fuel tube is radiographed, cut to proper length, and inspected.

Fig. 21—Cross section of a tubular aluminum fuel element containing 65 wt. % UO_2 in the fuel-bearing core section. (Magnification 15 $\times$.) (Courtesy of the Martin Company.)

Fig. 22—(a) As-polished section from 65 wt. % UO_2 –30 wt. % 1100-grade aluminum–5 wt. % aluminum–silicon eutectic tubular aluminum fuel tube which had received 45 min at 620°C. (b) Same as (a) except heat-treated for a total of 82 hr at 620°C. (Magnification 500 $\times$.) (Courtesy of the Martin Company.)

In the fabrication of 30 wt. % UO_2 sheet, the compacted billets are hot rolled to give a reduction in area of about 30 per cent and an elongation of about 70 per cent. The density of such sheet averages 4.95 g/cm^3 . Irregularities inherent in strip formation make any accurate measurement of physical and mechanical properties difficult.

A density value of 4.74 g/cm^3 has been measured on 65 wt. % UO_2 bushings. After sintering, the density is slightly lower owing to burn-off of the stearic-acid lubricant. Fuel tubes containing these bushings can be cold worked to give reductions in area in excess of 50 per cent and elongations of approximately 100 per cent without any deleterious effects. Figure 22 shows as-fabricated and long-time, heat-treated sections of fuel tubes containing 65 wt. % UO_2 -30 wt. % Al-5 wt. % aluminum-silicon eutectic alloy.

9 DISPERSIONS OF U_3O_8 IN ALUMINUM

Although some chemical instability is noted at 600°C , U_3O_8 appears to offer a greater potential than does UO_2 for incorporation of 20 per cent enriched fuel into aluminum-base fuel components. U_3O_8 , prepared by calcining $\text{UO}_3 \cdot \text{H}_2\text{O}$, reacts with aluminum at 600°C to form UO_2 and Al_2O_3 (reference 4). Figure 22 shows the rate of UO_2 formation with time at 600°C in plates containing 56.4 wt. % U_3O_8 -Al which had been previously hot rolled at 590°C , flux annealed at 610°C , and cold rolled. The values of UO_2 shown were determined by x-ray diffraction measurements. No uranium-aluminum intermetallic compounds were detectable by x-ray diffraction. Reaction products were not revealed by metallographic examination. Figure 23 shows

Fig. 23— UO_2 formation during heat-treatment of 56.4 wt. % U_3O_8 -balance aluminum plate.

Fig. 24 — Uranium-carbon constitution diagram.

the volume changes which occur during heat-treatment at 600°C of plates containing 55.7 wt. % U_3O_8 prepared by the same method. Unlike the UO_2 , volume changes of this low order of magnitude should offer no deterrent to fuel-element manufacture. Figure 20 shows that no warpage occurred in such a fuel plate after heat-treating for 24 hr at 600°C. Fuel plates and a brazed MTR type element have been successfully fabricated.

10 URANIUM-CARBIDE DISPERSIONS IN ALUMINUM

The constitutional diagram for the uranium-carbide system, illustrated in Fig. 24, shows the existence of three intermediate phases. Some pertinent data on the physical properties of these refractory compounds are listed in Table 1. All three compounds are characterized by a high concentration of uranium per unit volume which makes them attractive materials for incorporating fuel into aluminum-base fuel components.

10.1 Compound Preparation

Both the monocarbide (UC) and the dicarbide (UC_2) can be readily prepared by a variety of techniques. Uranium sesquicarbide (U_2C_3), on the other hand, is difficult to prepare; stressing is required to initiate formation of the intermediate compound from a mixture¹⁰ of UC and UC_2 . The available methods for preparing these carbides are summarized in Table 7. Of the methods available, the most promising technique for forming UC appears to be the reaction of

Table 7—PREPARATION OF URANIUM CARBIDES

Compound	Method of preparation	Temp., °C
UC	1. U + UC_2	>1800
	2. U + CH_4	625–900
	3. U + C	2100
	4. U_3O_8 + C	1800
U_2C_3	1. UC + UC_2 (with stressing)	1250–1800
UC_2	1. UO_2 + C	>2400
	2. U + C	2400
	3. U_3O_8 + C	2400

stoichiometric amounts of UC_2 and U at 1800 to 1900°C (reference 11). UC_2 can be manufactured in reasonable quantities (2 to 3 kg) by the reaction of UO_2 with C at 2400 to 2500°C (reference 12). In addition, arc melting the elemental components is ideally suited to the preparation of carbides having a wide range of carbon contents. The microstructure of both massive UC and UC_2 , prepared by arc melting, is shown in Figs. 25 and 26, respectively.

10.2 Thermal Stability with Aluminum

In order to evaluate the potential of these compounds for use in the preparation of aluminum-base fuel plates, the chemical and dimensional stability of UC and UC_2 in contact with aluminum at 620°C have been investigated. Behavior at 620°C is of prime interest because this level of temperature is the maximum encountered during brazing of the fuel plates into finished assemblies. Since U_2C_3 is difficult to prepare, it was not included in the scope of the present study.

Carbides, varying in carbon content from slightly less than stoichiometric UC to slightly greater than stoichiometric UC_2 , were prepared by arc melting the desired composition with a tungsten electrode in an argon atmosphere. The resultant massive carbides were comminuted to -100 mesh size by ball milling or hand grinding, again in an argon atmosphere. Compacts containing equiweight mixtures of the carbide under study and aluminum were prepared by cold compacting the blended charge in an 0.8-in.-diameter die. These compacts were then

Fig. 25—Micrograph of massive UC (4.46 wt. % C) prepared by arc melting of elemental constituents. Material at grain boundaries and in globules in matrix is α -uranium. Etchant: $\frac{1}{3}$ H_2O , $\frac{1}{3}$ HNO_3 , and $\frac{1}{3}$ CH_3COOH . (Magnification 1000 $\times$.)

Fig. 26—Macrograph of massive UC_2 (9.20 wt. % C) prepared by arc melting. Scattered graphite flakes are visible in carbide matrix. Etchant: $\frac{1}{3}$ H_2O , $\frac{1}{3}$ HNO_3 , and $\frac{1}{3}$ CH_3COOH . (Magnification 1000 $\times$.)

fired at 620°C in a dynamic vacuum of $<1\mu$ for various lengths of time. The stability of each compact was determined by micrometric measurements of dimensional changes, and in some cases, these measurements were supplemented with x-ray and metallographic studies.

The results of the stability studies are summarized in Table 8. The data indicate the following:

1. UAl_3 and UAl_4 form as the solid reaction products.
2. Reaction of the uranium carbides with aluminum is accompanied by a volume expansion of the compact owing to the release of gas.
3. Carbides containing more than 8 per cent carbon are dimensionally stable with aluminum at 620°C for at least 24 hr, and carbides which are essentially stoichiometric UC_2 are stable for at least 96 hr at 620°C. Small amounts of UAl_3 and UAl_4 are formed in specimens treated for 48 hr or longer, however.
4. Carbides near UC in carbon content exhibit marked chemical instability with aluminum at 620°C and compacts containing these carbides grow catastrophically in a time period of 10 hr or less. An example of this instability is shown in Fig. 27 which illustrates a compact at 50 per cent UC (4.86% C) + 50% Al heated in a dynamic vacuum for 10 hr at 620°C. Virtual disintegration of the compact is apparent.

Fig. 27 — Appearance of compact containing 50 wt. % UC (4.86 wt. % C) and 50 wt. % aluminum after treatment in vacuum for 10 hr at 600°C. (Magnification 1.5×.)

Similar studies with UC_2 , prepared by the reaction of UO_2 and carbon, indicated identical stability to that of UC_2 prepared by arc melting. Some further studies on compatibility of aluminum and UC prepared by several techniques yielded conflicting results and gave indications that the presence of gaseous impurities may effect the stability of the monocarbide.

Since UC_2 is more inert in the presence of aluminum than is UC, the dicarbide appears to be the more promising material for use in aluminum-base fuel elements.

10.3 Fabrication of Composite Fuel Plates

Techniques for producing composite fuel plates containing UC_2 investments of greater than 40 wt. % in the core or fuel-bearing section have been investigated. Results indicate that the

Table 8—GROWTH OF EQUIWEIGHT MIXTURES OF VARIOUS URANIUM CARBIDES AND ALUMINUM AT 620°C

Time at 620°C, hr	Uranium carbides													
	9.20% C		8.24% C		7.98% C		6.96% C		5.75% C		4.86% C		4.46% C	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
4	↓ NG*	↓	↓ NG	↓	↓ NG	↓	↓ NG	↓	↓ NG	↓	↓ NG	↓	↓ L = +0%, D = +0.4%	↓
10	↓ NG	↓	↓ NG	↓	↓ NG	↓	↓ NG	↓	↓ L = +22%, D = +18%	↓	↓ L = +30%, D = +20%	↓	↓ Disinte- grated	↓
16	↓ NG (0%UAl)†	↓	↓ NG	↓	↓ NG	↓	↓ NG (0%UAl)	↓	↓	↓	↓	↓	↓	↓
24	↓ NG (0%UAl)	↓ NG	↓ NG	↓ NG	↓ NG	↓ NG	↓ L = +1.6%, D = +1.4%, (5%UAl) ₄	↓ NG	↓	↓ L = +36%, D = +18%	↓	↓ L = +44%, D = +18%	↓	↓ L = +51%, D = +18%
48	↓ NG	↓ NG (5%UAl) ₃	↓ NG	↓ NG (5%UAl) ₃	↓	↓ L‡ = +0.4%, D§ = +0.1%	↓ L = +9.6%, D = +8.7%	↓ L = +1.6%, D = +1.1%	↓	↓	↓	↓	↓	↓
72	↓ NG	↓ NG (5%UAl) ₃	↓ NG	↓ NG (5%UAl) ₃	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
96	↓ NG (4%UAl) ₄	↓ NG (5%UAl) ₃	↓ NG	↓ NG (5%UAl) ₃	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓

*NG, no growth of compact.

†(%UAl), amount of U-Al intermetallic compound from x-ray studies.

‡L, increase in length of compact.

§D, increase in diameter of compact.

procedures developed and adopted for preparing the oxide-bearing plates are satisfactory, except that an evacuation step is probably required to prevent blister formation.

The initial attempts to clad UC_2 -bearing compacts with aluminum were thwarted by the presence of surface imperfections. Cold-pressed compacts of 35 to 45 wt. % UC_2 and aluminum powder were encased in a wrought aluminum-jacket by the picture-frame technique and preheated in air prior to hot rolling. After hot working and annealing for 1 hr at $610^\circ C$, inspection disclosed that more than 50 per cent of the plates had to be rejected because of surface defects. These defects were small and blister-like in appearance. Additional cladding tests were made on welded billet assemblies which had been evacuated at $300^\circ C$ to a pressure of less than 1μ prior to sealing the exhaust tube and hot rolling. Without exception, plates rolled from these evacuated billets blistered during fabrication.

Further exploratory work indicated that the surface defects were due to gas evolution rather than inadequate bonding or chemical interaction. Metallographic examination of sections taken from defective areas revealed the presence of small voids which were predominantly located in the fuel-bearing material rather than at the clad-core interface. The near-absence of chemical interaction was also observed. Moisture adsorbed on the surface of the UC_2 particles was suspected as the chief source of gas released during processing. This suspicion was substantiated by measuring the amount of water released from several UC_2 samples as a function of temperature in the range of 100 to $900^\circ C$. Analytical results revealed that 1.3 to 1.4 wt. % H_2O was removed on heating the carbide through this range and that 50 to 70 per cent of the total water content removed over the entire range occurred in the temperature increment of 100 to $600^\circ C$.

Two techniques have been devised for producing blister-free fuel plates containing cores of UC_2 dispersed in aluminum powder. One method entails the use of welded assemblies which are evacuated to pressure of less than 1μ at $600^\circ C$ for a period of 2 hr prior to sealing and hot rolling, whereas the other and more economical method involves batch sintering of the bare cores at $600^\circ C$ for 3 hr in a dynamic vacuum of less than 1μ . Following this treatment, the vacuum-sintered cores are assembled with frame and cover sheets and preheated in air prior to hot working. The feasibility of producing blister-free plates with excellent homogeneity by either method has been demonstrated on a pilot-plate scale. The appearance of a transverse section taken from an alclad- $UC_2 + Al$ powdered core plate is illustrated in Fig. 28.

The thermal stability and irradiation behavior of these UC_2 -bearing fuel plates are currently under investigation.

Fig. 28 — As-polished cross section of 50-mil-thick composite fuel plate composed of 50.8 wt. % UC_2 and 41.2% aluminum core and 1100-grade aluminum cladding. (Magnification 75 $\times$.)

11 OTHER FUEL DISPERSIONS IN ALUMINUM

The potential of only a few of the other high uranium-density compounds for use as fuel dispersants in the manufacture of aluminum-base elements has been investigated and limited results indicate that these compounds react with aluminum at elevated temperatures. It has been observed, for instance, that a compact of 50 wt. % U_6Fe and 50 wt. % aluminum distorted in a serious manner after $1\frac{1}{2}$ hr at $600^\circ C$ (reference 13). Another investigation reports that 50 wt. % mixtures of both U_3Si and U_3Si_2 and aluminum react after 24 hr at $620^\circ C$ in vacuum.⁵ Two studies on the use of UAl_2 as a fuel dispersant in aluminum report the transformation of UAl_2 to UAl_3 and UAl_4 in rather short periods of time.^{14,15} Composite fuel plates containing $UAl_2 + Al$ powder cores have been observed to increase 4 to 5 vol. % during fabrication by standard procedures.

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Manufacture of DIDO Fuel Elements

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[Illustrations referred to in this paper were not received for inclusion in this report.]

1 INTRODUCTION

DIDO is a heavy water cooled and moderated materials testing reactor that operates at 10 Mw with a neutron flux of 10^{14} neutrons/cm²/sec.

A fuel charge for DIDO consists of 25 fuel elements. These are shown assembled in the reactor (Fig. 1). Figure 2 shows a fuel element. The square box section, usually termed the fuel box, is an assembly of 10 fuel plates that are separated to form coolant channels (Fig. 3). The coolant enters the box via the lower tube and passes along the channels between the plates then out through the ports provided. Each fuel plate contains 10 g of U²³⁵ in a uranium-aluminum alloy that is clad in aluminum.

The manufacture of these fuel elements is divided into two stages: (1) fuel-plate fabrication and (2) fuel-element assembly.

1.1 Fuel-plate Fabrication

The plates are made by the now well-known picture-frame technique where fuel cores are first prepared from an enriched uranium-aluminum alloy and fitted into aluminum frames that are then sandwiched between aluminum cladding plates to form fuel packs. The longitudinal edges of the frames and cladding plates are argon-arc welded together to stop relative movement of components during heating and rolling of the packs into plate form. The main operations used in fuel-plate fabrication are shown in the flow sheet in Fig. 4.

1.2 Materials

The materials used are (1) highly enriched uranium in the form of 3-in.-diameter by 1½-in.-thick billets weighing approximately 2½ kg which are subsequently divided into 100-g pieces for alloying purposes, using the equipment shown in Fig. 5, and (2) 99.5 per cent pure aluminum according to B.S.5.1470/S1B with iron between 0.2 + 0.35 per cent, silicon 0.10 to 0.30, copper 0.02 per cent maximum.

1.3 Alloy Preparation and Billet Casting

The alloy is prepared direct from the metals uranium and aluminum which are melted *in vacuo* using the furnace shown in Fig. 6. It will be seen that the furnace design is basically the same as the conventional melting and casting furnace now in general use for uranium casting. Graphite is used for crucibles, the tundish, pouring spout, and molds which are assembled as shown diagrammatically in Fig. 7. This shows the crucible charged with 3.2 kg of aluminum and 800 g of enriched uranium for the preparation of the 20 wt. % uranium-aluminum alloy.

The aluminum is in the form of two blocks that are separated by a perforated graphite platform on which are placed small pieces of enriched uranium. This method of charging the crucible ensures that all the uranium goes into solution with the aluminum since the disks are fully exposed to the agitation occurring in the melt from the induced heating current. When the uranium has dissolved, the graphite platform floats to the surface of the melt. This allows the graphite rod, attached to the platform, to close an electric circuit that lights a lamp to provide an external indication that alloying is completed.

The crucible charge is heated to 900°C and held at this temperature for 30 min before allowing to cool to 865°C. The melt is then vacuum cast into the two graphite molds to form billets 2¼ in. wide by 1 in. thick and approximately 10 in. long.

The billets are then checked by X ray for homogeneity and soundness.

Figure 8 shows a longitudinal section of a billet that has been polished and etched to show the grain size, distribution, and shrinkage cavity beneath the pouring nozzles.

1.4 Manufacture of Fuel Cores

The billets are heated to 600°C in standard muffle furnaces and using a 6- by 10-in. two-high mill (Fig. 9); they are rolled to 0.065 in. thickness with reheating between passes. Thereafter the strip is cold-rolled to 0.056 ± 0.0005 in.

Core plates, each 7.750 in. wide and 2.32 in. long, are blanked out of the strips, chamfered on the trailing edge, and then weighed (53.8 ± 0.5 g). A number of samples of alloy are taken from the punched strip and used to determine (by chemical analysis) the uranium content at various positions along the length (Fig. 10). The cores are acceptable only when individual samples contain 20.0 ± 1 per cent uranium to give an average value of 20.0 ± 0.2 per cent for each billet.

The uranium content of each core is then assessed from its weight and the average value of the uranium content of the billet from which it was made.

1.5 Preparation of Pack Components

The aluminum frames and cover plates are punched from sheet. After degreasing, these are tested by heating in air-circulating furnaces at 600°C for 30 min. Fuel cores are similarly tested.

Each side of the fuel cores and frames is then scratch-brushed in the machine shown in Fig. 11.

The cores are then press-fitted into the frame with the leading edge hard against the frame. (The gap between the chamfered trailing edge of the core and the frame prevents air entrapment in the pack during rolling.)

Each cover plate is scratch-brushed on the face adjacent to the frame and core.

The frame and plates are then clamped together in a jig and are argon-arc welded along the two long edges only. This ensures that the components do not move relative to each other during rolling. Figure 12 shows a sectional view of a pack assembly.

1.6 Plate Rolling

This operation is done in a separate 6- by 10-in. two-high mill. The packs are heated for 15 min at 600°C in a muffle furnace and are then reduced to the final thickness of 0.058 ± 0.001 in. in three passes with reheating between passes. Unidirectional rolling is employed.

The plates are blister-tested by heating to 600°C for 20 min.

1.7 Radiography of Fuel Plates and Machining to Size

Projection fluoroscopy is used to measure the length, width, and possible bowing of the core and also to locate the core for removal of the surplus aluminum in the rolled plates. The X-ray generating equipment consists of a Solus-Schall 150-kv fine-focus shockproof unit with a 0.2-mm tube focal spot; the whole is controlled from a mobile desk type switchboard with kilovoltage, tube current, and focusing controls. Also suitably illuminated indicating meters,

overload relays, and a water-flow switch provided circuit protection. A calcium tungstate phosphor-base fluorescent screen was used with this equipment (Fig. 13). After measuring the core as above, two location holes are punched in the surplus aluminum on the longitudinal axis of the plates. A number of these are then mounted in a jig and machined to the required width (2.899 ± 0.010 in.). The plates are then sheared to length (25 ± 9.916 in.).

Fuel plates and cover plates are then cold-pressed to give a $5\frac{1}{2}$ -in. radial curvature and the $\frac{1}{4}$ -in.-wide flat edge (Fig. 14).

1.8 Plate Cleaning and Final Inspection

The plates are first degreased before pickling in a 5% w.v. solution of sodium hydroxide for 5 min at a temperature of 50°C . After a cold-water rinse they are immersed for 5 min in a 5% v.v. solution of nitric acid at 50°C and washed in cold water. After a further wash for 10 min in hot demineralized water, the plates are dried by an air blower. Every plate is checked for surface contamination, this being determined by measuring alpha activity with a proportional counter. The maximum permissible contamination over the total area of plate is $3\text{ }\mu\text{g}$ of U^{235} which is equivalent to 320 counts in 2 min. Plates showing higher counts are recleaned as above. If they again exceed the above standard, they are rejected and returned for refabrication.

At final inspection the plates are examined for superficial flaws that may be revealed by cleaning. Thereafter the radius of the plate curvature is checked with a gauge. The plates are then weighed (194 g) before sealing in polythene bags.

2 FUEL-ELEMENT ASSEMBLY

The fuel element is fabricated from four subassemblies: (1) the fuel box, (2) transin tube with guide nose, (3) fin assembly, and (4) nozzle tube assembly.

These are shown in an exploded view of the fuel element (Fig. 15). The box is assembled from 10 fuel plates and two aluminum cover plates. The plates are separated by U shaped aluminum spacer bars placed along the flat edges of the plates. The spacers are wrapped in very thin brazing foil made from an 8 per cent silicon-aluminum alloy.

These components are carefully assembled in a heat-resisting steel brazing jig with the cover plates in top and bottom positions (Fig. 16). Pressure is applied to the assembly to ensure good contact between brazing joints. The jig and contents are then preheated to 575°C in a muffle furnace and quickly transferred to a flux bath heated to 600°C and held therein for 1 min, during which time brazing occurs. After brazing, the jig and contents are cooled and then submerged in boiling water to remove adhering flux. The fuel box is then released from the jig and pickled for 15 min in 10 per cent nitric acid solution heated to 85°C to remove all traces of flux. It is then finally washed in cold demineralized water and carefully dried.

Following a weight check, the box is visually examined for obvious faults and then dimensionally inspected with particular attention to the coolant gaps between the plates. The box is finally pressure tested (3 psi) when submerged in water.

The transin tube is shaped to accommodate the square fuel box at one end and the circular guide nose at the other. It is fabricated from half pressings that are welded together. The guide nose is machined from bar stock. The fin assembly connects the fuel box to the nozzle tube assembly. It consists of a short square section conical tube and a narrow circular skirt which are separated by eight fins. The square conical tube, made from two pressings welded together, is provided with holes to accept projections on the fins for location purposes prior to brazing. The circular skirt is then fitted to the fins and torch-brazed into position.

The nozzle tube assembly consists of an outer seamless tube with a conical section at one end for attachment to the fin assembly. Inside the tube are three small tubes which are required for water sampling, upper tube water cooling, and thermocouple guiding purposes. The larger water-sampling tube is first welded to the top of the inner baffle cone. The other tubes are then positioned in this cone for torch brazing. After brazing the free ends of the tubes into a positioning plate, the baffle cone is brazed to the outer cone. The tubes are then inserted

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into the nozzle tube which is welded to the outer cone. All four subassemblies, including the bottom guide nose and top salvage joint flange, are washed in hot water and dried prior to assembly.

The transin tube is first torch-brazed to the fuel box. To this is welded the fin assembly and nozzle tube assembly. Finally the guide nose and salvage joint are then welded to the assembly (Fig. 17).

At each stage of the above assembly, the components are carefully positioned in jigs in order to attain the required dimensional tolerances.

Following assembly, the fuel element is washed in boiling water, pickled in a dilute nitric acid bath, thoroughly rinsed in distilled water, and then dried in air.

Final visual and dimensional inspection is then carried out.

The Metallurgy and Fabrication of Uranium-alloy Fuel Elements

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ABSTRACT

Uranium fuel alloys are discussed which have received considerable attention for use in power reactors. The alloy types discussed include the so-called "alpha-prime" alloys (containing 3 to 7 wt. % niobium and zirconium), gamma-phase alloys (containing 10 to 20 wt. % molybdenum or niobium), and epsilon-phase alloys (containing 3.8 wt. % silicon or 45 to 80 wt. % zirconium).

Each of these alloys has unique characteristics which dictate the methods that are used to process it to fuel elements. These characteristics are discussed, as are the processing methods suitable for each alloy.

The fabrication methods discussed are induction and arc melting for alloy preparation and brazing, roll bonding, and pressure bonding for cladding the fuel alloys. The discussion is confined to cladding with zirconium alloys metallurgically bonded.

Brief mention is made of end capping by welding. Other fabrication techniques which are not unique are not considered.

A summary of basic metallurgical information on the fuel alloys is added to provide background for the discussion of fabrication.

1 INTRODUCTION

The uranium alloys to be discussed are those with a large enough alloying addition to produce important changes in their properties, especially in corrosion resistance and radiation-damage resistance. The alloys to be considered are

1. Zirconium with 45 to 55 wt. % uranium, the epsilon phase in this alloy system
2. Zirconium with about 20 wt. % uranium
3. Uranium with 10 to 20 wt. % molybdenum or niobium, in which the gamma phase is metastable
4. Uranium with 5 wt. % zirconium and 1.5 wt. % niobium, which has a distorted alpha structure
5. Uranium with 3.8 wt. % silicon, the epsilon phase in the uranium-silicon system

These fuel alloys have been studied most intensively for use in pressurized-water reactors as zirconium-alloy-clad* fuel elements. However, their use is not restricted to

* The cladding normally has been Zircaloy-2 (zirconium-1.5 wt. % tin-0.12 wt. % iron-0.10 wt. % chromium-0.05 wt. % nickel) or Zircaloy-3 (zirconium-0.25 wt. % tin-0.25 wt. % iron). These cladding alloys are corrosion resistant in pressurized water. However, the information given on fabrication applies to other zirconium-base cladding materials as well.

water-cooled reactors. For example, the uranium-10 wt. % molybdenum alloy, clad with zirconium, is to be used in the PRDC fast breeder,¹ which is a sodium-cooled reactor. Highly alloyed fuels may also be of interest in gas-cooled reactors, although probably not in a gas-turbine cycle because of temperature limitations.

This discussion will pertain to the use of zirconium-alloy cladding on these fuels.* Such fuel elements are especially satisfactory for use in pressurized-water reactors and have been studied intensively in the United States. The characteristics desired in these fuel elements are as follows:

1. A fuel alloy which corrodes only slowly so that if the cladding develops defects in service, allowing the coolant to reach the fuel alloy, failure will be slow.
2. A highly corrosion-resistant cladding material.
3. A strong ductile corrosion-resistant bond between the core and the cladding.

Such a fuel element, made by a process of high reliability and inspected carefully, has little possibility of failing. If it does fail because of undetected flaws in the cladding or cracking of the cladding from growth of the core, it will corrode at a tolerable rate.

Two types of fabrication operations for these zirconium-alloy-clad uranium-alloy fuel elements will be considered. These are (1) alloy preparation and (2) cladding with a zirconium alloy.

Alloy preparation is discussed because all of the alloys are sensitive to composition and to contamination, some of them especially so, and great care must be taken in their preparation. Cladding the uranium-alloy core with a zirconium alloy is especially important, owing to the need for a high-integrity cladding, and will be discussed in considerable detail. Other fabrication operations—forging, rolling, machining, etc.—are not unusual and will not be treated. The fabrication requirements naturally depend on the detailed metallurgical characteristics of the materials. To avoid confusing the treatment of fabrication, detailed metallurgical information is collected in the Appendix. The information contained therein is referred to frequently.

2 CHARACTERISTICS OF FUEL ALLOYS

Although the detailed metallurgical data are given in the Appendix, it is desirable to call attention to a few of the metallurgical characteristics of the fuel alloys that are important to the choice of alloy-preparation and cladding methods.

2.1 Zirconium with 45 to 55 Wt. Per Cent Uranium

The epsilon phase in the uranium-zirconium system covers a composition range from about 45 to 55 wt. % uranium. At higher uranium contents, or with a few thousand ppm of nitrogen or oxygen, alpha uranium precipitates, causing adverse effects on corrosion resistance in pressurized water. The material is rather simply fabricated, and there are no special precautions to be taken. The low uranium content is an important disadvantage of this material.

*It appears desirable to explain the restriction in scope to zirconium-alloy cladding. Cladding with iron- or nickel-base materials is not discussed because weak, brittle bonds are formed. Furthermore, low-melting eutectics are formed with uranium alloys. Thermal bonding, as opposed to metallurgical bonding, avoids the bond brittleness problem, but it need not be discussed here. Cladding with titanium is dismissed as a subject for discussion because titanium has no important advantages over zirconium and, in addition, may form brittle bonds.^{2,3} Aluminum alloys as satisfactory as zirconium alloys at elevated temperatures have not yet been developed and are not discussed for that reason and because aluminum cladding techniques have been described elsewhere in this meeting. Finally magnesium, molybdenum, and niobium, other possible cladding materials, are not discussed because of the limited experience with these materials.

In view of these facts, the desirable characteristics of zirconium as a cladding material, and the large amount of information on methods for cladding with zirconium alloys, it seemed desirable to consider only zirconium-alloy cladding.

2.2 Zirconium with 20 Wt. Per Cent Uranium

An alloy of this composition was selected for discussion because it typifies the problems that exist in zirconium-20 to 45 wt. % uranium alloys. At equilibrium the alloy will consist of approximately equal amounts of alpha zirconium and epsilon zirconium-uranium phases. However, owing to the low temperature of transformation from gamma to epsilon phase (about 600°C), it is difficult to precipitate all alpha zirconium from the epsilon phase, and the alloy has a high hardness and is brittle if it is cooled rapidly from elevated temperatures. For this reason these alloys are especially sensitive to heat-treatment and require annealing or very slow cooling to be ductile.

This fact is important not only in the use of these alloys as core materials but also in cladding other uranium alloys with zirconium since alloys of this composition will exist in the bond layers. For that reason it is necessary to be careful of the heat-treatment of the fuel element in order to avoid brittle bond layers.

2.3 Uranium with 10 to 20 Wt. Per Cent Molybdenum or Niobium

Alloying uranium with 10 to 20 wt. % molybdenum or niobium stabilizes the gamma phase so that it is easily retained at low temperatures. These alloys have a high resistance to radiation damage and adequate corrosion resistance when properly clad with zirconium. Metallurgical factors that influence their fabrication are

1. The transformation rates of the alloys are sensitive to composition. Regions of low alloy content may transform and then corrode rapidly. Therefore a fairly high degree of homogeneity is required.

2. Cold work accelerates transformation and should be avoided or corrected for by annealing.

3. Some of the alloys in the diffusion layer between the zirconium cladding and the core alloy have a low corrosion resistance. However, this fact is not apparent when the diffusion zone is thin. Therefore cladding methods must be used which produce thin diffusion layers.

4. The corrosion resistance of the alloys in pressurized water is reduced by a few hundred ppm of carbon.

2.4 Uranium with 5 Wt. Per Cent Zirconium and 1.5 Wt. Per Cent Niobium

The uranium-5 wt. % zirconium-1.5 wt. % niobium alloy can be heat-treated so as to produce what is known as the alpha-prime or distorted alpha structure. This structure appears to be a supersaturated solid solution. The corrosion resistance and radiation-damage resistance of the material is much better than that of normal alpha uranium, although not so good as that of the other alloys. The alloy is sensitive to the same factors listed for the gamma-phase alloys, but they have a greater influence.

2.5 Uranium with 3.8 Wt. Per Cent Silicon

The epsilon phase has approximately the composition U_3Si . It is the stable phase at temperatures below 930°C, the peritectoid temperature, and is formed by annealing the cast structure consisting of uranium plus U_3Si_2 (or U_5Si_3 according to some investigators), below the peritectoid temperature. The epsilon phase has little ductility, although it can be coextruded with zirconium cladding. However, the as-cast and epsilonized material has better corrosion resistance than the fabricated alloy.

There is no appreciable solubility of the epsilon phase for either uranium or U_3Si_2 , so in order to achieve the desirable characteristic of the epsilon phase, it is necessary that the composition be nearly exact at all points.

Carbon lowers the peritectoid temperature markedly, 100°C for 1000 ppm, so that, when the alloy contains significant amounts of carbon, it is difficult to epsilonize the material.

Poorly corrosion-resistant layers form in solid-phase bonding to zirconium so that brazing is the preferred cladding method.

This brief discussion of the alloys may help to show the importance of the two processing operations that will be discussed in some detail, the melting and casting of homogeneous core alloys and cladding with a zirconium alloy.

3 PREPARING HOMOGENEOUS CORE ALLOYS

3.1 Vacuum-induction Melting

Owing to the chemical reactivity of the alloys, only two types of melting operations are feasible. These are vacuum-induction melting and cold-hearth arc melting. Vacuum-induction melting cannot be used for alloys containing large amounts of zirconium because there is no crucible material that does not severely contaminate such alloys. Uranium containing up to about 10 wt. % zirconium can be vacuum-induction melted.

High-uranium alloys can be vacuum-induction melted successfully in some types of crucibles. Uncoated graphite is not a satisfactory crucible material for these uranium alloys because of the high solubility of carbon in uranium. Haynes and Lorenz⁴ report a pickup of 0.3 to 0.4 wt. % carbon at 1500°C, far above the tolerable amounts since the corrosion resistance of a gamma-phase alloy, uranium-10 wt. % niobium, is reported to be adversely affected by carbon over the range 268 to 962 ppm.⁵

However, it is possible to melt uranium alloys in oxide crucibles because the oxygen has only a limited solubility in them. Melts can be made in crucibles of the more stable oxides or in graphite crucibles with an impervious coating of these oxides without serious contamination. In fact, Dickerson et al.⁶ report that the uranium-10 wt. % niobium alloy at 1565 to 1600°C rejects excess oxygen from solution as a crust containing about 1 wt. % oxygen and 8 wt. % niobium, suggesting that it is possible to limit the maximum oxygen content, even on repeated remelting. The uranium-10 wt. % niobium alloy was reported to be fluid in this temperature range of 1565 to 1600°C, although Haynes and Lorenz^{4,7} recommend pouring temperatures 100 to 150°C higher.

The crucible or coating material that gives least contamination and is usable to the highest temperatures is BeO. This has been used to temperatures of 1800°C. Zirconium dioxide coatings or crucibles and MgO can be used to about 1500°C (reference 4). Another crucible or coating material is MgZrO₃ (reference 8), which has been used to around 1500°C.

Recommendations for melting and pouring various uranium-base alloys are summarized below.^{4,7-10}

Alloy composition (balance uranium), wt. %	Superheating temp., °C	Pouring temp., °C	Crucible material	Coating material
3.8 Si		1600 to 1650	Graphite	BeO
3 to 6 Nb	1550 to 1750	1400	MgO	
10 Nb		1675 to 1700	BeO	BeO
12 Nb		1750	BeO	
12 Mo		1480	Graphite	ZrO ₂
5 Zr-1.5 Nb	1550	1450	Graphite	MgZrO ₃

In ZrO₂-coated graphite crucibles, carbon pickup is about 250 to 450 ppm for the uranium-12 wt. % molybdenum alloy,⁴ and zirconium pickup is less than 500 ppm. Less than 100 ppm beryllium is picked up by the uranium-10 wt. % niobium alloy in BeO-coated graphite or BeO crucibles.

Achieving proper average composition of the melt is not particularly critical with molybdenum or niobium alloys if care is taken to dissolve all of the alloying material because these alloys have adequate properties when the composition is held within normal composition limits.

However, the uranium-3.8 wt. % silicon alloy is extremely sensitive to composition because a slight excess or deficiency of silicon will cause the material to be significantly less

corrosion resistant. The practical melting range is ± 0.1 wt. % silicon,¹¹ and this variation has an important effect on corrosion. Carbon content is maintained below 300 ppm by using BeO-coated graphite crucibles.

3.2 Casting Induction-melted Alloys

After melting the alloys are cast in top-poured open molds to produce either cylinders or slabs of the alloy. The mold materials which have been used include graphite, oxide-coated graphite, and investment molds of SiO₂ or MgZrO₃. Molybdenum or tantalum inserts placed where the molten stream hits them will help to prevent mold erosion for large ingots.⁴ Different mold materials seem to be preferred for different materials as shown by the following tabulation:

Alloy composition (balance uranium), wt. %	Mold
Mo or Nb	Graphite ⁷ Water-cooled copper ¹⁰
3.8 Si	Investment ¹¹
5 Zr-1.5 Nb	Graphite ⁸

Ingots poured in this way are, of course, subject to central porosity, but this has been reduced by hot topping and by using gradient-heated molds. For the uranium-niobium alloy,¹² a hot top was used and the mold was heated to 1260°C at the top and 260°C at the bottom, so as to improve the feeding of the ingot. The yield of acceptable material was 55 per cent with this technique.

Segregation of niobium was the most difficult problem. The ingots generally have a low-niobium skin, and the top of the ingot is generally richer in niobium. Analyses obtained from various parts of an ingot are given in Fig. 1.

Top-poured ingots of this type tend to contain some central porosity and may require considerable cropping. To eliminate this, the ingots have sometimes been used as the electrode for a consumable-electrode arc-melting operation^{7,13} in order to increase soundness.

3.3 Tungsten-electrode Arc Melting

Arc melting is the only practical method for zirconium-uranium alloys. The process used is a cold-mold process in which the crucible is made of copper and is water cooled so that the alloy in contact with the crucible wall is solidified.

Heat is supplied by a tungsten arc, and the furnace atmosphere is helium or argon or a mixture of the two.¹⁴ The original cold-mold process was devised for melting titanium¹⁵ and has been adapted to the melting of reactor materials. Small quantities of the alloying materials, as 1/2-cm pieces, are added at intervals which are great enough so that each is melted before the next is added. Large ingots can be built up in this fashion, and the process is a great improvement over previous ones for the consolidation of zirconium because high purity can be achieved. A tungsten-electrode arc furnace is described by Lustman and Kerze.¹⁶

However, the process has several disadvantages. One of these is that if molten metal splashes against the tungsten electrode, it will alloy with it and cause tungsten contamination of the melt. Furthermore, the melts often contain gas bubbles, presumably because when the increments of the charge are dropped into the furnace, gas is frequently trapped, and, since the charge chills the melt, voids remain in the finished ingot. To avoid this, a melting procedure has been used in which the furnace power is reduced for a period of time before adding a new charge. This partially freezes the melt and the charge, when added, rests on top where it is melted by a subsequent increase of furnace power. Operated in this fashion, the tungsten-arc process is so slow that only a few hundred grams are melted in 6 min, the time for a charging cycle.¹⁴ Since constant operator attention is required, the process is expensive.

Fig. 1—The compositional variation in a chill-cast ingot of uranium-10.2 wt. % niobium.¹²

3.4 Consumable-electrode Arc Melting

The consumable-electrode arc-melting process avoids these disadvantages. It was originally developed¹⁷ to permit the melting of sponge (Kroll process) zirconium, which contains so much magnesium chloride that the charge would boil violently in the tungsten-electrode process and give serious difficulties with tungsten contamination.

In the consumable-electrode process, the electrode is formed of the metal or alloy that is to be melted. With this process melting rates are very high. For example, in a 20-lb furnace,¹⁸ the melting rate is about 4 lb/min.

The process has many advantages. Sponge zirconium can be melted directly, the ingots are sound, and melting rates are high. A laboratory type of consumable-electrode melting furnace is shown in Fig. 2 (reference 18).

Alloys may be produced in various ways. An alloy such as Zircaloy can be made by starting with pressed electrodes of zirconium sponge and dropping the alloying materials as small pellets or small pieces of wire into the melt at proper intervals. For alloys containing large

Fig. 2—Consumable-electrode arc-melting furnace.¹⁸

1. To rectifiers	7. Vacuum flange	13. Starter charge
2. To electrode controller	8. To rectifiers	14. Copper crucible
3. Electrode drive	9. To electrode controller	15. Water outlet
4. Electrode guide	10. Water outlet	16. Insulating ring
5. Water-cooled copper electrode	11. Electromagnetic coil	17. Furnace shell
6. Consumable electrode	12. Water inlet	18. Sight glass
		19. Threaded adapter

amounts of alloying addition, a composite electrode is made of the right amount of the two materials, as shown in Fig. 3, and used as the electrode.¹⁸ If the melting points of the two metals differ widely, as for uranium and niobium, the low-melting uranium will melt back considerably, as shown in Fig. 4 (reference 6), so that it is necessary to make an allowance for this meltback in designing the original electrode. By using formed electrodes, it is possible to produce alloys having good homogeneity which can be further improved by remelting. In the case of zirconium-uranium alloys, the standard deviation of the uranium content has been 0.24 wt. % in a zirconium-22 wt. % uranium alloy for a single melting.¹⁸

It has been mentioned that homogeneous alloys of uranium and zirconium can be prepared by arc melting. However, with alloys whose constituents have greater differences in melting points than uranium and zirconium, a type of inhomogeneity has been observed which is not related to insufficient mixing of the alloying materials in the molten pool. Instead, it seems to occur because of the fact that, with cold-hearth melting, solid and liquid alloys are in contact on a given interface long enough so that there is a tendency to separate liquid and solid phases of greatly different composition according to the constitution diagram. An illustration of this type of segregation is shown in Fig. 5. The melt was a small button arc melt of uranium-12 wt. % molybdenum. The bands of varying dendrite population seem to outline the molten pool as it existed at various times in the melting process. This kind of inhomogeneity is highly undesirable since it is not removed by homogenizing treatments.

3.5 Surface Conditioning Arc-melted Ingots

In both of the cold-mold melting processes, the ingot surfaces frequently contain folds that cause defects in the finished material unless they are removed. It is possible to remove them by machining, but this has the disadvantages of causing a loss of material and of contaminating the chips severely. An alternate method, which has been described for zirconium,¹⁸ and can be used for other alloys, is to fuse the surface by inert-electrode arc-welding methods. This gives a sound, dense surface suitable for forging and rolling. The ingot surface of a zirconium-20 wt. % uranium ingot, before and after surface conditioning, is shown in Fig. 6.

3.6 Homogenizing Cast Material

Microsegregation exists in the alloys, however melted, and must be eliminated for the alloy to have its best corrosion resistance. Figures 7a and 7b show the types of coring which exist in an as-cast consumable-electrode melt of uranium-12 wt. % molybdenum. The coring shows up in the heat-tinted material but not in the etched sample. Unless removed, this segregation persists through fabrication operations, as shown in Fig. 8a, where stringers are shown in extruded uranium-12 wt. % molybdenum alloy. The concentration differences in this type of material may be quite large. On extruded alloy Bauer²⁰ reports a variation from 3 to 12.5 wt. % molybdenum in extruded samples of a nominal uranium-10 wt. % molybdenum alloy, as determined by the Castaing microanalyzer.²¹ Coring also exists in the uranium-3.8 wt. % silicon alloy, and the phases that exist are alpha uranium and U_3Si_2 .

The microsegregation is eliminated by homogenizing treatments. Twenty-four hours at 900°C has been used¹³ for the uranium-molybdenum alloys, or shorter times at 1000°C. For the uranium-silicon alloy the treatment must be done below the peritectoid temperature of 930°C, and one week at 800°C has been used.¹¹

The effect of the homogenizing treatment is illustrated in Fig. 8b, where it is obvious that the stringers in the extruded unhomogenized material, Fig. 8a, have been eliminated. The homogenized material has better corrosion properties and probably has better radiation-damage resistance.

By these methods it has been possible to prepare fuel alloys of adequate quality for reactor use. For the uranium-molybdenum, niobium, and zirconium alloys, conventional fabrication operations are used to reduce the ingots to the required size for cladding operations. For the uranium-silicon alloys, it has been found that coextrusion, which is the only feasible fabrication method for the material, gives stringers of alpha-uranium in the material, greatly reducing its

Fig. 3—Rectangular type alloy consumable electrode.¹⁸ ■, uranium; □, zirconium.

Component	Number	Section
Zirconium rods	4	0.50 by 0.50 in.
Uranium strip	1	0.095 by 1.0 in.

Fig. 4—Typical electrode meltback of a box type consumable electrode.⁶ Niobium bar in center, uranium outside.

Fig. 5—Microsegregation in a button arc melt of uranium-12 wt. % molybdenum alloy. The zones of varying dendrite population have the shape of the molten pool.

Fig. 6—Consumable-electrode arc-melted ingots of zirconium-20 wt. % uranium before and after cropping and surface conditioning.

Fig. 7—Typical section of as-cast consumable-electrode arc-melted uranium-12 wt. % molybdenum ingot.¹⁹ Bright-field illumination. (a) Typical section. (Magnification 500x.) (b) Sample prepared by electropolishing and heat tinting to show coring. (Magnification 250 x.)

Fig. 8—Effect of homogenization prior to extrusion at 1000°C for 48 hr.¹³ (a) Extruded without prior homogenization. (Magnification 250 ×.) (b) Extruded with prior homogenization. (Magnification 250 ×.)

corrosion quality. For that reason the uranium-silicon alloy has its best properties as cast, and it has been used in that form.

4 CLADDING CORE ALLOYS WITH ZIRCONIUM ALLOYS

4.1 Required Bond Characteristics

All of the fuel alloys are clad to reduce the rate of corrosion and to prevent the escape of fission products. Since the hazards involved in a cladding failure are serious, a cladding of high integrity is required.

A metallurgical bond is essential so that, under the irradiation-induced growth of the core alloy, the cladding will be able to deform to accommodate the movements of the core without bond-line failure. The bond must be ductile since a brittle bond would probably fail over a large area when growth of the core occurred. This would cause overheating of the fuel and increase the probability of serious swelling of the core, or of a cladding break which would allow water to gain access to the core, causing rapid corrosion failure. Therefore the cladding methods to be described are aimed at achieving strong and ductile bonds.

4.2 Effect of Core-alloy Properties on Choice of Cladding Method

Another requirement which must be met by fuel elements is that the diffusion zone between the core and cladding alloy must corrode slowly—no more rapidly than the core alloy itself. In the case of the uranium-molybdenum alloy, a thick bond layer corrodes rapidly,¹³ and the bonding method must be one which produces thin diffusion layers. In the case of the zirconium-uranium alloy, corrosion-resistant bond layers are inherent, so any bonding method can be used. In the case of the uranium-silicon alloy, a corrosion-resistant metallurgical bond to zirconium cannot be obtained, so a brazing technique must be used to clad the fuel alloy with zirconium.

Therefore there are four important cladding methods that should be discussed: coextrusion, roll cladding, pressure bonding, and brazing.

4.3 Cold Drawing Coextruded Material

Extrusion-cladding methods have the advantage, for use with uranium-molybdenum alloys, of achieving very thin diffusion layers. The coextrusion techniques have been described in this

meeting by Kaufmann and will not be discussed here. However, two processes related to the use of extruded material will be discussed; these are cold drawing and end capping.

In order to achieve adequate tolerances for coextruded rods, it is desirable to draw the material to finish size. For the uranium-molybdenum alloy, Snyder²² reports that the uranium-12 wt. % molybdenum alloy can be cold drawn, in two passes of 30 per cent reduction each, from a starting size of 1.1 cm to a final size of 0.78 cm. No annealing is required even though the unclad alloy has only 7 per cent elongation and 43 per cent reduction of area in a tensile test.

However, the gamma-phase alloys are sensitive to cold work. It has been reported⁵ that transformation can be detected in a uranium-10 wt. % niobium alloy after 16½ per cent cold work. The uranium-molybdenum alloy is more stable and can withstand much greater cold work (50 to 60 per cent) but reveals the effect of cold work by transforming more rapidly at elevated temperatures. Heat-treatment at gamma temperatures is necessary to stabilize the material. For the cold-drawn material, a short treatment, 30 sec, at a high temperature, 870°C, has been found¹⁹ to be effective in recrystallizing the material, as shown in Figs. 9a and 9b. This short-time heat-treatment does not appreciably increase the thickness of the bond layer between the core and cladding.

4.4 End Capping Coextruded Material

The other fabrication method pertaining to the use of coextruded material is end capping. It has been mentioned by Kaufmann that coextruded end caps are possible. Nevertheless, it would be desirable to develop a good end-capping method because it would allow long bars to be coextruded, cut into sections, and end capped.

End caps can be sealed to the cladding without attempting to bond the end cap to the core. However, corrosion products force such an end cap off rapidly if water gains access to the unbonded area.

Therefore end-capping methods have been sought which produce a bond between the core and the end caps. It has been found that a low-melting-point core alloy (uranium-12 wt. % molybdenum) introduces problems that have not been solved with completely satisfactory results.

Welding methods have been used to avoid long-time heating of the coextruded material, which would give a thick, poorly corrosion-resistant diffusion zone between core and cladding. Of the various welding methods tried,²³⁻²⁴ resistance welding in a restraining sleeve of glass or other ceramic material has been most successful. However, using the best welding technique, which was resistance welding, a large number of failures (6 to 7 per cent) occurred in a 2700-hr corrosion test in 650°F water. In looking for the cause of these failures, it was found that in a number of Zircaloy-to-Zircaloy joints there was a thin layer of foreign material, as shown in Fig. 10. This was metallographically identified as a high-uranium alloy. Presumably, in some welds, this material penetrated to the surface and was corroded, forcing open a crack through which water could penetrate to the core. The core-alloy inclusions in the weld occurred because, in the early stages of welding, before the cladding-to-end cap joint was made, the relatively low-melting core alloy fused and entered the joint, as shown in Fig. 11.

The amount of uranium that gets into the joint is only a few micrograms, and it is probably possible to fusion weld the surface of the joint to alloy the small amount of uranium with the much larger amount of melted zirconium and thus avoid the corrosion weak spots.

It should be remarked that such end-capping difficulties as this are serious only when the core alloy melts at a much lower temperature than the cladding. If it were not for this factor, there would be no reason why end caps could not be attached satisfactorily.

4.5 Cladding by Roll Bonding

Another method for producing high-integrity bonds is roll bonding. This method has the advantage of cladding all core surfaces at one time, and it is capable of producing a fuel

(a)

(b)

Fig. 9—Effect of recrystallization heat-treatment on uranium-molybdenum fuel rod.¹⁹ Fuel rod was cold reduced 64 per cent. Bright field illumination. (a) Longitudinal section of fuel rod extruded after heating for 15 min at 1840°F. (Magnification 500 x.) (b) Longitudinal section of above sample after self-resistance heating for 30 sec at 1600°F and stretcher straightening. (Magnification 500 x.)

Fig. 10—Photomicrograph showing entrapped material at the end cap-to-cladding interface.²⁴
(Magnification 375 x.)

Fig. 11—Photomicrograph of an end-cap joint obtained with a relatively short welding time.²⁴
End cap above, cladding below on left, core allow below on right. Note melted core allow
between cladding and core. (Magnification 75 x.)

element containing a core having good geometry. The roll-bonding method is best adapted to the fabrication of plate type fuel elements.

In order to achieve good bonding, all surfaces must be completely free of contamination. This means that good cleaning of the components initially and preventing all contamination during roll bonding are essential.

The usual procedure for roll bonding is to place the core in a "picture frame" which will become the edge and end cladding of the finished fuel element and to place both core and picture frame between cover plates which become the face cladding of the fuel element. This assembly is placed inside a mild steel picture frame and between mild steel cover plates. The steel frame is welded shut and evacuated through a tube which is then sealed off. The assembly is heated to the rolling temperature and rolled hot at between 10 and 30 per cent reduction per pass until the final dimensions are attained. Total reductions are usually around 3 to 1 or 4 to 1, although more has sometimes been used.

Contaminated surfaces will not produce good bonds, and great attention is paid to preparation of the surfaces for bonding. The technique used for the preparation of the Zircaloy-2 for the Experimental Boiling Water Reactor fuel plates⁸ will illustrate the extreme care which has been used. The forged Zircaloy-2 is completely machined to remove all defects and is rolled 50 per cent oversize at 850°C. It is next wet-abrasive blasted, first with 100-mesh, then with 400-mesh Al_2O_3 , and then all remaining defects are removed by spot grinding. It is then rolled to nearly finish size at 600°C and again wet-abrasive blasted, after which it is pickled in boiling HNO_3 containing 1 vol. % HF, rinsed, and dried.

Unusual types of contamination may occur. One of these, first noted by investigators at WAPD, was that the zirconium surfaces would react with nitrogen that diffused from the mild steel. The surfaces then became contaminated with nitrogen and lost corrosion resistance. For this reason, they used a type of mild steel in which the nitrogen is fixed with a small addition of titanium. An alternative method used by ANL⁸ is to evacuate and weld the zirconium assembly so that ordinary mild steel (SAE-1020) can be used as the jacketing material. In this way contamination is avoided on the zirconium surfaces being bonded.

Another factor requiring close control in roll bonding is the relative hardness of the core and cladding materials. If there is a large difference between the hardness of the two materials, the core ends will have an unsatisfactory shape. If the core is harder than the cladding at rolling temperatures, the core ends will be enlarged and the cladding will be thin. If the core is softer, it may squeeze between the cladding, producing a long, tapering core end. Figure 12 shows the wide variation of core-end shapes which can occur. To obtain a good core-end shape, it is necessary to control the relative hardnesses of the core and cladding. Since the relative hardnesses change with temperature, rolling temperature may be used to control core-end shape, as shown in Figs. 13a and 13b (reference 26). In Fig. 13a a temperature of 1100°F was too low, and, in Fig. 13b, a temperature of 1450°F was too high for obtaining the optimum core-end shape.

It is not always possible to select a rolling temperature suitable for obtaining good core geometry. Unalloyed uranium cores are too soft, even at 1250°F (675°C) to produce a good core-end shape, as seen in Fig. 14. A temperature of 1250°F is a little low for good roll bonding with zirconium because bond-line contamination diffuses away too slowly. Alloying the uranium will harden it at elevated temperatures and allow more suitable rolling temperatures. Achieving the proper core hardness for roll bonding can be a factor in selecting the core alloy, as it was in the case of the uranium-5 wt. % zirconium-1.5 wt. % niobium alloy.⁸

The strength of the uranium-10 wt. % molybdenum alloy is too great at elevated temperatures for good roll bonding (see Sec. A.4). A harder cladding material would be desirable. No such harder alloys, corrosion resistant in pressurized water, have been developed, but in reactors cooled by other fluids, consideration could be given to harder zirconium alloys. One such is the zirconium-4 wt. % tin-1.6 wt. % molybdenum alloy, which was developed for high-temperature strength.²⁷ There is a fairly satisfactory hardness match between this alloy and the uranium-10 wt. % molybdenum alloy.

It has been found that measurements of hot hardness are a reasonably good indicator of the proper match of core and cladding hardness at rolling temperature. Hot-hardness data

Fig. 12—Samples of core-end sections with various shape factors.²⁵ The shape factor is the ratio of the thickness of the core end to the core thickness some distance away. (Magnification 1x.)

Fig. 13—Effect of rolling temperature on uranium-50 wt. % zirconium core-end shape.²⁶
 (a) Rolled at 1100°F with 3 to 1 reduction. (Magnification 30 x.) (b) Rolled at 1450°F with 3 to 1 reduction. (Magnification 30 x.) (c) Rolled at 1450°F with 7 to 1 reduction. (Magnification 30 x.)

(a)

(b)

Fig. 14—Effect on core-end shape of increased rolling reduction.²⁶ Unalloyed uranium core, zirconium-alloy cladding. (a) Rolled at 1250°F with 3 to 1 reduction. (Magnification 30×.) (b) Rolled at 1250°F with 6 to 1 reduction.

for a number of materials are given in Sec. A.4. An examination of these data shows that it is possible to obtain a rather good match of hardness between Zircaloy and uranium-zirconium alloys in the desirable range of rolling temperature, that is, 700 to 850°C.

If there is a hardness mismatch between core and cladding, the core-end shape will deteriorate as the rolling reduction increases, as shown in Figs. 13b and c and Fig. 14. The geometry of the core ends can be so unsatisfactory that it is necessary to make the cores longer than they need to be and cut them off to length, and weld on end caps. This was done to fuel plates for an in-pile-loop study of uranium-3 and 6 wt. % niobium⁹ but would be undesirable in a reactor for the reasons given previously in discussing end capping.

Obviously, roll bonding requires a longer time at temperature than extrusion cladding, and for that reason the bonding layers are apt to be thicker, and this may be undesirable. However, by roll bonding at as low a temperature as possible, the bond-layer thickness is minimized. Another approach to the problem is the use of barrier layers,¹³ such as niobium, molybdenum, etc., which may avoid diffusion layers of poor corrosion resistance. For a uranium-3.6 wt. % niobium core alloy, where bond-line corrosion was rapid for roll-bonded fuel plates, a niobium barrier layer was beneficial.⁹ The integrity of the barrier layer would, however, always be unknown for any process involving large deformation, like roll bonding.

The thickness of the diffusion layer is not a problem for the uranium-zirconium alloys where the only alloys that can be formed in the diffusion layer are more corrosion resistant than the core. However, it has been observed by WAPD²⁸ that bond brittleness may occur in roll-clad uranium-zirconium alloys. Separation of core and cladding occurred in bend testing roll-clad fuel plates. This is believed to be a result of the high hardness of alloys in the range of zirconium-20 wt. % uranium after rapid cooling, as shown in Sec. A.2. Heat-treating studies²⁹ show that annealing treatments just below the transformation temperature, approximately 600°C, soften alloys of this composition. Such heat-treatments, applied to the fuel plates, eliminated bond brittleness.

4.6 Cladding by Pressure Bonding

Another bonding method that is capable of producing good bonds between materials is pressure bonding. The metals that are to be bonded are pressed together at high pressures and elevated temperatures. Strong metallurgical bonds can be obtained, and it is sometimes possible to minimize the growth of brittle materials in the bond layers and obtain a stronger bond than with other methods.³⁰ The bonding has often been done in dies³¹ or by differential thermal expansion.¹¹

The properties of zirconium are such that more satisfactory pressure-bonding methods are possible for fuel plates. This is a method using hydrostatic pressures.³² The materials to be bonded are assembled in a pressure-tight evacuated envelope and heated in an autoclave at high temperatures and high gas pressures. Two characteristics of zirconium favor the formation of strong bonds under these conditions. First, zirconium, at the bonding temperature, dissolves most of the normal contaminants that might otherwise interfere with the bonding operation. Therefore it is not necessary to use a bonding process that plastically deforms the bonding surfaces in order to spread out and break up a layer of contaminants. Second, zirconium and its alloys deform plastically at an adequate rate at pressures that can be achieved in high-pressure autoclaves and at suitable bonding temperatures. For this reason the voids in the component to be bonded can, in a reasonable length of time, be reduced in size to the point where surface-tension forces can complete the closing of the voids.

The plasticity of zirconium and its alloys is apparent in Fig. A.29 in the Appendix, which gives data that were obtained by measuring the hot hardness of the material as a function of the time of load application. It is evident that considerable plastic flow occurs, as shown by the decrease of hardness with time. Flow continues down to relatively low pressures. From data such as these, it is possible to compute the flow rate as a function of pressure and then to deduce the time required for bonding. Computations of this sort have been made, and the results are given in Fig. A.30 in the Appendix. It is evident from these data that pressures of

a few hundred atmospheres or greater, at temperatures of 800°C or over, are sufficient to achieve bonding in a few hours. Higher pressures would decrease the bonding time greatly.

The preparation of components for pressure bonding is the same as for roll bonding. Studies of the bonds produced by pressure bonding show that removal of a considerable amount of the surface may be desirable. Figure 15 shows the excellent bond obtained when machined Zircaloy-2 components are used. Figure 16 shows that a vapor-blasted and pickled surface produces a poor bond. It is not yet known whether the poor bond results from contamination of the unmachined surface of the Zircaloy-2, which was not removed by vapor blasting and pickling, or contamination introduced in processing, possibly from the vapor-blasting treatment.

For pressure bonding, the components are machined to their finish size and assembled in an evacuated pressure-tight envelope made of any material, of sufficient plasticity, which will not bond to the components or contaminate them excessively. Steel, stainless steel, and copper all have been used successfully. The components are then placed in the autoclave, heated to the desired temperature, normally 850°C, at a pressure of 700 atm of helium or other inert gas. Bonding is complete in 4 hr.

Good pressure bonds can be obtained³² of zirconium to zirconium (Fig. 17) or of zirconium to core alloys. Figure 18 shows the bond obtained between zirconium and a zirconium-20 wt. % uranium alloy, and good bonds have also been obtained on uranium-10 wt. % molybdenum alloy.³³ Such bonds are as good as those produced by other methods and defy efforts to separate them at the bond line, as shown in Fig. 19.

Poor bonds may occur when process control is unsatisfactory. Figure 20 shows a dirty bond and Fig. 21 a bond-line flaw, both of which are caused by improper surface preparation. Figure 22 is an example of a bond which was incomplete because the pressure was inadequate to bring the surfaces into complete contact.

The pressure-bonding process has several advantages. One of the most important is that the amount of deformation occurring during bonding is small; so the accuracy of the finished components is high. Another advantage is that the bonding operation can be used with any core material regardless of its ductility or hardness. Thus, bonds can be made of zirconium to uranium-molybdenum alloy and of zirconium to zirconium, and it is possible to seal uranium dioxide cores in a pressure-bonded zirconium envelope without fracturing the cores.

The method also has obvious disadvantages. At pressures currently available, the bonding time required is a few hours at temperature. Thus, the diffusion zones are thicker than those obtained by extrusion cladding or roll bonding. For this reason the uranium-molybdenum fuel elements produced would not have characteristics suitable for use in a water-cooled reactor since the bond layer would corrode rapidly. This would not be a factor in the use of these fuel elements in a sodium-cooled reactor. With UO_2 cores a considerable amount of reaction occurs between zirconium and UO_2 (reference 34), and this is undesirable. To prevent such reaction, barrier layers would be required.

It is possible to use pressure-bonding methods with cladding materials other than zirconium alloys. Successful bonds have been made with stainless steel, and between aluminum and epsilon-phase uranium-silicon alloys.¹¹

4.7 Cladding by Brazing

Little work has been done on the brazing of fuel elements for use in high-temperature water. An exception to this is the case of the U_3Si alloy. Cladding by the only other feasible cladding method, coextrusion, gave a diffusion layer consisting of a layer of ZrSi_2 next to the cladding and a layer of alpha uranium next to the U_3Si (reference 11). This bond has extremely poor corrosion resistance and was considered unsatisfactory. Furthermore, the extrusion produced stringers of alpha uranium in the fuel so that its corrosion resistance was not so good as that of the cast alloy.

The best fuel elements of U_3Si clad with zirconium were obtained by brazing with aluminum-6 wt. % copper alloy. Some samples produced in this way had fairly good corrosion life as when tested with intentional defects in the cladding; however, difficulties were ex-

(a)

(b)

Fig. 15—Good pressure bond made by using machined Zircaloy-2 components, degreased.
(a) Polarized light. (Magnification 250 x.) (b) Bright field. (Magnification 250 x.)

(a)

(b)

Fig. 16—Poor pressure bond made with Zircaloy-2 components, using unmachined Zircaloy-2 cleaned by vapor blasting, pickled to remove 25 μ from the surface, and washed. (a) Polarized light. (Magnification 250 $\times$.) (b) Bright field. (Magnification 250 $\times$.)

Fig. 17—Interface of good pressure bond between zirconium and zirconium.³² (Magnification 500 x.)

Fig. 18—Interface of good pressure bond between zirconium-20 wt. % uranium alloy and zirconium.³² (Magnification 500 x.)

Fig. 19—Bend-test section with no observable separation between core and cladding.³² (Magnification 100 $\times$.)

Fig. 20—Appearance of a generally poor bond.³² (Magnification 250 $\times$.)

Fig. 21 —Flaw in bond line.³² (Magnification 250 x.)

Fig. 22—Poorly bonded section after 6 hr at 1650°F under 850 psi pressure.³² The pressure is inadequate to cause sufficiently rapid plastic flow. (Magnification 250 x.)

Fig. 23—Characteristic fractures that result in tensile testing of Zircaloy-2 clad uranium-12 wt. % molybdenum fuel rod.³⁵ Rod at right is metallurgically bonded; rod at left is unbonded.

perienced with the formation of brittle layers of UAl_3 . These difficulties were not solved before the work was stopped.

4.8 Evaluation of Bond Quality

By the methods that have been described, it is possible to produce strong ductile bonds on any of the ductile fuel alloys that have been discussed. A strong bond is considered to be one which defies all efforts to separate the core and cladding at the bond line. Thus, a composite material with a strong bond can be cold drawn, broken in a tensile machine, swaged, bent, or chisel tested without separation along the bond line. Fracture, when it occurs, will always be some distance from the bond line. Figure 23 shows a well-bonded uranium-alloy-clad rod that was broken in a tensile machine, with considerable reduction of area, without any cladding separation. With the poorly bonded rod, the cladding separated completely.

The important difference between such a strong bond and a weak one is that a weak one will not tolerate such deformation without bond-line failure. Although there are all degrees of weak bonding, the defining characteristic is that bond-line separation can occur. Unfortunately, the difference between the two types may be so subtle that tests other than those involving deformation may be unable to detect them. It is recognized that this opinion is not held by all investigators,⁸ but there are others who do have this view.³⁵

The difference between strong bonds and weak ones is vital. Core alloys swell during irradiation, requiring that the cladding be deformed to accommodate the swelling. The bond layer must be strong enough to transmit the forces to deform the cladding plastically. Otherwise, bond rupture will occur, followed by rapid fuel-element failure.

The task of inspecting bonds in finished fuel elements is tremendous. A poor bond may result from a small fraction of tiny unbonded areas, small scattered areas of dirt, or a thin layer of brittle material. Finding any such defects by nondestructive testing is at least difficult and may be impossible.

Proof-testing methods seem to hold more promise of detecting subtle types of bond defects because they can reveal directly the characteristics which are important. Typical methods might be cold swaging in straightening machines or shot blasting. These are ways of obtaining the plastic working of the bond which can cause poor bonds to fail so that nondestructive inspection can detect them.

Proof-testing methods cannot always be used. In such cases the best guarantees of good bonding are (1) rigid process control with frequent destructive examination of the bonds and (2) the tendency of zirconium, given favorable conditions, to produce good bonds.

Obviously, because of the importance of good bonds, all pertinent nondestructive tests should be applied to the materials routinely to provide a further check on process control. One should not assume, however, that such tests will detect all bonds which may fail in service.

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Appendix

Frequent mention was made in the body of this discussion of the metallurgical characteristics of the materials which affect the fabrication operations. The details of the metallurgy were not presented there but are given in the following sections.

A.1 CONSTITUTIONAL DIAGRAMS

Data are given for five systems, uranium-zirconium, uranium-molybdenum, uranium-niobium, uranium-silicon, and uranium-niobium-zirconium. The discussions of the features of the diagrams have been taken verbatim either from BMI-1000 (reference 36) or from a revised version of this report as prepared by F. A. Rough and A. A. Bauer.³⁷

The phase designations used in these diagrams are those of the uranium metallurgist and do not always agree with the phase designations used in the preceding discussion, which were those of the laboratories whose work was being reported. Thus, in the uranium-zirconium, -molybdenum, and -silicon systems, the phase called epsilon above appears as δ in the diagram, while epsilon designates the next unique phase of higher alloy content.

A.1.1 Uranium-Zirconium System

(a) *Constitutional Diagrams.* The system uranium-zirconium has been studied by a number of investigators. The diagram shown in Fig. A.1 is based largely on the work of Saller³⁸ and Rough³⁹ and their coworkers, but the principal features of the system were reported earlier by Kaufmann⁴⁰ and by Carlson and Peterson.⁴¹ The diagram is based on work with alloys prepared by arc melting selected biscuit uranium and Grade 1 crystal-bar zirconium.

There is agreement that complete solid solution exists between gamma uranium and beta zirconium.³⁸⁻⁴³ Until recently there was some question concerning the stability of the intermediate delta phase. However, results of recent studies by Rough,³⁹ Kearns,⁴⁴ and Holden⁴⁵ confirm the stability of the phase. Oxygen and nitrogen, in ternary-alloy combination with the delta phase, have been shown³⁹ to cause its decomposition. Features in this region of the diagram are based upon the work of Rough, Austin, Bauer, and Doig.³⁹ The uranium-zirconium-oxygen system is reported in the uranium-ternary system section of this compilation.

The gamma-plus-epsilon region of the diagram has been studied by several investigators.³⁸⁻⁴⁶ Variations in the gamma boundary values reported have been explained recently as arising from oxygen and nitrogen contamination. The value of solubility of uranium in alpha zirconium (0.3 at. %) at the isotherm was determined by McGeary⁴⁶ and was based on precision dilatometric measurements of a series of alloys.

The features of the high-uranium end of the system have been confirmed by a number of investigators.^{38,40-42,47} Refinement of this area to include the gamma₁-plus-gamma₂ region is indicated by more recent works.^{38,42} The details shown are based largely on the work of Saller, Rough, and Bauer³⁸ who have used quantitative lineal analysis of metallographic samples, thermal analysis, and, more recently, high-temperature x-ray techniques⁴⁸ to establish the various phase regions.

The solubility of zirconium in alpha and beta uranium has been reported by Ziegler and Chiswick⁴⁹ to be between 0.2 and 0.4 wt. % at 675, 700, and 750°C in the beta phase and between 0.09 and 0.2 wt. % from 500 to 640°C and slightly in excess of 0.2 wt. % at 660°C in the alpha phase. These values were determined by metallographic examination of annealed and quenched low-zirconium alloys, the solubilities being less, particularly in the beta phase, than were determined by quantitative lineal measurements.

(b) *Crystallography.* Holden and Seymour⁴⁵ report that the gamma-to-delta transformation is an ordering reaction. Complete agreement on the crystal structure has not been reached, however.

Peterson⁵⁰ reports the delta phase to be body-centered cubic with $a_0 = 10.678$ Å. The data given below are from the work by Mueller⁵¹ who, on the basis of single-crystal and powder-

Fig. A.1—Constitutional diagram for the uranium-zirconium system.

diffraction work, also reports the phase to be cubic with $a_0 = 10.69$ Å. However, Mueller reports that although powder photographs can be indexed according to this cubic cell, a few high-angle lines show a regular displacement which indicates an increase in a_0 . Upon this basis, Rough³⁹ reports a hexagonal or rhombohedral pseudocubic structure with $a_0 = 8.793$ Å and $c_0 = 9.212$ Å at 575°C in a uranium-72 at. % zirconium alloy.

Phase	Type	Unit cell		Number of molecules	Density, g/cm ³		Space group	Remarks
		Dimensions, Å			X-ray	Other		
Delta	Body-centered cubic	$a = 10.69$				9.7		

A.1.2 Uranium-Molybdenum System

(a) *Constitutional Diagram.* The uranium-molybdenum was first studied by Ahmann⁵² who interpreted the system much as it is now, except that the gamma phase was reported to be stabilized to room temperature in the vicinity of 25 to 30 at. % molybdenum. A somewhat similar report was issued independently by Pfeil.⁵³ It was then shown that the gamma phase is metastable; and, although relatively long periods of time are necessary to transform the gamma, a different phase is stable below about 575 to 600°C.⁵⁴⁻⁵⁶

Recent work by Halteman and Lustman⁵⁷ and by Pfeil and Brown⁵⁸ has been concentrated on the region of metastable gamma alloys. Early results indicated that the intermediate delta

phase exhibited a wide solubility range from about 20 to 33 at. % molybdenum at the isotherm temperatures. When annealing times on the order of a month are involved, this wide solubility range is observed. However, Halteman⁵⁹ has since demonstrated that with a still more prolonged annealing period the region narrows to about 31.5 to 32.5 at. % molybdenum. The diagram shown in Fig. A.2 is based upon these results and confirms the earlier interpretation of Saller, Rough, and Vaughan.⁵⁴

There appears to be some difference of opinion regarding the solubility of molybdenum in alpha uranium. Pfeil⁵³ has reported a peritectoid alpha formation with a solubility of about 3 or 4 at. % molybdenum in alpha. This report is contrary to the work of both Ahmann⁵² and Saller, Rough, and Vaughan⁵⁴ who carried out an intensive study of this region. It is true that several atomic per cent of molybdenum can be retained in what might be described as a super-saturated, or distorted, alphas-like structure. However, cold working followed by annealing for a long period produces two-phase structures which indicate a maximum solubility of about 0.5 at. % molybdenum, or less, in the alpha. Thermal analyses also indicate a lowering of the beta-to-alpha transformation even during heating.⁵⁴ The maximum solubility in the beta phase is about 1.0 at. % molybdenum. It has been demonstrated that the beta phase can be retained to room temperature by quenching alloys of about 1 at. % molybdenum. The retained structure is metastable and transforms slowly during long periods of room-temperature aging.⁵⁴

The solubility of uranium in molybdenum is quite limited and appears to be a maximum of about 2 at. % uranium at 1285°C (reference 60).

(b) *Crystallography.* The delta phase has been studied by a number of investigators, and it is generally agreed that it is an ordered structure. The data in the following tabulation are from the work of Halteman⁵⁹ who reports that the tetragonal delta phase is of the C11b MoSi₂ type and can be considered as an ordered form of gamma in which the molybdenum atoms assume special positions in a unit cell composed of three body-centered pseudocubes.

Pfeil and Brown⁵⁸ had earlier reported the structure to be body-centered tetragonal with $a = 3.425$ Å and $c = 3.282$ Å, which is the same structure reported by Tucker.⁵⁵ However, the diffraction pattern reported by Tucker was found to be incomplete; also, the observed intensities could not be accounted for on the basis of this structure. Upon this basis Saller⁵⁴ and Halteman⁵⁷ and their coworkers had proposed a body-centered tetragonal phase with $a = 6.84$ Å and $c = 6.55$ Å. However, the more detailed analysis of Halteman⁵⁹ leads to the tetragonal cell with $a = 3.427$ Å and $c = 9.839$ Å.

Phase	Type	Unit cell		Density, g/cm ³		Space group	Remarks
		Dimensions, Å	Number of molecules	X-ray	Other		
Delta	Tetragonal	$a = 3.427,$ $c = 9.839$			16.63	14/mm	C11b type isomorphous with MoSi ₂ , WSi ₂ , ReSi ₂ , AlCr ₂ , MgH ₂

A.1.3 Uranium-Niobium System

(a) *Constitutional Diagram.* The diagram shown in Fig. A.3 is from Rogers et al.⁶¹ and represents essential confirmation of work of earlier investigators⁶²⁻⁶⁴ although revisions in certain phase boundaries have been made.

The complete solubility of gamma uranium and niobium is agreed on by all investigators.⁶¹⁻⁶⁵ Sawyer⁶² had reported the gamma₁-plus-gamma₂ region as extending from about 11 to 78 at. % niobium at 645°C, whereas data from the United Kingdom indicated limits of 16.5 and 66 at. % niobium for the same temperatures. Dwight,⁶⁵ on the other hand, reports the monotectoid to occur at about 19 at. % niobium and 634°C.

There appears to be agreement at the high-uranium end of the system. Rogers et al.⁶¹ interpret the system as having a eutectoid reaction when alpha is formed. This supports

Fig. A.3—Constitutional diagram for the uranium-niobium system.

Fig. A.2—Constitutional diagram for the uranium-molybdenum system.

the results of Saller and Rough.⁶³ However, Sawyer⁶² and Dwight⁶⁵ indicate a peritectoid rather than a eutectoid reaction. In any case, it is agreed that the solubilities in the alpha and beta phase regions are limited.

If diffusion samples are prepared in this system and are annealed first in the gamma region and then in the alpha temperature range, an intermediate layer is observed. After very long periods of annealing, this layer decomposes. Similar material has been observed during annealing of gamma-treated alloy samples. The appearance of this layer may be explained simply as a microstructural phenomenon which occurs at a certain composition and treatment, or it may be explained by the formation and decomposition of a metastable phase. It appears certain, however, that after long-time annealing at alpha temperatures (500 to 600°C) there is no intermediate phase in this system.

(b) *Crystallography.* There are no compounds in the uranium-niobium system.

A.1.4 Uranium-Silicon System

(a) *Constitutional Diagram.* The constitutional diagram for the uranium-silicon system has been determined by Kaufmann et al.^{66,67} as shown in Fig. A.4. Undoubtedly, some correction of this diagram is necessary. However, until the changes are fully understood, it is best

Fig. A.4—Constitutional diagram for the uranium-silicon system.

to leave the diagram as it is shown. Recent work by Zachariassen⁶⁸ has indicated the existence of U_3Si_2 instead of U_3Si_3 , and two forms of USi_2 are reported. It is not readily apparent whether eta ("alpha" USi_2) and theta ("beta" USi_2) are allotropic modifications of USi_2 or slightly different stoichiometrical ratios as shown in the diagram (U_2Si_3 and USi_2).

There is no disagreement about the compounds delta (U_3Si) (references 66 to 68), and iota (USi_3) (references 66 to 70). Kaufmann and Bitsianes,⁶⁷ however, report that delta (U_3Si) actually

has a very narrow composition range near 23 at. % silicon, rather than a stoichiometric ratio of U_3Si . There is evidence that the bonding in this phase may be metallic in nature.⁶⁸

(b) *Crystallography*. Data on the uranium silicides are tabulated below. The data are from Zachariasen,⁶⁸ except for iota (USi_3), which is from Kaufmann.⁶⁶ The discrepancies between these data and the constitutional diagram are explained above.

The structure of iota (USi_3) has been determined by others^{69,70} and is reported to be the L12 type, isomorphous with UGa_3 , UIn_3 , UGe_3 , UPb_3 , UAl_3 , and USn_3 (reference 69).

Zachariasen⁶⁸ reports that delta (U_3Si) is the only one of the intermetallic compounds in this system which does not have covalent bonds between silicon atoms. This generalization presumably excludes USi_3 since Zachariasen did not report on it.

In epsilon (U_3Si_2) the silicon atoms are bonded together to form pairs normal to the four-fold axis. In zeta (USi) the silicon atoms are bonded together to form endless zigzag chains along the c-axis. In theta ("beta" USi_2) the silicon atoms form "graphite layers" normal to the sixfold axis; and in eta ("alpha" USi_2) a three-dimensional network of silicon atoms occurs, with uranium atoms in the interstices.

Phase	Type	Unit cell		Density (X-ray), g/cm ³	Space group	Remarks
		Dimensions, A	Number of molecules			
Delta (U_3Si)	Body-centered tetragonal	a = 6.029 ± 0.002, c = 8.697 ± 0.003	4	15.58	14/mcm	
Epsilon (U_3Si_2)	Tetragonal	a = 7.3298 ± 0.0004, c = 3.9003 ± 0.0005	2	12.20	P4/mbm	
Zeta (USi)	Orthorhombic	a = 5.66 ± 0.01, b = 7.66 ± 0.01, c = 3.91 ± 0.01	4	10.40	Pbnm	Isomorphous with FeB
Eta ("alpha" USi_2)	Body-centered tetragonal	a = 3.98 ± 0.03, c = 13.74 ± 0.08	4	8.98	14/amd	Isomorphous with $ThSi_2$ and $PuSi_2$, $CeSi_2$ and $NpSi_2$
Theta ("beta" USi_2)	Hexagonal	a = 3.86 ± 0.01, c = 4.071 ±	1	9.25	C6/mmm	Isomorphous with AlB_2 and TiB_2
Iota (USi_3)	Cubic	a = 4.03	1	8.15	Pm3m	L12 type, $AuCu_3$ -ordered structure

A.1.5 Uranium-Niobium-Zirconium System

(a) *Constitutional Diagram*. The uranium-rich portion of the uranium-niobium-zirconium system has been investigated by Dwight.⁷¹ A ternary section showing the phase boundaries as they exist at 630°C is shown in Fig. A.5. The dotted lines appearing in this figure trace the limits of the γ_1 -plus- γ_2 regions, found in both binary systems, at the respective binary monotectoid temperatures.

With increasing temperature, solubility of zirconium and niobium in the gamma phase increases.

Fig. A.5 — Constitutional diagram for the uranium-niobium-zirconium system.

Studies below the temperature of 630°C were not reported.

(b) *Crystallography*. No new phases were reported.

A.2 TRANSFORMATION KINETICS AND HEAT-TREATMENT

A.2.1 Uranium-Zirconium Alloys

Transformation from gamma-phase uranium-zirconium solid solution to epsilon phase is extremely rapid. According to data from Kearns,⁷² the time required for 25 per cent completion of the transformation is a few seconds at 400 to 500°C. His time-temperature-transformation diagram for a uranium-50 wt. % zirconium alloy is shown in Fig. A.6. The alloy contained 565 ppm oxygen and, on that account, rejected small amounts of alpha uranium, as shown by the dotted line.

The gamma phase can be retained at room temperature by a drastic quench. The hardness of the retained gamma phase is low but increases rapidly during transformation. When transformation has largely been completed, hardness is high, as shown in Fig. A.7, and very long times are required to anneal the material fully and obtain a low hardness. Kearns attributes the high hardness to the extremely small epsilon particle size (~100 Å) of the transformed material and the softening to growth of the epsilon particles.

For alloys containing less than 50 wt. % of uranium in zirconium, down to 20 wt. % uranium, it is more difficult to retain the gamma phase. Alloys at about 20 wt. % uranium transform martensitically and, on quenching, become extremely hard.

The response of alloys of various uranium contents to hardening on quenching is shown in Fig. A.8, which gives the results for Jominy end-quench bars.⁷³ The hardness of some of the materials produced can be reduced by an annealing treatment. The effects of 550 and 700°C annealing treatments are shown in Fig. A.9. Even furnace cooling from a high-temperature anneal does not decrease hardness or increase ductility as much as possible. Very slow

Fig. A.6—Time-temperature-transformation diagram for uranium-50 wt. % zirconium alloy, from dilatometric data.¹²

Fig. A.7—Hardness of beta-quenched zirconium-49 wt. % uranium alloy isothermally transformed at 500°C (930°F) (reference 29).

Fig. A.8—Hardness of zirconium-uranium end-quench bars quenched from 900°C (reference 73).

Fig. A.9—Hardness of zirconium-uranium end-quench bars quenched from 900°C and annealed.⁷³ Hardness $\frac{1}{8}$ in. from quenched end.

cooling is required throughout the two-phase region between the gamma phase and the alpha zirconium-plus-epsilon phase regions, to allow time for precipitation of alpha zirconium from the gamma solution and formation of coalesced or softened epsilon. The hardnesses attained by slow cooling in this region are shown in Fig. A.10.

Fig. A.10—Hardness of zirconium-uranium alloys heated for $\frac{1}{2}$ hr just below the upper limit of the transformation range, furnace cooled to 610°C for 4 hr, and furnace cooled at 25°C/hr.⁷³

The uranium-zirconium alloys are capable of a great variety of microstructures on heat-treatment. Some of the microstructures which have been obtained in a zirconium-22 wt. % uranium alloy are shown in Figs. A.11 to A.13.

A.2.2 Uranium-Molybdenum and Uranium-Niobium Alloys

In both of these alloy systems gamma solid solutions may be retained at room temperature. Time-temperature-transformation data for various molybdenum alloys are given in Fig. A.14

Fig. A.11—Zirconium-22 wt. % uranium warm rolled at 1000°F and alternately annealed at 1000°F and cold swaged.⁷⁴ Final treatment was 1000°F anneal. (Magnification 250 x.)

Fig. A.12—Zirconium-22 wt. % uranium held 36 hr at 1550°F and furnace cooled to room temperature.⁷⁴ Rate, 1°F/min between 1550 and 1200°F. (Magnification 250 x.)

Fig. A.13—Zirconium-22 wt. % uranium held 36 hr at 1550°F, water quenched, annealed two weeks at 1020°F, and furnace cooled.⁷⁴ (Magnification 250 x.)

Fig. A.14—Time-temperature-transformation diagrams illustrating initial resistivity decrease for uranium-molybdenum alloys.⁷⁵ [From ASM Trans., 49: 598 (1957).]

Fig. A.15—Time-temperature-transformation diagrams illustrating initial resistivity decrease for uranium-molybdenum-X alloys.⁷⁶ [From ASM Trans., 49: 576 (1957).]

(Van Thyne and McPherson),⁷⁵ for ternary uranium-molybdenum alloys in Fig. A.15 (reference 76), and for uranium-niobium alloys in Fig. A.16 (reference 76).

Fig. A.16—Time-temperature-transformation diagrams illustrating initial resistivity decrease for uranium-niobium alloys.⁷⁶ [From ASM Trans., 49: 576 (1957).]

The continuous-cooling transformation diagram for a uranium-10 wt. % niobium alloy on cooling at various constant rates is shown in Fig. A.17 (reference 77). The critical-cooling rate is 7.5 to 8°C/min.

The uranium-molybdenum gamma phase decomposes eutectoidally to form alpha phase and the ordered epsilon phase. The uranium-niobium gamma phase decomposes to alpha uranium and the niobium-rich gamma phase.^{75,76} WAPD (reference 78) says this phase is essentially pure niobium.

Cold work in either of these materials has an effect on transformation. In the case of uranium-10 wt. % niobium alloys, samples which were cold rolled as low as 16½ per cent⁵ show transformation by metallographic or X-ray examination. In cold-worked samples, the transformation that normally occurs on grain boundaries is on slip planes. The uranium-molybdenum alloy is less sensitive to cold work, and this would be expected in view of the greater stability of the uranium-molybdenum gamma phase, as shown by the transformation diagrams.

A.2.3 Uranium-5 Wt. Per Cent Zirconium-1.5 Wt. Per Cent Niobium

This alloy, as gamma quenched, transforms martensitically. On aging of martensitic structures, which are generally called alpha prime or distorted alpha phase, hardening occurs and on overaging a second phase is precipitated from the metastable solid solutions.⁷⁹ The properties of the alpha-prime phase are much different than those of normal alpha uranium. For example, a quenched 5 wt. % zirconium alloy has a hardness of 534 VHN and 1000 times better corrosion resistance in boiling water than alpha uranium. A time-temperature-hardness diagram for the uranium-5 wt. % zirconium-1.5 wt. % niobium alloy is given in Fig. A.18 (reference 80).

The best heat-treatment of this alloy for corrosion resistance is a gamma quench from perhaps 800°C in the as-cast condition.⁸¹ Overaging of the material is detrimental to the corrosion resistance. The best treatment for resistance to radiation damage is to heat the material to 800°C, then reduce the temperature to 650°C and hold for 24 hr, and quench. If the treatment for radiation stability is followed by an 800°C treatment for corrosion resistance, dimensional stability is lost. The material loses corrosion resistance upon irradiation. In

the EBWR, the material is used as treated for radiation stability.⁸¹ Although the corrosion resistance is not high in this condition, corrosion failure through a defect is still much slower than for unalloyed uranium⁸¹ and allows time for corrective measures to be taken.

A.2.4 Uranium-3.8 Wt. Per Cent Silicon Alloy

This alloy is heat treated to produce the epsilon phase by diffusion from the uranium and U_3Si_2 existing in the cast structure. The best epsilonizing treatment is one week at a temperature of 800°C (references 11 and 82). This treatment is satisfactory if the carbon content is less than 300 ppm. Carbon reduces the peritectoid temperature (100°C for 1000 ppm carbon), which requires that the epsilonizing treatment be done at a lower temperature. The reaction then becomes sluggish and epsilonizing is impractical.

A.3 DIFFUSION DATA

Data on the diffusion of oxygen in alpha and beta zirconium are given in Figs. A.19 and A.20 (reference 83). The large diffusion coefficient for oxygen shows the rapidity with which oxidized surface layers can be diffused away during bonding operations. The nitrogen diffusion coefficient is a factor of 10 lower, as given by Lustman.¹⁶ Data on the diffusion of uranium in zirconium and Zircaloy are given in Fig. A.21 (reference 29). More recent data on gamma-phase diffusion over a range of composition have been obtained by Adda and Philibert.⁸⁴ Their results are summarized in Table A.1.

Fig. A.17 — Continuous-cooling transformation diagrams for the uranium-10 wt. % niobium alloy based on metallographic and hardness data (solution treated at 950°C for 1 hr).⁷⁷ (From paper by S. J. Parry, R. J. Thyne, and D. J. McPherson, Continuous Cooling Transformation Studies for the Uranium-10 Wt. % Niobium Alloy, courtesy of AIME, prepared for the Nuclear Engineering and Science Congress.)

Fig. A.18—Effect of time and temperature of tempering on the hardness of water-quenched uranium-5 wt. % zirconium-1.5 wt. % niobium alloy.⁸⁰ (From the Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 9, Paper 555, Physical Metallurgy of Uranium and Its Alloys, by F. G. Foote, August 1955.)

Fig. A.19—Temperature variation of the diffusion coefficient for oxygen in alpha Zircaloy-2 and Zircaloy-3.

Fig. A.20—Temperature variation of the diffusion coefficient for oxygen in beta Zircaloy-2 and Zircaloy-3.

Fig. A.21—Diffusion of uranium in alpha and beta zirconium.²⁹

Table A.1—GAMMA-PHASE DIFFUSION DATA
FOR URANIUM IN ZIRCONIUM

Zirconium content, at. %	Q, kcal/mole	D ₀ , cm ² /sec
10	32	9.5×10^{-4}
20	28.6	1.3×10^{-4}
30	26.3	3.5×10^{-5}
40	27.4	4
50	29.7	8
60	29.7	6.3
70	29.7	5.5
80	34.3	3.2×10^{-4}
90	41	7.8×10^{-3}
95	47	8.7×10^{-2}

These results are given in a form which will permit computation from the equation

$$D = D_0 \exp \left(- \frac{Q}{RT} \right)$$

The data show a pronounced effect of composition. More recently, diffusion in the uranium-zirconium system has been measured⁸⁵ at 1000°C with the following results:

Uranium, at. %	5	10	20	25	30	40	50	60	75	85	90
D, 10 ⁻¹⁰ cm ² /sec	9.2	6.2	5.7	5.1	5.7	6.6	7.5	10.3	16.1	25.2	49.8

These results correlate fairly well with those of Adda and Philibert.

For uranium-molybdenum, uranium-silicon, and uranium-niobium alloys, diffusion zones between the alloys and zirconium claddings have poor corrosion properties, and it is desirable to minimize the thickness of the diffusion zone. Measurements made on the rate of growth of the diffusion zone between zirconium and a uranium-10 wt. % molybdenum alloy are given in Fig. A.22 (reference 20). At 900°C the diffusion-zone thickness is proportional to the square root of time, showing that this is a normal diffusion process. At lower temperatures, however, this proportionality is not maintained, and the investigator suggests that barrier layers, perhaps a layer of the compound ZrMo₂, are being formed and interfering with the diffusion process. Other investigators have not found this lack of proportionality at the same temperatures and for the same length of time.¹³ Data for diffusion between zirconium and uranium-12 wt. % molybdenum, uranium-10 wt. % niobium, and uranium-3.8 wt. % silicon are given in Fig. A.23. From these data for the uranium-12 wt. % molybdenum alloy, an activation energy of 55,000 cal/mole has been found for the process as shown in Fig. A.24. The investigators point out that the diffusion of uranium and zirconium is the same, whether the alloy is uranium-molybdenum or uranium-niobium, suggesting that molybdenum and niobium have little effect on the diffusion process.

There has been some study of the composition of the diffusion layer between zirconium and uranium-12 wt. % molybdenum.⁸⁶ The diffusion layer formed in a period of 48 hr at 985°C is shown in Fig. A.25. Layers were machined from the diffusion zone as indicated by the numbers beside the photomicrograph. Analyses of the various layers are shown in Table A.2. Also indicated in this table are the corrosion properties of the various layers as determined on some of the alloys, which were button-arc melted. The compound ZrMo₂ was formed in the interface. This compound itself has good corrosion resistance, but its formation may deplete the solid solution of molybdenum, possibly accounting for the reduced corrosion resistance of some alloys in the diffusion layer.

Data are given by WAPD¹³ on the effect of barrier layers in preventing the formation of diffusion layers subject to rapid corrosion. The barriers studied were chromium, iron, molyb-

Fig. A.22—Rate of growth of diffusion zone in coextruded uranium—10 wt. % molybdenum alloy clad with zirconium.²⁰

Fig. A.24—Rate of diffusion-layer growth as function of temperature for uranium-12 wt. % molybdenum-Zircaloy-2 couple.¹³

Fig. A.23—Isothermal diffusion-layer growth in Zircaloy-2 for uranium-base alloys clad with Zircaloy-2 (reference 13).

Fig. A.25—Alloy layers present in interface of a specimen pressure bonded at 1400°F using a 600-psi pressure for 4 hr and diffusion annealing for 48 hr at 1800°F (reference 86). (Magnification 250 X.)

Table A.2—ANALYSES OF LAYERS PRESENT IN THE INTERFACE FORMED BETWEEN ZIRCALOY-2 AND URANIUM-12 WT. % MOLYBDENUM⁸⁶

Layer	Analysis, wt. %				Remarks
	Mo	Sn	U	Zr	
1	0.15	1.45	2.1	94.0	Layer adjacent to Zircaloy-2
2	3.1	1.3	18.6	84.0	
3	7.4	0.65	45.8	43.0	
4	9.2	0.5	59.1	35.0	Some corrosion attack on this layer after 72 hr
5	12.3	<0.5	78.0	18.0	Corrosion failure in 1/2 hr
6					Identified by X-ray as ZrMo ₂
7	12.5	<0.5	85.3	1.5	Corrosion failure in this layer near ZrMo ₂ layer
8	12.8	<0.5	85.3	1.5	
9	12.3		89.0		Core alloy

denum, nickel, niobium, tantalum, and uranium-10 wt. % niobium alloy. None were successful, possibly owing to fabrication difficulties.

The diffusion layer formed between uranium-3.8 wt. % silicon and zirconium has been found to be produced by the diffusion of silicon from the fuel into the zirconium, forming a layer of ZrSi₂ and leaving a layer of alpha uranium at the surface of the fuel, so that there is rapid corrosion at the zirconium-to-U₃Si bond.¹¹

A.4 MECHANICAL AND PHYSICAL PROPERTIES

A.4.1 Hot Hardness

Measurements of the hot hardness of materials serve as an important indicator of the suitability of various fabrication operations. For example, in the roll-bonding process it is necessary that a fairly good hardness match be obtained between core and cladding alloys in order to maintain good core configuration. For this reason, values for the hot hardness of various materials are given.

Data for the hot hardness of alloys in the zirconium-uranium system are presented in Fig. A.26 (reference 29) and the data for the uranium-molybdenum alloys in Fig. A.27 (reference 87). From data such as these, it is possible to select temperature ranges that are satisfactory for roll bonding these alloys and zirconium.

It is apparent that the uranium-10 wt. % molybdenum alloy is much harder than zirconium at all temperatures, so a poor hardness match is inevitable. It appears that, for applications not involving water corrosion, cladding with a stronger zirconium alloy like zirconium-4 wt. % tin-1.6 wt. % molybdenum (which was developed in an effort to produce a zirconium alloy of good high-temperature strength)²⁷ would be desirable. Hot-hardness data for this material at temperatures of 700 and 800°C are given in Fig. A.28, and it is apparent that its short-time hardness is much closer to that of uranium-10 wt. % molybdenum than is that of zirconium.

The hardness data given in Fig. A.28 were obtained as a function of time to provide an approximate indication of the resistance to creep of this material at these temperatures. It is quite evident that the creep resistance is not good at 700 and 800°C, as indicated by the steep slope of the curves. However, it is much better than other zirconium alloys at a temperature of 500°C, as will be apparent in the next section.

Hot-hardness data obtained as a function of time of load application also have value in estimating the rate of flow of the material in the pressure-bonding operation. Such data obtained for zirconium are given in Fig. A.29 (reference 18). It is apparent in this figure that plastic flow occurs at all of the indicated temperatures. From such data it is possible to calculate the rate of flow at various pressures. This has been done for a number of alloys, and

Fig. A.26—Hardness-temperature relation in the zirconium-uranium system.²⁹ (DPH, kg/mm².)

Fig. A.27—Hot hardness of uranium-molybdenum alloys gamma quenched from 900°C (reference 87).

Fig. A.28—Hot hardness versus time of indentation for zirconium and zirconium-3.9 wt. % tin-1.6 wt. % molybdenum.²⁷

Fig. A.29—Hot hardness versus time for arc-melted sponge zirconium (No. X-290).¹⁸

Fig. A.30—Plasticity of zirconium alloys.¹⁸

Fig. A.31—Tensile behavior of zirconium-uranium alloys prepared by induction and arc melting.²⁹

Table A.3—TENSILE PROPERTIES OF HEAT-TREATED ZIRCONIUM-22 WT. % URANIUM ALLOY⁷⁴

Heat-treatment*	Test temperature, °C	0.2 per cent offset yield strength, psi	Ultimate strength, psi	Uniform elongation, %	Elongation in 1 in., %	Reduction of area, %
A	25	112,000	129,200	1.9	2	2
B	25	†	57,700	0.5	0	0
C	25	48,300	87,900	13	16	17
D	25	†	60,800	0.4	0	0
E	25	†	55,400	0.4	0	0
F	25	64,000	97,200	7.4	8	9
A	500	12,000	25,600	8.4	75	92
B	500	41,800	55,200	5.1	14	13
C	500	29,200	44,200	6.2	34	32
D	500	38,400	54,500	3.7	12	18
E	500	34,200	47,500	4.9	25	38
F	500	35,100	48,000	5.7	18	22

* Heat-treatments:

A, as rolled at 1000°F

B, 36 hr at 1550°F, furnace cool at 25°F/min from 1550 to 1200°F, and then furnace cool to room temperature

C, 36 hr at 1550°F, furnace cool at 1/2°F/min from 1550 to 1200°F, and then furnace cool to room temperature

D, 36 hr at 1550°F, furnace cool; reanneal 1 hr at 1550°F, quench to 1020°F, hold 1/2 hr, reheat to 1300°F, hold 10 hr, water quench; and anneal 1 hr at 1020°F, water quench

E, 36 hr at 1550°F, water quench; anneal 1/2 hr at 1020°F, water quench; and anneal 10 hr at 1400°F, furnace cool

F, 36 hr at 1550°F, water quench; and anneal 22 days at 1020°F, furnace cool

† Brittle failure.

Table A.4—TENSILE PROPERTIES OF URANIUM-12 WT. % MOLYBDENUM TESTED AT 0.05 IN./MIN STRAIN RATE

Condition	0.5 per cent yield strength, 1000 psi	Tensile strength, 1000 psi	Total elongation, %	Reduction of area, %
A. At 25°C (Y257 alloy)				
1. 900°C/24 hr/WQ	166	166	9.0	41.9
2. 1 + 500°C/72 days	156	157	10.4	32
B. At 316°C (Y257 alloy)				
1. 900°C/24 hr/WQ	106	107	3.8	23.3
2. 1 + 500°C/72 days	99	100	4.0	32
C. At 260°C (Y256 alloy)				
1. As extruded	114	120	6.1	15.4
2. 900°C/24 hr/WQ	102	104	6.8	50
3. 2 + 500°C/40 hr	113	116	5.2	37
C. At 316°C (Y256 alloy)				
1. As extruded	108	118	6.8	14.8
2. 900°C/24 hr/WQ	100	103	5.0	33
3. 2 + 500°C/3 hr	102	104	5.5	45

Table A.5—EFFECT OF TEST TEMPERATURE ON TENSILE PROPERTIES OF URANIUM-12 WT. % MOLYBDENUM ALLOY (Y256) ANNEALED 24 HR AT 900°C AND WATER QUENCHED AND TESTED AT 0.05 IN./MIN STRAIN RATE

Temperature, °C	0.5 per cent yield strength, 1000 psi	Tensile strength, 1000 psi	Total elongation, %	Reduction of area, %
-65		226	0	0
-31		167	0	0
-15	189	189	3.6	36
0	179	180	4.9	7.8
260	102	104	6.8	50
316	100	103	5.0	33

Fig. A.32—Tensile properties of uranium-10 wt. % molybdenum.²⁰ —, gamma phase; 24 hr, 900°C, water quenched. - - -, transformed 24 hr, 900°C, water quenched, two weeks, 500°C water quenched.

Fig. A.33—Effect of temperature upon the hardness and tensile properties of zirconium-3.9 wt. % tin-1.6 wt. % molybdenum.²⁷

Table A.6—PHYSICAL PROPERTIES OF URANIUM ALLOYS*

	$\gamma > 570^\circ\text{C}$, $\text{U}\alpha + \epsilon < 570^\circ\text{C}$	$\gamma > 600^\circ\text{C}$, $\text{U}\alpha + \text{Nb} < 600^\circ\text{C}$	$\epsilon < 930^\circ\text{C}$, $\text{U}\gamma + \text{U}_3\text{Si}_2$	Zr-45 to 55 wt. % U
Crystal structure	γbcc , $a_0 = 3.396 \text{ \AA}$ for 12 Mo $\text{U}\alpha$ orthorhombic (very limited solubility of Mo); ϵ -ordered tetragonal, $a_0 = 3.427 \text{ \AA}$, $c_0 = 9.834$, $c/a = 2.871 \text{ \AA}$	γbcc , $a_0 = 3.40 \text{ \AA}$; $\text{U}\alpha$ orthorhombic (very limited solubility of Nb); Nb bcc, $a_0 = 3.3 \text{ \AA}$ limited solubility of U	ϵ tetragonal, $a_0 = 6.018 \text{ \AA}$, $c_0 = 8.681 \text{ \AA}$	Possibly bcc, $a_0 = 10.69$
Metastable phase at room temperature	γ retained in 8 Mo, cooled in 1 hr from 900°C , and 12 Mo 1 day from 900°C	γ retained by slow cooling	ϵ thermodynamically stable below 930°C	ϵ thermodynamically stable below 593°C
Thermal conductivity (10– 100°C), cal/(sec)(cm)($^\circ\text{C}$)	0.034 for 8 Mo, 0.033 for 12 Mo		0.036 at 25°C , 0.042 at 65°C	0.014 at 35°C
Thermal coefficient of expansion (100– 400°C), $10^{-6}/^\circ\text{C}$	13.8 ± 0.5 for 8 Mo, 13.0 ± 0.5 for 12 Mo		13.8 ± 0.5	9–11
Electrical resistivity, $\mu\text{ohm-cm}$	73 at 25°C , 65 after 42 days at 400°C		56 at 25°C	164 at RT
Specific heat (300– 400°C), cal/(mole)($^\circ\text{C}$)	7–8 for 12 Mo			
Melting point, $^\circ\text{C}$	1150 for 12 Mo	~ 1300 for 10 Nb	985°C	$\sim 1500^\circ\text{C}$
Density, g/cm ³	17.5 for 8 Mo, 16.9 for 12 Mo		15.5 ± 0.1	9.7
Diamond pyramid hardness	180 for 6 Mo, 300 for 12 Mo; 630 and 500 maximum, respectively, depending on heat-treatment	180 for 8 Nb, 350 for 12 Nb; 600 and 575 maximum, respectively, depending on heat-treatment	220 ± 10	~ 250 annealed ~ 400 maximum

* For gamma phase of uranium-molybdenum and uranium-niobium unless indicated.

the results are plotted in Fig. A.30 (reference 18). The quantity plotted in this figure is the pressure required for essentially complete closing of voids during the pressure-bonding operation and can be considered to be the pressure required to cause plastic flow at a selected rate. Such data indicate that pressures of 700 atm or so are required in the pressure-bonding operation for temperatures of 800°C and above.

A.4.2 Other Mechanical Properties

Data for the tensile properties of various uranium-zirconium alloys are given in Fig. A.31 (reference 29). It was mentioned previously that alloys of 20 wt. % uranium in zirconium are very sensitive to heat-treatment. Data in Table A.3 (reference 74) show the room-temperature and high-temperature tensile properties for the zirconium-22 wt. % uranium alloy in several heat-treated conditions. Such data are a useful indicator of the heat-treatment required to obtain good ductility at room temperature to permit cold working. Obviously, heat-treatment C is the best for this purpose. At temperatures high in the alpha-phase region, most of the materials have moderately good ductility. Photomicrographs of the materials with heat-treatments A, C, and F were given in Figs. A.11 to A.13 (reference 74).

The tensile properties for uranium-12 wt. % molybdenum are given for three heat-treated conditions in Table A.4 (reference 78). In Table A.5 the effect of temperature on the properties of the gamma-quenched material is given over a range of temperatures.⁷⁸ Figure A.32 shows the tensile properties to higher temperatures. It is noteworthy in these tables that the tensile ductility of the molybdenum alloy is not high. Nevertheless, as clad, it is possible to cold draw the materials by large amounts, as was noted in the section on fabrication.

Hot-hardness data for the zirconium-4 wt. % tin-1.6 wt. % molybdenum alloy are given in Fig. A.33 (reference 27). The creep characteristics of this material at 500°C compared to those of zirconium are given in the following tabulation.

Stress to produce 1 per cent deformation, psi		
Test time, hr	Iodide zirconium	Zirconium-4 wt. % tin- 1.6 wt. % molybdenum
100	3700	16,000
1,000	1800	11,000
10,000	900	4,000

It is apparent in this tabulation that the creep strength at 500°C is four or five times that of iodide zirconium.

A.4.3 Physical Properties

The physical properties of the important fuel alloys have been assembled from various sources^{29, 78} and are given in Table A.6.

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SESSION IV

Nonmetallic Fuel Elements

Preparation and Properties of Uranium Dioxide Powder

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ABSTRACT

The physical properties of UO_2 powder are discussed in relation to their importance in fuel-element application. Various methods of commercial preparation of the dioxide are described with particular emphasis on the two methods which have had the widest application in the actual production of the material for fuel-element raw material. Data are presented showing the relation between method of manufacture and properties of interest.

1 INTRODUCTION

Highly purified UO_2 is in many respects an ideal material for the fabrication of fuel elements for atomic reactors. Although its density is not equal to that of the metal or many possible alloys, it compares very favorably with most other stable compounds of the element which might be chosen. Its very high melting point, complete stability in the thermal range up to its melting point, and very high resistance to corrosion by those materials with which it is likely to come into contact (for example, water and metals of cladding and construction) for many purposes offset the advantage of density that the metal and alloys have.

It is interesting here to note that the first self-sustaining nuclear chain reactor, put into operation on Dec. 2, 1942, at the University of Chicago, was fueled with compressed UO_2 with the exception of about 6 tons of uranium metal which was available at the time. This UO_2 had been purified at St. Louis in the first uranium refinery ever built for such high purity, and the uranium metal had been made from the product of this refinery by methods that led to a lesser degree of purity than that of the starting material. Thus even the disadvantage of lower density was to some extent offset by the higher purity of the oxide in this first reactor. It is still difficult to prepare metal of as high a nuclear purity as the dioxide without excessive expense.

2 PHYSICAL PROPERTIES OF URANIUM DIOXIDE

Uranium dioxide is a dense, brown substance of high melting point. Some of its physical properties are given in Table 1.

As a powder, the properties of UO_2 are dependent on its method of preparation. Chemical reactivity, bulk density, surface area, crystallite size, porosity, and even O/U ratio are grossly affected by the history of the powder.

Table 1—PROPERTIES OF UO_2

Melting point	2750°C
Density, x-ray	10.97 g/cm ³
Refractive index ¹	2.35
Specific heat, ¹ cal/g-°C	0.056 (0 to 200°C)
Thermal conductivity, ¹ cal-cm/°C-cm ² -sec	0.02 (20°C) 0.008 (1000°C)
Expansivity, ¹ C ⁻¹	~10 ⁻⁵ (0 to 1000°C)
Tensile strength ¹	~5000 lb/sq in.

The phase relations of uranium oxides of compositions between UO_2 and UO_3 are quite complex, as indicated in Table 2.

For reactors involving very high temperatures, the use of UO_2 fuel elements offers distinct advantages. Uranium dioxide not only has a high melting point and a relatively high density, but its lattice will accommodate foreign atoms to a marked degree without a change in crystal structure. This permits the accommodation of fission products without large dimensional changes. It is relatively stable to the action of high-temperature water, as compared to uranium metal or alloys. Since UO_2 is isotropic, it is not subject to oriented dimensional changes when subjected to thermal cycling or irradiation. Its oxygen content is of low-neutron cross section. These properties are sufficient to make it the material of choice for power reactors, where both high temperature and high burn-up are involved.

Table 2—PHASE RELATIONS OF URANIUM OXIDES

Formula	Cell type	Lattice, A	Reference
$\text{UO}_{2.00}$	FCC	5.4704	2
$\text{UO}_{2.00}$	FCC	5.4682	5
$\text{UO}_{2.20}$	FCC	5.4462	2
$\text{UO}_{2.25}$	FCC	5.4411	2
$\text{UO}_{2.60}$	Orthorhombic	a = 6.734, b = 3.966, c = 4.144	2
$\text{UO}_{2.67}$	Orthorhombic	a = 6.7198, b = 3.983, c = 4.1462	2
$\text{UO}_{2.82}$	Cubic	4.138	4
$\text{UO}_{3.0}$	Amorphous (yellow)		
$\text{UO}_{3.0}(\text{I})$	Hexagonal (red to black)	a = 3.963, c = 4.160	3
$\text{UO}_{3.0}(\text{II})$	Poorly crystallized (red)		6
$\text{UO}_{3.0}(\text{III})$	Orthorhombic (orange)	a = 13.01, b = 10.72, c = 7.51	6
$\text{UO}_{3.0}(\text{IV})$	Cubic	4.146	4

The absolute density of UO_2 , although high for a nonmetal, is still low enough to make it imperative to approach its full utilization in fuel elements compacted from powders. The suitability of a UO_2 powder for fuel-element fabrication, therefore, is judged partly by its behavior on compaction and sintering. Details of current practice in this field will be given in another paper.^{7,8} For the purposes of this paper it will be necessary to consider those properties of UO_2 powders which promote ready attainment of high densities of ceramic bodies sintered in a hydrogen atmosphere (sinterability).

It was evident early that the well-known tendency of UO_2 to oxidize at low temperatures was related to its sinterability. Early practice of high-temperature reduction to promote stability toward oxidation led to difficult sintering. The O/U ratio was close to theoretical, in general, being less than 2.05. Methods of preparation giving products of higher O/U ratio resulted in a material that sintered more readily. Some of these methods are described as follows:

Schwartz and Vaughan of Battelle Memorial Institute,⁹ working in cooperation with our laboratory, have found two types of UO_2 , an active form which retains cubic symmetry up to an O/U ratio of 2.4 and over the temperature range 25 to 700°C, and an inactive form whose cubic symmetry is lost at an O/U ratio of 2.12 at 180°C in oxygen. At higher oxygen contents the inactive form becomes tetragonal. It is postulated that the active oxide can be further oxidized throughout the lattice, whereas the inactive can be oxidized only at preferred sites. That oxidation itself is not necessary to promote easy sintering is shown by an experiment in which an active form of UO_2 was sintered with and without exposure to air, with essentially the same results. These workers have further shown that the active form of UO_2 can be made by hydrogen reduction of either amorphous or Type II UO_3 . This is consistent with the well-known effect of UO_3 properties on the reactivity of UO_2 in its reaction with anhydrous hydrogen fluoride.

Other work indicates that the physical condition of UO_2 particles is of great importance in determining the sinterability of a UO_2 powder. According to Belle and Jones,¹⁰ powders with large surface area, high density, large "roughness factor," and narrow pore-size distribution have excellent sintering characteristics. Comminution of poorly sintering powders greatly improves their sintering characteristics. Work at Battelle on ball milling and at Mallinckrodt on "Micronizing" is consistent with these conclusions. It is evident that two independent and self-consistent sets of data do not agree as to what controls the sinterability of UO_2 powders. It is probable that both lattice and surface effects are important, but more work is necessary to assess properly their individual contribution to sinterability of UO_2 powders.

Whatever the explanation, experience shows that the UO_2 made by 800°C hydrogen reduction of Type III UO_3 is difficult to sinter. Comminution of this material improves its sinterability markedly.

3 PREPARATION

3.1 Denitration of Uranyl Nitrate and Hydrogen Reduction

Some of the most important methods of preparation of UO_2 will now be reviewed.

By far the largest quantities of UO_2 have been prepared by denitration of uranyl nitrate followed by hydrogen reduction, and this may well be considered as the historical or classical method of preparation. Although most of this oxide has been converted to tetrafluoride and then to either metal or hexafluoride, sizable quantities have been used directly in fuel-element work. Such oxide may be used directly as obtained from the reduction furnaces or subsequent to certain aftertreatments to be discussed later in this paper.

Denitration may be carried out in batch kettles or continuously. Most production work has been done in gas-heated stirred stainless-steel pots differing from one plant to another chiefly in size. The smallest size in use has a capacity of 45 to 50 U. S. gal, whereas the largest sizes are about 250 U. S. gal. This is mentioned because the resulting products appear to differ in reactivity. The denitration cycle is longer, and hence the denitration slower, in the larger pots. The product from the smaller pots has a larger proportion of the Type III UO_3 . Such differences in type of trioxide and in reactivity affect the reduction to dioxide and the final properties of the dioxide powder. The exact relation between these effects and the quality of the dioxide for ceramic purposes is not yet fully understood but is recognized to be an important factor worthy of continued investigation.

The continuous methods for the denitration of UNH generally depend upon the addition of concentrated uranyl nitrate solutions to a hot layer of UO_3 powder, either in a horizontal stirred bed or in a fluidized bed. The UO_3 is drawn off at a point as remote from the addition of the uranyl nitrate solution as practicable. To date such continuous methods of UO_3 production have not been important in preparing the forerunner for UO_2 for use as such but may well become important as they tend to give a rather different particle shape from that obtained by batch methods.

The reduction of the trioxide to dioxide at high temperature by hydrogen or by cracked ammonia (75 per cent H_2 , 25 per cent N_2) may also be carried out continuously or in batches. Historically this was originally done by loading trioxide powder in stainless-steel trays about $1\frac{1}{2}$ in. deep and placing these trays in a stainless-steel box in an electric oven at $800^\circ C$. Hydrogen gas was passed through the boxes for 6 hr to effect the reduction, and the product was cooled in hydrogen to nearly room temperature to prevent reoxidation upon exposure to air. However, continuous methods have almost completely replaced the batch methods for this step. The UO_3 , produced by the thermal denitration of uranyl nitrate as described above, is fed into one end of a horizontal cylindrical tube 22 ft long and 16 in. in diameter. This tube rests in an electric furnace and has an agitator that slowly moves the UO_3 toward the discharge end. Cracked ammonia gas is passed through the reactor countercurrent to the powder. About one and one-half times the theoretical amount is required, and the excess is burned at the gas discharge end. Dust carried through is collected in a bag type collector from the cooled combustion gases. The quality of the product may be controlled somewhat by the temperature in the furnace which is normally from 650 to $800^\circ C$. The material made at the lower temperature is very reactive and partially reoxidizes on exposure to air even when thoroughly cooled. However, this may not be important since, when ceramic elements of dioxide are fired in a reducing atmosphere, reconversion to UO_2 will occur. Nevertheless, material reduced at 750 to $800^\circ C$ has most generally been used for ceramic work since it is more stable and its properties are better understood.

Figure 1 shows the two most common denitration kettles in use. It will be seen that they are the same in principle and differ only in size.

Figure 2 shows the general construction of the continuous reduction reactor.

Fig. 1—Denitration pots.

PREPARATION AND PROPERTIES OF URANIUM DIOXIDE POWDER

Fig. 2—Continuous reduction reactor.

Fig. 3—ADU flow sheet.

3.2 Ammonium Diuranate Precipitation and Hydrogen Reduction

Most power reactors are designed for a fuel enriched in U^{235} content. Therefore, any fuel-element material for such reactors must be made from a UF_6 starting material. The production of a brown oxide from the hexafluoride is carried out through an ammonium diuranate intermediate, and, when made from this intermediate, it is frequently referred to as ADU type brown oxide. The use of this ADU intermediate has proved convenient for the hydrolysis of the hexafluoride and also has led to a UO_2 of especially good ceramic properties.

At a plant near St. Louis,¹¹ ADU type brown oxide is manufactured commercially in either of two enrichment ranges. With material containing up to 3 per cent U^{235} , protection against criticality accidents is obtained by simply limiting the quantity of material in any one batch. In the enrichment range of 20 per cent and up, all equipment is designed to provide always-safe geometry. The shape of all containers is such that under no conditions can a critical situation be obtained irrespective of the enrichment or concentration of the material being worked. Cylindrical vessels for liquors are limited to 5 in. in diameter, and trays of powders are restricted to a maximum of $1\frac{1}{4}$ in. thick.

Although the scale of equipment is quite different depending on whether one is processing high- or low-enrichment material, the basic flow sheet employed for the production of ADU type UO_2 is identical. This flow sheet is shown in Fig. 3 together with the reactions involved. Basically the process consists in the hydrolysis of the UF_6 , supplied by the United States Atomic Energy Commission, with a dilute ammonia solution to give a precipitate of ammonium diuranate. This ADU is filtered, washed, and dried. The dried powder is pyrohydrolyzed with steam at 800 to 850°C, and at the same time the ammonium diuranate is converted to black oxide. This U_3O_8 is finally reduced to brown oxide with hydrogen or cracked ammonia at 800°C. Incidentally, this U_3O_8 intermediate provides a convenient means of preparing various other compounds of enriched uranium of interest in the power reactor field. If the oxide is to be compressed into solid UO_2 fuel elements, the reduced product is simply ground and packaged. On the other hand, if the end use is as a component in a matrix type fuel element, the ground product is fired at temperatures up to 1700°C, cooled, ground, and screened before packaging.

Figure 4 is a picture of the equipment used in the hydrolysis step. The UF_6 is vaporized in its cylinder by heating and is passed into a stream of recycling ammonia solution. Aqueous ammonia is continuously fed to the hydrolysis reactor at about the same rate as the hexafluoride. These feed rates are controlled such that the aqueous slurry always contains an excess of ammonia, and at the end of the precipitation this excess is increased somewhat. A heat exchanger in the recirculation line removes the heat of reaction, maintaining a temperature of 30 to 40°C. The equipment used for the high-enrichment batches is identical in principle with that shown except for scale; for example, the vessels are limited to 5 in. in diameter.

Filtration of low-enrichment batches of ADU is done on a rubber-lined filter press, and filtration of high-enrichment batches is done on stainless-steel Buchner type funnels. The ease of filtration, as well as the bulk density and ultimate particle size of the final product, is very sensitive to the manner in which this precipitation and the washing of the cake are carried out. By careful control of these factors the bulk densities of the product ceramic UO_2 can be controlled over the range 1.5 to 5.0 g/cm³.

The washed ADU is placed in an electric circulating-air oven in stainless-steel trays at 175°C. This oven is fitted with a liner that prevents stacking of trays, as shown in Fig. 5.

The dried ADU is crushed in a cone type mill and loaded into Inconel or Hastelloy-C trays. These trays are introduced into a box of the same material which fits into an electric muffle furnace as shown in Fig. 6. Air is swept from the box with a nitrogen stream, and a mixture of steam and ammonia is introduced. The temperature is increased to 800°C, and the ammonia flow is continued at this temperature until reduction is complete. The box is withdrawn from the furnace, cooled to essentially room temperature with a water spray, and the product removed. This step involving simultaneous pyrohydrolysis and reduction is used only for the larger scale low-enrichment batches. High-enrichment batches are pyrohydrolyzed and reduced in separate operations. The steam cycle is stopped before the ammonia is introduced, and the ammonia is cracked before introduction into the box, in the case of high-enrichment batches.

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Fig. 4—Hydrolysis equipment.

Fig. 5—Drying ovens.

Fig. 6—Muffle furnace.

Fig. 7—View of high-enrichment area.

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The UO_2 is removed from the trays and milled again in a cone mill. If the brown oxide is to be fabricated into ceramic fuel elements, it is ready for shipment at this point. For some purposes, such as inclusion in a stainless-steel matrix fuel element, a high-fired product is desired. For this purpose, after crushing the reduced product, it is introduced into molybdenum trays and fired for 4 hr at 1700°C in a molybdenum wound resistance furnace. After milling the product is screened, and the minus 200 mesh plus 325 mesh fraction is used for fuel-element production. The oversize from this screening operation is recycled to the mill, and the fines are returned to the high-firing operation.

Table 3 shows an analysis of the type of product from this process. It is possible that, if sufficient demand existed, the amount of some of these impurities could be considerably decreased. Note that the tap density of the ceramic type product may be controlled at will over the range 1.5 to 5.0 g/cm^3 for any special application. The particle size of the product may also be controlled.

Table 3—COMPOSITION OF ADU TYPE UO_2

Composition	$\text{UO}_{2.096}-\text{UO}_{2.016}$
Ni	70 ppm
F	100 to 300
Fe	60
Cr	30
B	0.2
Cu	10
Si	50
Ag	0.1
Sn	1
Pb	2
Tap density	1.5 to 5.0 g/cm^3
Mean particle size	0.5 to 2μ

Because of the great value of highly enriched uranium, it is necessary to avoid all losses. All work with high enrichments is carried out in dryboxes that permit recovery of all dust. A panoramic view of the area in which high-enrichment material is processed is shown in Fig. 7. Here the drybox type operation, the wide separation of the units, and the standards of cleanliness required for this type of operation can be seen.

3.3 Steam Oxidation of Metal

The reaction between uranium metal and water has been studied extensively from the standpoint of corrosion. Several variations in the conditions of this reaction have been utilized as a means of producing UO_2 . As ordinarily carried out, the reaction is between low-pressure steam and metal held at 150 to 225°C . This has been done both with metal chips and with the metal powder obtained by thermal decomposition of UH_3 .

Recent work¹² indicates that, although the above methods produce an oxygen-excess oxide, the use of high-pressure steam (2200 psig, 343°C , 24 hr) produces a slightly oxygen-deficient oxide. All of these oxides, except in the case of the hydride intermediate, have low surface areas and show only moderately good sinterability. None of these methods appears to give sufficient advantage over other methods to offset the cost burden of going through the metal step.

3.4 Aftertreatments

Grinding UO_2 improves its sinterability quite markedly. This is presumably due primarily to an increase in surface area and a reduction of the number of closed pores, allowing the material to be more easily compacted into a continuous mass. The most effective means of such grinding are ball milling and Micronizing.

Ball milling¹³ is usually carried out as a dry operation, although wet milling has been studied to some extent. Dry milling has been accomplished by operating a 10-in. rubber-lined mill one-third full of 1¼-in.-uranium balls (or short rods) for 48 hr. A 14-lb batch of UO₂ was handled under these conditions. This treatment increased the sinterability at 1600°C in 10 hr from 82 to 91 per cent in a typical experiment. At 1400°C for 2 hr in steam, the difference was smaller, i.e., 77.6 per cent unmilled and 78.5 per cent milled.

Micronizing is essentially a self-attrition process carried out by means of turbulent high-velocity air streams. ("Micronizer" is the trade name of an instrument sold in the United States.) In experiments¹⁴ with an 8-in. Micronizer the air supply was 120 cu ft/min, the air pressure 100 psig, and the UO₂ feed rate 28 lb/hr. The sinterability at 1400°C for 2 hr in steam was increased from 77.6 to 83.8 per cent. In other experiments where the UO₂ was extruded and fired in H₂ at 1700°C, the densities obtained were as high as 96 to 97 per cent of theoretical with Micronized UO₂.

Grinding methods always contaminate the product to some degree, although this is minimal in the case of Micronizing. To study the effect of contamination independently, deliberate additions of various other oxides have been made.¹⁵ The effects are negligible in some cases, e.g., NiO, ZrO₂, and MoO₃; moderate in others such as Al₂O₃, CaO, and V₂O₅; and striking in the case of TiO₂. In the latter case, at 1800°C, small percentages such as 0.25 to 0.5 per cent are more effective than 1 to 3 per cent. This is because of the tendency for too rapid sintering of the outer portion of the samples to trap gases internally, causing bloating during firing. Also TiO₂ additions are less effective at high temperatures than at lower (1400°C) temperatures, with the more reactive oxides such as ammonia precipitated material. From these results, it would appear that trace contamination introduced by grinding is not an important factor in the effect of grinding on sinterability.

3.5 Flame Chemistry Methods

A method of producing UO₂ by direct reduction in a high-temperature flame has recently been developed at the AEC plants in St. Louis. There are many ways in which this new technique can be applied. The general objective is to obtain UO₂ of extremely high density, often approaching the theoretical x-ray density of 10.97 within the limit of measurement. Although this method may eventually be used for the production of solid fuel elements directly, it is mentioned here as a method of production of UO₂ since this can be a direct step from UO₃ or even uranyl nitrate with the dioxide in powder form never appearing as an intermediate.

Figure 8 shows the general arrangement of the apparatus. A very high-temperature flame is maintained by burning hydrogen or methane. The feed material (UO₃ powder, uranyl nitrate solution, or even UO₂ powder where only further densification is wanted) is fed through a tube directly onto the top of some already fused UO₂ which is maintained in the hottest part of the flame by the drive mechanism which continuously lowers the rod, or boule, of fused UO₂ as it forms. The solidified rod which is obtained by this method is polycrystalline, but the individual crystals are fairly large in size (1 to 5 mm). It is believed that if such material were used in a fuel element it would have a decided advantage in heat transfer over compacted and sintered powders which have very small crystallite sizes. It is also possible to grind the fused material to give a coarse powder of very high density for use in cermet type fuel elements.

In various experimental runs UO₂ closely approaching UO_{2.00} has been made starting from the trioxide, the nitrate, and from the powdered dioxide. The mechanical control necessary for the growth of large single crystals has not yet been perfected, but it is believed that this will be an interesting outcome of this technique.

At the flame temperature the dioxide is the stable form, and a chemical reducing agent is not really needed in this technique, although the hydrogen or methane feeding the flame may well serve in this capacity.

The atomic hydrogen flame, or arc, has also been used successfully. The same apparatus is used, except the electrodes for the dissociation are located at the point where the hydrogen enters just above the fused pool of dioxide. Evaluation of the advantages of the atomic hydrogen arc over the chemical flame is not yet sufficiently advanced for a comparison to be made.

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Fig. 8—Flame reactor.

Fig. 9—Standard oxide from nitrate. (Magnification 10,000×.)

Fig. 10—Vacuum denitrated oxide. (Magnification 10,000×.)

Fig. 11 — ADU oxide. (Magnification 10,000×.)

Fig. 12 — Micronized oxide. (Magnification 10,000×.)

4 SUMMARY

Table 4 tabulates some of the effects of methods of preparation and particle size on the density of the fired ceramic body. These data have been assembled from various experiments done in our laboratories and do not represent a controlled set of conditions; thus the data may not be quantitatively reproducible. However, the qualitative differences shown are real, and they show the importance of the physical state of the particles.

Table 4—PROPERTIES OF UO_2 POWDERS

Preparation	O/U ratio	Tapped bulk density, g/cm ³	Average particle size, μ	Density of fired pellets, % of theory
Pyrohydrolysis and denitration of UNH to UO_3 , followed by high-temperature reduction to UO_2 with hydrogen	2.01 to 2.03	4.95	4.05	88.7
Dry milling of above in rubber-lined mill with uranium rods	2.10			90.2
Wet milling of UO_3 in rubber-lined mill with uranium rods before reduction to UO_2	2.01 to 2.04		1.48	93.2
Micronized UO_2 prepared as in first entry above	2.01 to 2.05	2.74	0.48	92.8
Hydrolysis and precipitation of ADU, followed by high-temperature reduction to UO_2 with hydrogen	2.02 to 2.10	2.18	3.00	89.9

Figures 9 to 12 show the particle size and shape of oxide made from nitrate by the standard process, from nitrate by vacuum denitration, from fluoride solution by the ADU process, and the effect of Micronizing.

It appears to be evident that UO_2 powder suitable for the fabrication of fuel elements can be made by several different processes. The important considerations are not the particular chemical steps preceding the reduction to dioxide but rather the physical conditions which control the ultimate crystallite size, and the aftertreatments which affect the agglomerate size and roughness factor. The effect of additives is also important in the fractional percentage range.

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Production of Uranium Dioxide for Ceramic Fuels*

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ABSTRACT

Uranium dioxide powder suitable for forming and sintering into high-density ceramic fuel may be prepared by hydrogen reduction of ammonium diuranate. Some of the variables in the preparation of ammonium diuranate and in its subsequent reduction to uranium dioxide have been investigated. The aim was to define the conditions for making a readily sinterable uranium dioxide powder of consistent properties.

Ammonium diuranate was prepared by both batch and continuous precipitation. The effect of varying the precipitation conditions was shown by determining the sintered density of the uranium dioxide pellet prepared from the ammonium diuranate under standard conditions. The effect of varying the reduction conditions was demonstrated.

The results show that the sintering properties of the uranium dioxide are insensitive to reduction conditions but are affected grossly by variations in the ammonium diuranate preparation.

Methods of preparing uranium dioxide that will sinter to a density consistently greater than 10.0 g/cm^3 are given for both batch and continuous precipitation.

Two relatively simple measurements, air permeability and tap density, were made routinely on both ammonium diuranate and uranium dioxide powders. These measurements can be used to segregate powders of poor sintering characteristics but are not useful in predicting minor differences in sinterability.

1 INTRODUCTION

The use of ceramic fuels in nuclear power reactors could result in safe, reliable operation because of certain characteristics inherent in such fuels. Uranium dioxide (UO_2), in particular, has two major attributes that make its use attractive. Experience to date has shown it to be dimensionally stable to both thermal and irradiation effects, and it is resistant to corrosion by hot water. This latter property is a desirable one in fuel for use in pressurized water power reactors, since, in the event of sheath defect or failure, the reactor may be taken off load sufficiently slowly to prevent undue thermal shock or stress to the reactor components without incurring severe contamination of the coolant. Other factors that favor UO_2 are that satisfactory uranium density can be achieved in the fuel and no elements of significant parasitic cross sections are introduced with it. These last two factors are important considerations in the Canadian power reactor program, which is based on the use of natural uranium fuel.

* This paper may also be identified as Report CRL-45.

The cost of fueling a power reactor is a significant fraction of the total cost of power produced. It is necessary, therefore, that any processes used in the manufacture of UO_2 fuels be as cheap as possible, commensurate with reliability in operation. The steps involved in the manufacture of a UO_2 fuel element generally include the following operations:

1. Preparing a sinterable UO_2 powder
2. Forming the powder into pellets
3. Firing the pellets at high temperature to achieve satisfactory densification
4. Grinding the pellets to required dimensions and tolerances
5. Loading and sealing of the pellets into a suitable sheath
6. Inspecting the finished fuel element

These steps are related in several ways, but preparation of sinterable oxide with consistent properties is essential to economic production of fuel by this method.

The initial Canadian work on the production of ceramic-grade UO_2 powder was done at the Department of Mines and Technical Surveys, where Bright, Gow, and Prince¹ defined, in the laboratory, techniques for preparation of ammonium diuranate (ADU), reduction of ADU to UO_2 , pellet forming, and sintering to high density.

Commercial production was attempted by the Carbonyl Division of Canadian General Electric Co., Ltd., using, as starting material, ADU prepared by Eldorado Mining and Refining, Ltd. Production of pellets of consistent density and size was found to be very difficult for reasons subsequently determined to be associated with variation in the properties of the ADU.

Since methods of preparation of ADU and of reduction of ADU to UO_2 had not been thoroughly investigated, the Chemical Engineering Branch of Atomic Energy of Canada, Ltd., carried out a short empirical study of the variables in these two steps and their effect on the production of sintered UO_2 pellets in order to advise on the design of a commercial process.^{2-4*} The rather broad specifications for product and processing were defined as follows:

1. The sintered density of the UO_2 pellets should be consistent and greater than 10.0 g/cm^3 .
2. The methods of preparation of both ADU and UO_2 should give consistent materials and should be capable of being carried out in commercial equipment.
3. The process should be economically attractive. In particular, pressures in the cold-forming step and temperatures in the sintering step should be as low as possible. Suggested values were 20 Tsi and 1600°C , respectively.
4. Shrinkage on firing should be small and reproducible to a few thousandths of an inch in order to minimize scrap and grinding.
5. Methods of assessing the probable characteristics and behavior of the powders should be developed.

The work summarized in this report was devoted primarily to a study of some of the variables in the precipitation of ADU and in the reduction of ADU to UO_2 . Some data typical of those obtained by two methods of powder assessment are included.

2 PROCEDURES USED AND VARIABLES STUDIED

2.1 Assessment of Powders

The specifications listed above, if met, automatically require that the sintered density be controlled within $\pm 0.1 \text{ g/cm}^3$. Therefore any method that is useful in assessing the sintering properties of UO_2 should be capable of detecting differences which result in changes of sintered density of this magnitude.

Bright, Gow, and Prince¹ used several methods in attempting to determine the sintering potential of UO_2 powders. These methods included differential thermal analysis, surface area determined by nitrogen absorption (the Brunauer-Emmet-Teller method), surface area esti-

* This report summarizes work that is described considerably more in detail in a following report that will be issued in the near future.

mated from an air permeability measurement, oxygen-uranium ratio after reduction, density of unfired (green) pellets, and sintered density achieved in a standard firing cycle. An examination of their data showed that, although any of the above measurements could be used to demonstrate differences between UO_2 powders capable of sintering to grossly differing densities, none could predict the density to within $\pm 0.5 \text{ g/cm}^3$. It was obvious that only measurement of the sintered density could differentiate between effects of variables which yielded density differences of this magnitude. However, in order to determine over-all trends resulting from variation in conditions, measurements of tap density, air permeability (Blaine method), green density, linear shrinkage on firing, and sintered density were done routinely on all samples. The methods used in making the air permeability and tap-density determinations are described in Appendix A.

2.2 Preparation of ADU

(a) *Batch Precipitation.* ADU was precipitated from uranium nitrate solution on the scale of 1 to 16 liters/batch. All experimental data reported here were obtained by precipitating ADU by addition of NH_4OH or NH_3 to the uranium nitrate solution. Variables studied were uranium concentration, NH_4OH concentration, solution temperature, effect of excess NH_4OH , and rate of precipitation.

(b) *Continuous Precipitation.* ADU was precipitated by pumping NH_4OH and uranium nitrate solution simultaneously and continuously into a small well-agitated precipitation vessel. The resulting ADU slurry overflowed into a second tank in which it could be treated with additional NH_4OH or from which it could be drained to a filter. The pH of the liquid in the precipitation vessel was measured continuously and was maintained at any desired value by adjusting the flow of NH_4OH from the metering pump. Uranium nitrate concentration in the feed solution was kept constant at 100 g uranium/liter. The pH of precipitation was varied, and the effect of conditioning with additional NH_4OH was determined.

No continuous precipitations were done using NH_3 gas.

2.3 Filtration of ADU

All samples of ADU were filtered through Whatman No. 5 filter paper on a Büchner filter.

2.4 Drying of ADU

The standard drying procedure was to transfer the ADU cake from the filter paper to a tray in which the ADU was dried in a natural convection oven operated at either 60 or 200°C. The effect of variation in drying temperature was investigated as well.

2.5 Reduction of ADU to UO_2

All samples of ADU made during the investigation of precipitation conditions were reduced batchwise in an atmosphere of flowing hydrogen according to the following cycle. The ADU was inserted into the furnace, and air was displaced by argon. The temperature was raised to approximately 200°C, and the gas flow was changed from argon to hydrogen. The temperature was raised to 900°C over a period of 3 to 4 hr and was held at 900°C for 1 hr. The UO_2 was then cooled to room temperature in a hydrogen atmosphere. The hydrogen was then displaced with argon, and the samples were removed from the furnace. Since some samples tended to be pyrophoric after this treatment, all were stored for about 1 hr under an atmosphere of CO_2 obtained by evaporation of solid CO_2 . After this treatment the samples could be handled in the air with no difficulty.

The variables in reducing ADU to UO_2 were studied on ADU of three types using an appropriate variation of the technique described above. The maximum temperature of reduction was varied between 750 and 1000°C, and the length of time this temperature was maintained was varied from 1 to 6 hr. Depth of the ADU bed was varied from 1 to 5 in. The effect of including a thermal decomposition step prior to reduction was investigated. Rate of

heating during reduction was varied from 100 to 200°C/hr. Several different atmospheres were used during cooling of the UO_2 after reduction. The effect of comminution of the ADU before reduction was examined.

2.6 Cold Pressing

The technique for forming pellets was not varied. The UO_2 powder was brushed through a 170-mesh stainless-steel screen, the larger aggregates being ground in a mortar and pestle as necessary. Each sample was mixed with 2 wt. % paraffin wax added as a solution in CCl_4 . The CCl_4 was removed by vacuum desiccation or by drying overnight in air.

The waxed powder was pressed from one end in a 0.773-in.-diameter die at a pressure of 40,000 psi for 10 sec. The thickness of the green pellet was about 0.25 in., depending on the weight of UO_2 used and on its characteristics.

At least two pellets were pressed from each sample of UO_2 . The dimensions were determined with a micrometer, and these, along with the weight of the pellet and that of the wax added, were used to calculate the green density of the pellets.

2.7 Sintering

All pellets were sintered in hydrogen. The wax was removed by heating slowly to 300°C and holding at that temperature for up to 18 hr. The temperature was then increased to 1600°C at either 100 or 400°C/hr, depending on the type of UO_2 . The temperature was held at or above 1600°C for 1 hr. Cooling was controlled at a rate no greater than the heating rate down to 1200°C, after which the sintering furnace was allowed to cool at its natural rate, 100 to 200°C/hr.

2.8 Pellet Assessment

The pellets were examined visually for flaws, cracks, bulges, and other obvious defects. The diameter and height of each pellet were measured to ± 0.0005 in., and the weight was determined to ± 0.5 mg. These measurements were used to calculate the sintered density of the pellets.

The densities of portions of a few pellets that broke or bulged during firing were determined by an immersion technique.

3 RESULTS AND DISCUSSION

3.1 Assessment of Powders

The relation of the Blaine Nos., as determined by air permeability measurements on both ADU and UO_2 powders, to the sintered density of the UO_2 pellets made from them is given in Fig. 1. Although there is considerable scatter in the data, there is a clear trend toward higher sintered density as the Blaine No. increases. Since the Blaine No. is a measure of the surface area of the powder, it is apparent that, for the methods of pressing and sintering used in these experiments, high surface area is one of the prerequisites to high sintered density. The actual surface area of these samples has not been measured.

The data plotted in Fig. 2 relate the sintered density of the UO_2 pellets to the tap densities of the ADU and UO_2 from which they were made. The scatter in the data is again considerable, but it is obvious that powders of low tap density must be used to obtain pellets of high sintered densities.

Neither of the powder assessment methods used is capable of indicating the density to which a given powder will sinter within the desired limits (± 0.1 g/cm³). It is possible, however, to pick limits that will ensure that practically all accepted powders will achieve sintered densities greater than 10.0. These limits may be selected as ADU (tap density, <1.0; Blaine No., >9000) and UO_2 (tap density, <2.2; Blaine No., >5000). Unless other more precise assessment techniques are developed, controlled processing must be relied upon to produce ADU or UO_2 powders that will sinter to sufficiently consistent dimensions and density to minimize or avoid grinding the pellets to final size.

Fig. 1—Correlation of UO₂ sintered densities and Blaine numbers of ADU and UO₂.

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Fig. 2— UO_2 sintered density related to tap densities of ADU and UO_2 .

3.2 Precipitation of ADU

(a) *Batch Precipitation.* The results of varying certain of the conditions during batch precipitation of ADU are presented in Figs. 3 to 7. In each experiment conditions other than the one being studied were kept constant, and the ADU was filtered, washed, dried, reduced, pressed, and sintered in the standard manner described previously. The sintered density of the UO_2 pellet is related to the variables being studied in each case. There are several anomalous results, but, in general, the trends are clear.

The data in Fig. 3 show that, when either 2.6N NH_4OH or NH_3 is used as precipitant, it is advantageous to precipitate the ADU from a dilute solution of uranium nitrate.

The sintered density of the UO_2 probably increases with increasing NH_4OH concentrations as shown by the data plotted in Fig. 4.

The effect of solution temperature during precipitation is shown in Fig. 5. If NH_4OH is the precipitant, higher temperatures tend to result in higher sintered densities, but with NH_3 as precipitant the sintered density is independent of precipitation temperature. Two samples of ADU precipitated with each reagent were aged in the mother liquor at the precipitation temperature for 2 hr without affecting the sintered density. It was concluded that no lowering of density would occur as a result of aging during a reasonable time required for filtration.

Rapid precipitation generally results in fine precipitates and that this is advantageous is shown in Fig. 6. The effect is one again more pronounced for ADU precipitated with NH_4OH than for that precipitated with NH_3 .

Precipitation of ADU is complete before the pH of the liquor is 7. The effect of adding additional precipitant is shown in Fig. 7. When NH_4OH is used to precipitate ADU at room temperature, the sintered density is increased when the pH of the liquor is increased to 9 to 10. This requires up to a fivefold excess of precipitant. The increase in sintered density is not obtained when excess NH_4OH is added at 60°C , since increasing the temperature has in itself increased the sintered density.

On the basis of the data presented, it is concluded that when NH_4OH is used for batch precipitation of ADU, factors that contribute to high sintered density are uranium concentration below 300 g/liter, high NH_4OH concentration, increased temperature, rapid precipitation, and use of an excess of NH_4OH . The flow sheet devised to meet these conditions and adapted to certain process conditions in the manufacturer's plant (Eldorado Mining and Refining, Ltd.) specifies the following:

Uranium nitrate solution	100 to 150 g uranium/liter
Ammonium hydroxide	13N (28%)
Temperature	60°C
End pH	9

The uranium nitrate solution is agitated thoroughly in a tank, and the NH_4OH is added as rapidly as is convenient.

This flow sheet has been used many times in the laboratory to make kilogram quantities of ADU and three times by Eldorado Mining and Refining, Ltd., to produce 100-lb batches of ADU. The UO_2 produced from these ADU samples has been demonstrated to sinter in the laboratory to consistent density of 10.3 to 10.6 g/cm³. A thorough test in commercial reducing, pressing, and sintering equipment is in progress.

The precipitation of ADU with NH_3 is generally less sensitive to changes in process conditions since sintered densities above 10.0 g/cm³ were obtained on almost all samples. This is interpreted to mean that the particle size of ADU precipitated with NH_3 is invariably very small. In order to obtain good pellets from the UO_2 produced from this material, it was necessary to limit the heating rate during sintering to 100 rather than 400°C/hr which was satisfactory for the NH_4OH precipitated ADU. This feature was considered a disadvantage from the point of view of continuous commercial production. No additional work was done on NH_3 precipitated ADU, although it is quite probable that a completely satisfactory process could be developed by varying conditions in the precipitation or other processing operations.

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Fig. 3—Effect of uranium feed concentration on sintered density of UO_2 . Precipitation to pH 7 in approximately 1 hr.

Fig. 4—Effect of precipitant concentration on sintered density of UO_2 . Precipitation to pH 7 in approximately 1 hr at room temperature.

Fig. 5—Effect of precipitation temperature on sintered density of UO_2 . Precipitation to pH 7 in approximately 1 hr. ●, aqueous ammonia; ○, gaseous ammonia: $\text{U} = 300$ g/liter; $\text{NH}_4\text{OH} = 2.6\text{N}$.

Fig. 6—Effect of rate of precipitation on sintered density of UO_2 . Precipitation to pH 7 at room temperature. Aqueous ammonia (300 g U/liter): ●, 2.6N NH_4OH . ▲, 13N NH_4OH . Gaseous ammonia: ○, 100 g U/liter. △, 200 g U/liter.

Fig. 7—Effect of excess ammonium hydroxide on sintered density of UO_2 . $NH_4OH = 13N$.

(b) *Continuous Precipitation.* Precipitation pH has a major effect on the sintered density of UO_2 prepared from ADU prepared by continuous precipitation. However, the data plotted in Fig. 8 show that ADU precipitated at a pH controlled above 6.7 will yield highly sinterable UO_2 . The conditioning of the slurry with excess NH_4OH to increase the liquor pH to 9.0 has no effect comparable to that obtained with batch precipitated ADU.

Other variables that affected batch precipitated ADU were shown to have little or no effect on the ADU prepared by continuous precipitation. These included temperature and NH_4OH concentration.

The continuous precipitation technique is useful for preparation of enriched UO_2 for use in test fuel elements, since it can be made ever-safe in operation. The flow sheet is simple. The mixing of the reagent streams is accomplished in a small precipitation vessel. The pH of the slurry in the vessel is controlled at 7 to 8 by controlling one reagent stream while the other is held constant. The ADU slurry overflows from the precipitation vessel to a suitable filter.

3.3 Filtration of ADU

Since small ADU particle size apparently is essential if the resulting UO_2 is to sinter to high density under the pressing and firing conditions chosen, it is to be expected that the ADU will be difficult to filter. No actual filtration data were obtained. However, batch precipitated ADU was filtered satisfactorily on Büchner filters in the laboratory and on box filters on the larger scale. For continuously precipitated ADU, it was noted that, as the pH of precipitation was increased, the filtration rate decreased rapidly. It is advisable, therefore, to operate at a pH between 7 and 8 and preferably close to 7.

3.4 Drying of ADU

As judged by the sintered density achieved on the UO_2 prepared from it, ADU was unchanged in properties by drying at temperatures from 60 to 400°C. The physical properties such as tap density and Blaine No. were altered because of partial or total decomposition of the ADU to UO_3 or intermediate compounds.

The drying temperature recommended, 200°C, was chosen only on the basis of speed and convenience.

3.5 Reduction of ADU to UO_2

The three samples of ADU used to investigate the effect of varying conditions in the reduction process have been designated E-11, P-54, and P-55. E-11 and P-54 were made at Eldorado Mining and Refining, Ltd., and Chalk River, respectively, according to the recommended batch precipitation flow sheet, and P-55 was made at Chalk River by a variation of the flow sheet known to produce an ADU of somewhat inferior quality. The normal sintered densities achieved with UO_2 prepared from these samples by reduction by the standard technique were E-11, 10.63 g/cm³; P-54, 10.54 g/cm³; and P-55, 10.13 g/cm³.

The effect of varying the maximum temperature attained during reduction is shown in Fig. 9. ADU, which on normal reduction at 900°C yields highly sinterable UO_2 , is little affected by change in reduction temperature over the range 750 to 1000°C. An inferior ADU such as sample P-55 yields less sinterable UO_2 as the reduction temperature is increased.

UO_2 powders made by reduction of ADU at the lower temperatures tend to be pyrophoric. An ADU of type E-11 or P-54 may be reduced at a temperature as high as 1000°C to eliminate pyrophoricity without sacrificing sintered density, but treatment of the inferior ADU in the same manner results in a serious loss of density.

Varying the time at which the UO_2 was held at 900°C from $\frac{1}{2}$ to 6 hr had no effect on the sintered density achieved with any of the powders.

The depth of ADU in the containers used in the reduction operation is apparently a critical variable, although the reason for this has not been ascertained. It may be seen from Fig. 10 that the sintered density decreased rapidly as the depth of ADU powder was increased from

Fig. 8—Influence of ADU precipitation pH on UO_2 sintered density.

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Fig. 9—Effect of maximum temperature during reduction on sintered density.
 O, E-11. □, P-43. ×, P-55.

Fig. 10—Effect of depth of ADU bed on sintered density of UO_2 . Tests done on E-11 ADU. O, reduced in tray. ×, reduced in $5\frac{3}{4}$ -in. diameter pot. ⊗, reduced in $\frac{3}{4}$ -in. pipe.

1 to 4 in. To obtain UO_2 of maximum sinterability, it is necessary to restrict the depth of ADU charged in trays to the reduction furnaces to less than 2 in. Presumably this limitation could be avoided in a continuous reactor such as a fluidized bed. Continuous reduction was not studied.

The other variations of technique studied were decomposition in argon, carbon dioxide, and steam for various times at 600°C prior to reduction; cooling in hydrogen, argon, or carbon dioxide for 1 or 18 hr; comminution of the ADU to -50 mesh prior to reduction and rate of heating during reduction (100 to 200°C/hr). Generally, none of these techniques had significant effect on either of the good ADU samples (E-11 or P-54), but the poorer grade of ADU (P-55) gave scattered density values.

The results show conclusively that the properties of a UO_2 are determined primarily in the ADU precipitation. If a good ADU is made, the sintering qualities of the UO_2 reduced from it are little affected by relatively major changes in the reduction procedure. UO_2 prepared from an ADU of poorer quality may, however, give inconsistent sintered densities if the reduction conditions are not closely controlled.

For ADU prepared by the batch precipitation flow sheet, it is recommended that the reduction be done in hydrogen to a maximum temperature of 900 to 950°C and that the UO_2 be cooled in hydrogen. The maximum temperature may be as high as 1000°C to decrease the tendency for the UO_2 powder to be pyrophoric.

All samples of UO_2 prepared in the laboratory were transferred from the reduction furnace to a container with a CO_2 atmosphere supplied by evaporating carbon dioxide. After storage in this atmosphere for $\frac{1}{2}$ to 4 hr, they could be handled freely in air, although slow oxidation still occurred. A plot of oxidation as a function of time for a typical UO_2 powder prepared from ADU is given in Fig. 11. It is the very high initial rate of oxidation that can result in sufficient heat generation to burn the powder.

3.6 Cold Pressing

If the UO_2 is ground to pass a 150-mesh screen prior to waxing, the sintered pellets will have a better over-all appearance, although the density is unchanged.

The conditions used in cold pressing the UO_2 to form pellets were not varied. The density achieved in the pressed pellets depended, therefore, on the characteristics of the powder and generally was between 5.0 and 5.7 g/cm^3 . Highest sintered densities were usually obtained with pellets of cold-pressed density between 5.0 and 5.3 g/cm^3 , but there was no good correlation between cold-pressed density and sintered density.

3.7 Sintering

The work that has been described was undertaken with the major aim of determining methods of producing readily sinterable UO_2 powder, but a systematic study of the sintering of the pellets was not undertaken. The results of investigation of some of the variables in sintering UO_2 of this type will be available from the work of others.^{5,6}

It was possible to sinter UO_2 made from ADU precipitated batchwise with NH_4OH at a heating rate up to 400°C/hr , but that made by batch precipitation with ammonia gas or by continuous precipitation could not be sintered satisfactorily at a heating rate much greater than 100°C/hr without encountering pellet failure. Typical faults encountered with the latter materials were cracking, crazing, capping, and bulging when the more rapid heating rate was used, but these were essentially eliminated at the slower rate.

The maximum temperature during sintering varied from 1600 to 1700°C and was maintained for 1 hr. It was shown that this variation in temperature had essentially no effect on the sintered density of the pellet.

3.8 Pellet Assessment

The sintered pellets were measured for density and diametrical shrinkage. Pellets made from any one batch of material were very uniform in both density and diameter, but some

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Fig. 11—Spontaneous oxidation of UO_2 .

batch to batch variation was encountered. Pellets that sintered to high density ($>10.0 \text{ g/cm}^3$) shrank 19 to 22 per cent, based on the green diameter. It is anticipated that these variations will be reduced in commercial-scale operation. No problem is seen in the commercial sintering of pellets of the same approximate size, but, if the size is increased greatly, some difficulty may be encountered owing to the high shrinkage on firing.

4 CONCLUSIONS

Readily sinterable UO_2 powder can be made by hydrogen reduction of ADU.

The properties of the UO_2 are determined primarily by the properties of the ADU. Small particle size, as determined by the air permeability measurement, is necessary to the development of high sintered density.

In batch precipitation of ADU with NH_4OH , the conditions that contribute to development of small particle size are low uranium concentration, high NH_4OH concentration, increased temperature, use of excess NH_4OH , and rapid precipitation. When ammonia gas is used as the precipitant, the properties of the ADU powder are essentially independent of precipitation conditions. When ADU is precipitated continuously with NH_4OH only, control of pH at a value greater than 6.7 is necessary.

The use of temperatures up to 400°C in drying the ADU does not affect the sintered density of the UO_2 made from it.

The sintering properties of UO_2 prepared from ADU made by the recommended flow sheets are little affected by rather gross changes in reduction conditions.

UO_2 made from ADU precipitated batchwise with NH_4OH may be sintered using heating rates as high as 400°C/hr . UO_2 made from ADU precipitated continuously with NH_4OH or batchwise with ammonia gas must be sintered with greatly reduced heating rates, i.e., about 100°C/hr .

The sintering potential of an ADU or a UO_2 sample can be estimated roughly by measurement of either the tap density or the air permeability of the sample.

The recommended methods of preparation of UO_2 are the following three methods:

1. Batch Precipitation with NH_4OH : To a well-agitated solution of uranium nitrate (100 to 150 g uranium/liter) at 60°C , add 13N NH_4OH rapidly to an end pH of 9. Filter off the ADU precipitate and wash with water. Dry the ADU at 200°C , and load into trays to a maximum depth of 2 in. Reduce the ADU to UO_2 in a hydrogen atmosphere furnace, taking the UO_2 to a maximum temperature of 900 to 950°C and maintaining this temperature for 1 hr. Cool the UO_2 to room temperature under hydrogen before exposure to air.

2. Batch Precipitation with NH_3 : To a well-agitated solution of uranium nitrate (100 to 150 g uranium/liter) at 20 to 60°C , add NH_3 rapidly to an end pH of 7 or higher. Filter, wash, dry, and reduce as in 1.

3. Continuous Precipitation with NH_4OH : Into a small agitated vessel run simultaneously uranium nitrate solution (100 to 150 g uranium/liter) and NH_4OH (4N to 13N). Control the pH in the vessel at 7 to 8. The ADU slurry may overflow to a holding tank or direct to a filter. Filter, wash, dry, and reduce as in 1.

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Appendix A

A.1 AIR PERMEABILITY TEST

The method of assessing the powders was adapted from the procedure given in Am. Soc. Testing Materials, C204-255, 1955. The general formula used was

$$S = \frac{S_s \rho_s (1 - e)_s \sqrt{e^3} \sqrt{T}}{(1 - e) \sqrt{e_s^3} \sqrt{T_s}} \quad (1)$$

where S = specific surface in square centimeters per gram of the test sample

S_s = specific surface in square centimeters per gram of the standard sample used in calibration of the apparatus

T = time interval in seconds of manometer drop for the test sample

T_s = time interval in seconds of manometer drop for standard sample used in calibration of the apparatus

e = porosity of the prepared bed of the test sample

e_s = porosity of the prepared bed of the standard sample used in calibration of the apparatus

ρ = specific gravity of the test sample

ρ_s = specific gravity of standard sample used in calibration of apparatus

The apparatus used was a commercial Blaine Test Apparatus that was calibrated with National Bureau of Standards cement sample No. 114i. The densities accepted for UO_2 and ADU were 10.97 and 5.8 g/cm³, respectively.

On insertion of the data pertinent to the standard sample and the appropriate densities, Eq. 1 becomes

$$\text{UO}_2 \text{ Blaine No.} = 143 \frac{\sqrt{e^3} \sqrt{T}}{1 - e} \quad (2)$$

$$\text{ADU Blaine No.} = 271 \frac{\sqrt{e^3} \sqrt{T}}{1 - e} \quad (3)$$

The numbers obtained by substitution of the measured porosities and times in Eqs. 2 and 3 are used in the report as Blaine Nos. rather than surface areas because the apparatus was not calibrated with standard ADU or UO_2 samples.

Powder samples were prepared in a standard fashion by grinding in a mortar and pestle to pass a 165-mesh screen. This grinding served only to break agglomerates but was necessary to provide reproducible results.

A.2 TAP DENSITY

The powder samples were ground in a mortar and pestle to pass a 165-mesh screen. The tap density was calculated from the volume occupied by a known weight of powder in a 25-ml graduate after dropping 150 times onto a cork mat from a height of 2 in.

Sintering of Uranium Dioxide

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In Sweden the interest in UO_2 as a reactor fuel has become very great. The main reason is the fact that the two existing industrial reactor projects both are planned to use D_2O as coolant and moderator. The temperatures are so high that the danger of a fast reaction between D_2O and natural uranium metal is too great for permitting the use of the metal as a fuel.

The demand for sintered compacts of UO_2 for different kinds of experiments suddenly increased rapidly, and the department of materials testing and research of the Atomic Energy Company had to develop methods and facilities for this sintering. We were fortunate enough to find a partner in the powder-metallurgy industry, i.e., Kohlswa Jernverk, and it is the result of this joint effort which will be described.

It is important to point out that the results by no means give an extensive description of all the different methods of sintering or explain the mechanism. A special powder was used which was produced according to the regular production method, and from the beginning some special types of furnaces used in the production at Kohlswa Jernverk could be adapted for a convenient way of manufacture. Some of the general lines that have been learned may be of interest at this conference.

The sintered compacts of UO_2 are used as very simple fuel elements for subcritical assemblies. They had to have:

1. A high and uniform density; 95 per cent of the theoretical density for crystalline UO_2 was chosen as a convenient value (about 10.4).
2. A high chemical purity, giving a maximum of $\sim 1/2$ ppm boron equivalents of impurities.
3. A microporosity such that small and uniformly distributed pores were obtained and local big voids were avoided which could have a serious influence on the density distribution of UO_2 in the fuel elements.
4. Good macroproperties, e.g., be free from inner and outer cracks, have an outer shape with such tolerances that a grinding operation could be avoided, and have a strength such that they could be handled during the canning operation.
5. A good chemical resistance to the heavy water used as moderator in the experiments.

For the future development of fuel elements for power-producing reactors, more rigid demands are valid. The purpose of the present UO_2 program is to make possible the production of UO_2 fuel elements for the two Swedish power-reactor projects: the R3 reactor of the Atomic Energy Company and the "ADAM" reactor, a joint effort between the Atomic Energy Company, the big electric concern ASEA, and the Royal State Power Board. This means for the UO_2 program that additional problems have to be solved, and the present program includes especially the following additional steps:

6. Find the rules which govern the formation and distribution of pores in the sintered compacts and the relation between the porosity of the sintered compact and its fission-gas release.

SINTERING OF URANIUM DIOXIDE

7. Find the relation between heat conductivity and properties of the sintered compacts such as grain size, pore size, and pore distribution at different temperatures and neutron fluxes. These problems are touched upon by Mr. Flinta in his paper at this conference.

8. Find methods to produce sintered UO_2 with very close tolerances. The present method is to grind the ends and the cylindrical surface of sintered compacts according to mass-production technique, but a precision sintering might be possible in the future.

9. Study the compatibility of UO_2 with different canning materials (aluminum, Zircaloy, and stainless steel) and with high-temperature water and water vapor.

10. Find the rules which govern the cracking of sintered UO_2 under temperature gradient. The cracking of sintered UO_2 in the fuel elements of a power reactor seems to be unavoidable, and a great advantage should be obtained by a predetermined cracking pattern.

The properties of the UO_2 powder are of fundamental importance. The starting material for our UO_2 production has been an ammonium uranate precipitated by so-called homogeneous precipitation.¹ After precipitation, the uranate is heated in air to about 300°C, where some water and ammonia are given off and a trioxide, containing small amounts of water and ammonia, is obtained (formula about $\text{UO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} \cdot \frac{1}{2}\text{NH}_3$). This oxide is reduced by hydrogen at about 800°C, giving a dioxide, the composition of which can be varied between $\text{UO}_{2.05}$ and $\text{UO}_{2.20}$.

The powder consists of spherical agglomerates with an average diameter of 40 to 50 μ , composed of small crystallites with a size in the range of 0.1 to 1 μ . Typical photographs of this powder are shown in Figs. 1a and b. In Fig. 1a, the powder is shown in low magnification as obtained after reduction, and the spherical agglomerates with their uniform size are shown. Figure 1b is a fraction of a crushed agglomerate in very high magnification (electron microscopy), showing the crystallites of UO_2 out of which the spherical agglomerates are composed.

Additional information about this type of powder has already been given in a paper by one of the authors.²

Some general conclusions for the sintering of UO_2 may be drawn from our work with this powder:

1. The shape and size of the powder agglomerates are mainly determined by the step of chemical precipitation. Different variables during the heating of the uranate and the reduction of UO_3 , such as temperature and time, have only a minor influence. This is illustrated by Figs. 2a to c and 3a to d, where agglomerates of two different kinds have passed the whole chain $\text{UO}_3\text{-U}_3\text{O}_8\text{-UO}_2\text{-UF}_4$ (fluorination through gaseous HF). Although several chemical reactions are involved in these steps, the general shape and size of the agglomerates are preserved. The "inheritance" of the grain properties, which has been observed, for example, in the hard-metal industry for the steps $\text{WO}_3\text{-WO}_2\text{-W-WC}$, is thus also valid here. The reduction temperature does not play the same role.

2. Also, the shape and size of the crystalline particles, which together form the agglomerates, are mainly determined by the chemical precipitation. The reduction temperature of UO_3 has, however, an influence, but has to be changed considerably. It thus seems that a rapid increase in crystalline particle size is noted, beginning at a reduction temperature of about 1100°C, but this temperature also seems to depend on the type of powder used.

3. Although the crystallites in a spherical agglomerate are only mechanically bound together, the bridge formation between the crystallites is important. The crystallites within an agglomerate grow together, forming one or a few single crystals much more easily than crystallites in adjoining aggregates. This is shown in Figs. 4a and b, where the structure of the sintered compact consists of clusters of rather big crystals. Each cluster is formed from the original agglomerates of UO_2 .

Another example of the influence of shape and size of the agglomerates on the properties of the sintered product is shown in Figs. 5a and b. Three samples from the same powder have been treated under exactly the same conditions except for the pressure applied during the cold pressing of the powder before sintering. There is a marked difference in grain size of the sintered pellets, with a maximum for a medium pressure. Also, the densities vary in the same way, with a maximum for a medium pressure. According to our opinion this phenomenon is explained in the following way:

(Text continues on page 411.)

Fig. 1a— UO_2 -powder agglomerates as reduced. (Magnification 100 X.)

Fig. 1b— UO_2 -powder crystallites as reduced. (Magnification 30,000 X.)

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Fig. 2—Uranate (a), UO_3 (b), and UO_2 (c) from the same powder. The agglomerates are preserved through the different reactions involved. (Magnification 100 X.)

Fig. 3—Uranate (a), U_3O_8 (b), UO_2 (c), and UF_4 (d) from the same powder. The agglomerates are preserved through the different reactions involved. (Magnification 100 $\times$.)

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(a)

(b)

Fig. 4—Part of a badly sintered compact, showing how the crystallites within the former agglomerates have grown together. (a) Unpolarized light. (b) Polarized light. (Magnification 500 x.)

(a)

(b)

(c)

Fig. 5—Grain size of sintered UO_2 that has been cold-pressed before sintering to (a) 2 tons/cm², (b) 4 tons/cm², and (c) 5 tons/cm². (Magnification 1000 x.)

SINTERING OF URANIUM DIOXIDE

(a)

(b)

Fig. 6—Different pore types in sintered UO_2 . (Magnification 500 $\times$.)

(a)

(b)

Fig. 7—Uranium carbides in sintered UO_2 , formed through the influence of hydrocarbons (a) in the sintering atmosphere and (b) from the lubricant. (a) Magnification 250 $\times$. (b) Magnification 100 $\times$.

SINTERING OF URANIUM DIOXIDE

The effect of an increased pressure is, in the beginning, to increase the bridge formation within the agglomerates still more, as well as the bridges between different particles. Therefore a rapid formation of single crystals, consisting of all those crystallites which form an agglomerate, is obtained at the sintering temperature. They grow faster the higher the compacting pressure has been. If the pressure of the cold compact has exceeded a certain value, however, the agglomerates have been crushed to smaller fractions at the cold-pressing operation, rendering a formation of single crystals from the small crystallites more difficult.

4. Also, the formation and type of pores are dependent on the agglomerates. Two kinds of pores seem to exist, those within the former agglomerates and those between the former agglomerates (Figs. 6a and b). The first type consists of small, round pores with diameters of about 1 to 5 μ . It seems to be possible to control these pores by a convenient time-temperature sintering. The second type consists of pores that are bigger (5 to 20 μ) and irregular in shape. These pores remain even after prolonged heating as high as 2000°C. The method of controlling these pores seems to be that of mixing the original agglomerates with a fraction of small crystallites.

5. The atmosphere during sintering is of fundamental importance. Different methods have been used, e.g., hydrogen in carbon furnaces, hydrogen in molybdenum furnaces, hydrogen and water vapor in molybdenum furnaces, and vacuum sintering. Some 1000 kg of UO_2 has been sintered in hydrogen in carbon-tube furnaces. Although this sintering makes use of a cheap type of furnace existing in several powder-metallurgical factories and although the product obtained has had a density and purity well fulfilling the requirements for subcritical assemblies, this method of sintering has been abandoned. The main reason has been the formation of small amounts of uranium carbides (UC and UC_2) in the sintered UO_2 pellets. Even if it has been possible to work out the sintering in such a way that a surface layer of uranium carbides is avoided, small amounts of the UC phase will appear as evenly distributed grains inside the pellets. A thorough investigation has shown that two carbon sources are responsible for the formation of uranium carbides, namely, hydrocarbons present in the atmosphere of a carbon-tube furnace and hydrocarbons formed through the cracking of organic lubricants in the UO_2 pellets.

The first type of hydrocarbons reacts with the UO_2 pellets, mainly on their surface, and the result is a surface layer of carbides, whereas the amount of carbide grains inside the pellets decreases toward their center (Fig. 7a). Hydrocarbons formed through cracking of residues of organic lubricants in the UO_2 pellets react mainly with the central parts of the pellets, giving small amounts of uranium carbides which decrease toward the surface of the pellets (Fig. 7b).

The first type of carbide formation can be avoided to a large extent if a convenient time-temperature program for the sintering is followed and also by embedding the pellets in different oxides. The second type of carbide formation can be avoided if the lubricant is vaporized before the final stage of sintering. On a technical scale, however, it is difficult to eliminate

Fig. 8— UO_2 pellets after corrosion in distilled water at 100°C. (a) and (b) Surface carbide layer present; time, 1 hr. (c) and (d) No surface layer of carbides (the pellets have been ground); time, 10 hr.

Fig. 9a—Typical relation between density obtained for sintered pellet and temperature of sintering. The temperature obtained from the extrapolated curve at a density of d_p indicates the temperature at which sintering starts (d_p = density of cold-pressed compact). The theoretical $d_s = 10.95$.

Fig. 9b—Typical relation between grain size ϕ_m of sintered pellet and sintering temperature ($\log \phi_m$ vs. $1/T$). The temperature obtained from the extrapolated curve at a grain size equal to the size of the crystallite powder particles indicates the temperature of recrystallization.

the carbide formation completely. For example, a carbide formation was observed in the central parts of UO_2 pellets which had been heated for one week at 200°C in vacuum after pressing but before sintering. (Alcylalcohols had been used as lubricants.)

UC and UC_2 both react with water or water vapor, and therefore UO_2 pellets containing these phases may crack even after a short contact with water. The most marked effects are observed if pellets with and without a surface carbide layer are compared (Fig. 8). The carbide grains inside the pellets, however, are also of importance.

Another disadvantage is the greater tendency for pellets containing uranium carbides to crack, owing to thermal gradients or mechanical tension, than for pellets free from carbides.

Vacuum sintering has the advantage that no carbon activity due to hydrocarbons in the furnace atmosphere exists. Still, the carbide formation due to cracking of the lubricants is a problem. One of the main disadvantages is the volatility of UO_2 at higher temperature in vacuum ($\geq 1700^\circ$), often resulting in a marked change of shape of the pellets during sintering. Even if vacuum sintering has many advantages for other systems, it seems to be of less importance for the sintering of UO_2 . The presence of a gaseous phase seems to be of special importance for this system in order to make a surface diffusion of the ions possible.

The method now in use is a sintering in molybdenum or molybdenum disilicide furnaces in an atmosphere of hydrogen. Small amounts of water vapor are sometimes added to the hydrogen and have the advantage of decreasing the sintering temperature, probably because of a reaction with the surface of the UO_2 pellets.

6. Many different variables have influence on the sintering process, e.g., temperature, time, oxygen contents of the oxide, and shape and size of the crystallites. Many of these problems, especially that of the oxygen contents, have been discussed by Murray and Livey.³ In order to get a better understanding of the sintering mechanism and also to be able to control a sintering process on a technical scale especially, two temperatures are of interest for the powder used. They are the temperature for the beginning of sintering and the temperature for the beginning of recrystallization.

In order to determine the first temperature, the density (d_s) of pellets pressed at different pressures and sintered for a certain time at different temperatures (T) has been measured. If d_s is plotted against T , curves like that in Fig. 9a are obtained. They may be extrapolated to lower temperature values, and the intersection of this extrapolated curve with d_p (density of pressured compact) indicates the temperature of the beginning of sintering for the powder used.

In Fig. 9b the diameters (ϕ_m) of the UO_2 grains in pellets sintered at different temperatures for a certain time have been measured. If $\log \phi_m$ is plotted against $1/T$, straight lines are obtained. They have been extrapolated to lower temperatures, and the intersection of these curves with ϕ_m of the initial powder indicates the temperature of recrystallization for the special powder and sintering process studied.

No full control of the sintering process is achieved before the two mentioned temperatures have been determined, and they are also of great theoretical interest in order to make possible an understanding of the diffusion mechanism of sintering. Much of the present research in our laboratory is concentrated on methods to determine these temperatures and also on variables that have an influence on them.

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Fabrication and Enclosure of Uranium Dioxide

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ABSTRACT

Uranium dioxide compacts of high density can be economically produced by conventional ceramic processes such as cold pressing, isostatic pressing, hot pressing, extrusion, and slip casting. Greatly reduced costs and improved quality have been made possible by new powder treatments and fabrication techniques. Typical of the recent developments are (1) powder activation by reduction in a fluidized bed, (2) combined powder compaction and cladding by swaging, without subsequent sintering, and (3) finishing of sintered ware by belt centerless grinding.

To overcome the disadvantage of poor neutron economy, UO_2 fuel assemblies require not only high-density oxide but also an efficient arrangement of the fuel. It is now economically feasible to fabricate UO_2 cores for relatively simple fuel assemblies which will meet this requirement.

Problems of providing safe, durable, and economical enclosures for UO_2 fuel cores are rapidly being solved. Techniques have been developed for forming and assembling tubing, end fittings, and supporting members from alloys of zirconium, iron, and aluminum. Less conventional techniques, such as vacuum casting of zirconium alloys and high-frequency welding, are being studied. Standardization of fabricating processes and fuel-element designs is an extremely desirable objective which will be partially realized as the operating behavior of UO_2 fuel elements becomes better understood.

1. INTRODUCTION

The development of large power-producing reactors in the U. S. shows a growing trend toward the use of UO_2 fuel materials. Although metallic fuels have higher thermal conductivity and better neutron economy, their use in reactors of high specific power is limited by low strength at elevated temperatures, chemical reactivity, and radiation damage.

Uranium dioxide has been used as a fuel in the form of slurries, powders dispersed in ceramic or metallic matrices, and pellets, tubes, or other massive shapes clad with zirconium, iron, or aluminum alloys. The principal advantages offered by the oxide are its chemical stability toward cladding materials and high-temperature coolants, a high melting point, isotropic crystal structure, resistance to radiation damage, and amenability of the irradiated oxide to established processing methods.

2 FABRICATION OF URANIUM DIOXIDE

The principal objective in fabricating UO_2 fuel-element components is a compact which is sufficiently dense to provide adequate neutron economy, chemical stability, and fission-product retention. The shape of the fuel components depends, of course, upon the design of the reactor. Figure 1 shows some typical fuel-element cores which were fabricated at the Hanford Atomic Products Operation. The short cylindrical rods, or pellets, are similar to those employed in

Fig. 1—Sintered massive UO_2 fuel-element cores.

the first Pressurized Water Reactor (PWR) loading of blanket fuel elements.¹ The large-diameter tubes are being fabricated for the first loading of the Plutonium Recycle Reactor.²

Conventional techniques that are generally applicable to UO_2 fabrication include cold pressing, hot pressing, hydrostatic pressing, extrusion, and slip casting. Most of these compaction processes require a subsequent sintering operation, in either an inert or a reducing atmosphere, to increase the density and strength of the green compact.

Less conventional compaction techniques (such as rotary swaging, vibratory compaction, and tamping) have also been considered. The success of these techniques depends primarily upon the properties of the raw material; consequently, methods for producing, characterizing, and activating UO_2 powders are now being investigated in a number of laboratories.

2.1 Preparation of Uranium Dioxide Powders

Methods for the preparation of UO_2 powders include precipitation with H_2O_2 or NH_4OH ; steam oxidation of metallic uranium or hydrided uranium chips; reduction of U_3O_8 , UO_3 hydrates, or UO_3 spheres obtained by spray drying and decomposing $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; fusion of UO_2 by the carbon-arc process; agglomeration of fine UO_2 powders; and reduction of UO_3 crystals.³ The powders most extensively employed in the U. S. are (1) "PWR-grade" oxide, prepared by reduction of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and (2) "ceramic-grade" material prepared by converting UF_6 (from gaseous diffusion plants) to $(\text{NH}_4)_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$, which is then reduced to UO_2 .^{*} The first type was used in fabricating the first loading of blanket fuel elements for the PWR. The ceramic-grade material is used in fuel elements for the Dresden Boiling Water Reactor and other reactors.

^{*}Both types of UO_2 powder are manufactured by Mallinckrodt Chemical Works (MCW).

2.2 Characterization of Uranium Dioxide Powders

Physical and chemical characteristics of UO_2 powders have been investigated to understand and better predict their fabrication behaviors. Differential thermal analyses, electron-microscopy studies, and measurements of particle* diameter and surface area are typical methods that have been employed to characterize UO_2 powders.

The electron micrographs in Fig. 2 illustrate the wide variation in surface characteristics of UO_2 powders from various sources. The morphology and relative sizes of UO_2 particles can be observed and correlated with differences in fabrication behavior.

The agglomerate, or spongelike structure, of the ceramic-grade UO_2 results in pressed compacts of low green density. This structure also explains the low bulk density of this powder (2.5 g/cm^3 as compared to 4.3 g/cm^3 for PWR-grade UO_2). Ceramic-grade UO_2 compacts pressed at 25 tsi or more usually fractured during sintering because of pressure laminations presumably caused by the air entrapped in the agglomerates. Differences in surface texture and particle size, as observed in the electron micrographs, also account for variations in the sintering behavior of the UO_2 powders. The small particle size and the large surface area of powder c in Fig. 2 explain the excellent sintering of this powder. Better sintering would be expected with powder a than with powder b because of the rougher surface and higher surface area of powder a, despite the fact that the particle sizes of the two powders are about the same.

Thermogravimetric and differential thermal analysis techniques also have been useful^{4,5} in characterizing oxide powders prepared by various processes. When a sample of UO_2 is heated in air, the differential thermal analysis curve shows two peaks corresponding to the two exothermic reactions: $3\text{UO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{U}_3\text{O}_7$ and $\text{U}_3\text{O}_7 + \frac{1}{2}\text{O}_2 \rightarrow \text{U}_3\text{O}_8$. Depending on the method of raw-material preparation, the peaks may be shifted in position and may vary in sharpness. For material of finer particle size and greater surface reactivity, the peaks occur at lower temperatures and with a higher degree of separation.

Specific surface area, average particle diameters, and surface roughness factors have been widely used to characterize UO_2 powders and have been very helpful in predicting the sintering behavior of these powders.⁶

Specific surface areas are measured by B. E. T. gas-adsorption techniques,⁷ and particle diameters are measured by air-permeability methods. The surface-roughness factor is the ratio of the specific surface area to the average particle diameter.

Fig. 2— Electron micrographs of UO_2 powders. (a) MCW PWR-grade UO_2 . (b) MCW ceramic-grade UO_2 , lot 5. (c) MCW ceramic-grade UO_2 , lot 9.

*The term "particle" is used in this discussion to describe either UO_2 crystallites or agglomerates of crystallites.

2.3 Activation of Uranium Dioxide Powders

High-density UO_2 bodies can be fabricated with relatively low pressures and low sintering temperatures if the powder is first activated to obtain the desired particle diameter, surface area, and structure. Wet or dry ball milling, Micronizing, hammer milling, and oxidation-reduction treatment in a fluidized-bed reactor are typical methods that have been investigated. The appearance of UO_2 powder after such treatments is illustrated in Fig. 3.

Uranium rods or alumina balls are used in rubber-lined ball mills to break down agglomerates of UO_2 particles to form a powder that sinters relatively easily. The effect of ball milling upon the densities of UO_2 compacts, before and after sintering, is illustrated in Fig. 4. Surface areas, compacting pressures, sintering temperatures, and sintered densities are correlated in Fig. 5.

Micronizing is a grinding method in which powder agglomerates are broken up by the action of a high-velocity fluid jet. The method has been employed to prepare UO_2 with particle diameters^{8,9} of less than $1\ \mu$. These powders can be pressed or extruded into compacts easily sinterable to 95 per cent of theoretical density.* Contamination of the UO_2 by metallic impurities from the stainless-steel Micronizer has been eliminated by lining the interior of the Micronizer with rubber.

Mechanical activation of UO_2 powder by high-speed hammer milling in a Mikro-Atomizer is being investigated.¹ Contamination of the UO_2 by the Stellite-lined hammers is negligible, and the mill is capable of high production rates.

Recent studies have demonstrated that the sinterability of most UO_2 powders can be significantly improved by an oxidation-reduction cycle in a fluidized bed.^{6,10} The temperatures used for the oxidation and reduction were 450 to 500°C and 525°C, respectively.

Untreated PWR-grade UO_2 and PWR-grade UO_2 subjected to the oxidation-reduction cycle were compacted to 60 per cent of the theoretical density by cold pressing at 25 tsi. The two powders sintered to 85 and 91 per cent of the theoretical density, respectively. The oxidation-reduction cycle increased the surface area, and particularly the surface roughness, as illustrated in Fig. 3.

2.4 Compacting Uranium Dioxide Powders

The most common method of fabricating UO_2 involves pressing UO_2 powder in a metal die and subsequently sintering the compacted powder to obtain a high density. This method has been applied to the fabrication of pellets, bars, crucibles, and tubes. The addition of an organic binder to the powder is required to give the green oxide compact sufficient strength for subsequent handling. Various organic binders have been employed, including polyvinyl alcohol, polyethylene glycol, paraffin, and camphor. Sterotex, a hydrogenated vegetable oil, is usually added as a lubricant. The binder and lubricant volatilize during subsequent sintering of the compacts.

A compacting pressure in excess of 100 tsi was employed to compact PWR-grade UO_2 into pellets having approximately 70 per cent of the theoretical density for the first PWR loading. Reinforced tungsten carbide dies are necessary at such pressures to reduce abrasion of the die by the UO_2 powder. The pellets were sintered at 1725°C for 10 hr to obtain 92 to 94 per cent of the theoretical density.^{11,12} More than 2 million of these UO_2 pellets were required for the first loading of PWR blanket fuel elements. High sintered densities can be obtained at relatively low compacting pressures with UO_2 powders activated by processes such as Micronizing or ball milling, as indicated in Fig. 4.

The fabrication of UO_2 , alone or mixed with zirconium powders, by hot pressing has been investigated.^{4,13-15} In general, this method does not appear to compete favorably with cold pressing and sintering.

Extrusion of UO_2 has been investigated at several sites (references 1, 9, 16, and 17) as an alternate method of forming tubular, cylindrical, and ribbon fuel cores of relatively long lengths. The UO_2 powders are usually activated by Micronizing, ball milling, or an oxidation-reduction

*Theoretical density = $10.97\ \text{g/cm}^3$.

Fig. 3—Typical electron micrographs of activated UO_2 powders. (a) MCW PWR-grade UO_2 , ball milled for 64 hr. (b) MCW PWR-grade UO_2 , Micronized. (c) Ceramic-grade UO_2 , reoxidized and reduced in a fluidized bed.

Fig. 4—Effect of ball milling on densities obtained by cold pressing and sintering UO_2 (5000 g of UO_2 milled with 4000 g of alumina balls in a 2-gal-capacity mill).

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Fig. 5—Sintered density of UO_2 (MCW PWR grade) as a function of compacting pressure, sintering time, and particle surface area.

cycle¹⁶ prior to blending with an organic plasticizer, water, and glycerine. With adequate powder preparation, rods 0.7 in. in diameter in long lengths can be fabricated to 95 per cent of theoretical density by sintering at 1650 to 1700°C for approximately 8 hr. Uranium dioxide tubes 0.829 in. O. D. by 0.555 in. I. D. have been fabricated by extrusion.¹ These dimensions are representative of those contemplated for PWR core 2 blanket fuel elements.

Fabrication of ceramics by isostatic pressing involves compacting preformed or loose ceramic powder in an evacuated rubber mold or envelope. Massive UO_2 shapes such as the long, large-diameter tubes in Fig. 1 are in this way easily compacted to high densities. PWR-grade UO_2 milled for 48 hr was isostatically formed at 40,000 psi into rings of 65 per cent theoretical green density.¹⁸ These rings reached 95 per cent of the theoretical density after sintering at 1600°C for 8 hr. Burdick and Parker¹⁹ have prepared high-density UO_2 test specimens by preforming at 10,000 psi and isostatically re-pressing at 100,000 psi.

Since the pressure is uniformly applied to all surfaces, density gradients in isostatically pressed oxide are minimized. The green strength of the compacts is sufficient to permit conventional machining operations subsequent to the pressing operation. High-density wares such

as alumina spark-plug insulators and alumina pellets for ball mills are mass produced by isostatic pressing.

In studies on the use of vibratory compaction techniques,^{20,21} rods were compacted which sintered to 89 per cent of the theoretical density during 10 hr at 1725°C. Mechanical difficulties were encountered in regulating the powder feed, however, and it was concluded that the process does not compete favorably with cold-pressing and extrusion techniques.

Crucibles, cylinders, and other UO_2 shapes can be fabricated by slip casting. Rods were cast from a slip made up of ball-milled UO_2 , 1.0 wt. % bentonite, 0.2 wt. % Daxad-23, 0.25 wt. % polyvinyl alcohol, and 10 per cent water.^{22,23} Hydrochloric acid can also be added as a defloculent. The castings were considerably improved by milling the UO_2 for 10 hr and deairing the slip. Densities greater than 90 per cent of the theoretical density were obtained by sintering at 1600°C for 6½ hr.

An atomic hydrogen torch has been used to melt and form UO_2 rods by a flame fusion technique²⁴ similar to the Verneuil process for making sapphire rods. By adding up to 6 per cent Al_2O_3 to the UO_2 powder, short rods having densities up to 91 per cent of the theoretical density were achieved. With improved mechanical controls, it may be possible to increase the density.

Simultaneous compaction and cladding of UO_2 powders by rotary swaging offers promise of relatively low-cost manufacturing of fuel elements.²⁵ This technique eliminates the usual ceramic forming and sintering processes. Swaged fuel elements have been fabricated with claddings of stainless steel, Zircaloy, and aluminum alloys. Several types of UO_2 powders were investigated. Compacted-powder densities were uniform and reproducible within 1 per cent. Maximum compacted-powder densities of 90 per cent were achieved by cold swaging, and maximum densities of 94 per cent were achieved by hot swaging at 600°C. Massive recrystallization occurs in hot-swaged (600°C) UO_2 powders as illustrated in Fig. 6. This low-temperature sintering phenomenon is being investigated. Structurally sound Zircaloy jackets of high strength are obtained in the swaging process, with degrees of cold work as great as 75 per cent, because the cold work occurs in compression rather than in tension. In preliminary tests fuel elements made by rotary swaging have been irradiated in the Materials Testing Reactor to exposures of approximately 10^{20} nvt.

2.5 Sintering of Uranium Dioxide Compacts

In the sintering process, tiny particles of UO_2 which have been brought into intimate contact with one another by a forming operation become rigidly bonded by diffusion and grain growth. Organic binder and lubricant materials are eliminated by vaporization if they have not previously been removed in a separate decarbonizing furnace. If a reducing atmosphere of hydrogen is present, the excess oxygen initially associated with the UO_2 is removed. Growth of single crystals proceeds until the original particles lose their identities and the bulk density of the part being sintered approaches that of a single crystal of UO_2 . This condition is desirable in a UO_2 fuel element because, in addition to increasing the amount of uranium in the fuel element, it improves the thermal conductivity, erosion resistance, and fission-gas-retention characteristics of the core material.

The sintered cylindrical UO_2 pieces employed for the blanket-fuel-element rods in the PWR were first decarbonized at approximately 800°C to remove the organic binder and lubricant materials used in cold pressing the compacts. The pellets were then heated to 1725°C in a molybdenum-wound, hydrogen-atmosphere, pusher type furnace and were held at that temperature for 5 to 10 hr. The rates of heating and cooling were closely regulated to prevent cracking or spalling of the pellets.¹²

Tubular pieces such as those illustrated in Fig. 1 are currently sintered in a hydrogen atmosphere at a temperature of 1600°C for 4 hr to obtain a minimum density of 93 per cent of the theoretical density.

Recent experiments indicate that UO_2 can be sintered to a high density in a steam atmosphere at a relatively low temperature.^{8,26-29} For example, comparable densification rates have

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UO₂ particles (6 ×) swaged at 25°C (left) and at 600°C (right)

UO₂ swaged at 600°C (1200 ×)

Electron micrograph of UO₂ swaged at 600°C (4000 ×)

Fig. 6 — Typical UO₂ samples after swaging.

been observed for cold-compacted UO_2 sintered in steam at 1200°C and in hydrogen at 1700°C . Uranium dioxide pieces compacted to 55 per cent of theoretical density were sintered to 90 per cent density in 1 hr in 1400°C steam. Identical compacts reached only 70 per cent of theoretical density after sintering 24 hr at the same temperature in hydrogen.

The increased sintering rates observed in steam atmospheres are thought to be a result of several secondary phenomena that are more important than the mere replacement of atmosphere. Most important of these are the increase in the oxygen to uranium ratio to as much as 2.15 and the attendant surface-activation effects. Reduction of the oxygen to uranium ratio to 2.00 obviously requires a final cooling in hydrogen.

Substantial reductions in sintering costs would be made possible by the successful development of steam sintering. For example, furnace maintenance costs are reduced approximately 50 per cent for every 100°C decrease in the operating temperature below 1700°C . Ultimately, however, the feasibility of steam sintering of UO_2 fuel cores will depend upon the irradiation behavior of the oxide. At the present time, the effect of oxygen to uranium ratios greater than 2.00 is suspected to be detrimental to the irradiation stability of UO_2 .

Porosity changes associated with sintering have recently been investigated.⁸ Closed and open pores in sintered UO_2 change rapidly during the initial stages of sintering. A small decrease in the closed porosity is observed in densities up to approximately 87 to 88 per cent of the theoretical density, after which there is a rapid increase at densities of approximately 91 to 92 per cent. This is followed by a linear decrease at higher densities. The open porosity decreases rapidly with increasing density, especially at approximately 91 to 92 per cent of the theoretical density; thereafter little change occurs. This may be due to the decrease in pore size and the transformation of open to closed pores. The pore-size distribution of unsintered UO_2 is narrowed, and smaller pores are formed as the green density increases. Narrow distribution of pores and small pore sizes are associated with easily sinterable powders having high surface areas.

Various inorganic compounds have been investigated as additives to UO_2 in an attempt to lower sintering temperatures and to increase the sintered density.^{26,27} Of the materials considered, TiO_2 and CeO_2 were the most effective. At 1600°C , the addition of 0.25 wt. % TiO_2 increased the sintered density from 85 per cent of theoretical density to 96 per cent. Titania additions above 1 per cent did not further increase the sintered density.

2.6 Finishing

Because of the hardness and fragility of sintered UO_2 , it is difficult to finish the material to close tolerances with low reject rates. Conventional hard-wheel grinders have been used to grind small cylindrical pieces,³⁰ but, for shapes such as the massive tubular elements, this type of grinder is not satisfactory.

With belt type grinders, UO_2 cylinders, rods, plates, and other shapes can be finished rapidly and economically. Rejects caused by chipping or cracking of the UO_2 are practically eliminated because of the resilient contact wheel, the low grinding temperatures, and the low-pressure free-cutting characteristics of abrasive belts.¹⁶

3 ENCLOSURE OF MASSIVE URANIUM DIOXIDE SHAPES

Enclosure of UO_2 cylinders, thick-walled tubes, and other massive shapes in metallic cladding or sheathing is necessary to support the fissionable material in the desired geometry, to protect it from the high-temperature coolant, and to contain any fission products that are not retained within the oxide. Enclosure of the UO_2 involves, principally, problems of fabricating cladding components, assembling the core and cladding components, and nondestructively testing the fuel assembly prior to irradiation.

Most of the effort in massive UO_2 fuel development has been expended on rod bundles such as that illustrated in Fig. 7. This fuel geometry is employed in the first PWR loading and is similar to those being developed for the Yankee Pressurized Water Reactor and the Dresden

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Fig. 7— Typical fuel assemblies containing massive UO_2 cores.

Boiling Water Reactor.³¹ Additional details of the Shippingport Pressurized Water Reactor fuel design and of preliminary reference fuel designs for the Yankee Pressurized Water Reactor and the Dresden Boiling Water Reactor are summarized in Table 1. Each of the three fuel assemblies is designed to fit in a square coolant channel.

The thick-walled, nested tubular fuel element illustrated in Fig. 7 is being developed for the Plutonium Recycle Program Reactor at Hanford. Massive tubular oxide fuel elements are also being considered for the Atomics International Sodium Graphite Reactor³² and the Shippingport Pressurized Water Reactor.¹ The thick-walled tubular geometry is proposed because, compared to geometries such as rod bundles, the coolant is more efficiently distributed, less cladding material is used, and more UO_2 can be accommodated. The use of thick-walled tubular elements may permit savings in coolant pumping costs and fabrication costs.

Tubular oxide fuel elements composed of relatively short sections, such as those illustrated in Fig. 8, are also being considered for the Plutonium Recycle Program Reactor. These

Table 1— UO_2 FUEL DESIGNS

Reactor	UO_2 fuel pellet		Fuel assembly length, in.	Material	Cladding		No. of rods per channel	Max. UO_2 temp., °F
	Diameter, in.	Length, in.			Thickness, in.			
Shippingport	0.4	0.4	72	Zircaloy-2*	0.027		120	2500
Yankee	0.3	0.3	102	Stainless steel	0.015		305	4000
Dresden	0.5	0.5	106	Zircaloy-2	0.030		36	3000

*1.5 wt. % tin—0.25 wt. % each of iron, nickel, and chromium; the rest is zirconium.

Fig. 8—Zircaloy-clad tubular oxide fuel elements (magnification 1×).

and similar fuel elements clad in Zircaloy-2 or aluminum-1 wt. % nickel alloy have been irradiated with heat generation rates of approximately 50 kw per foot of element.

3.1 Components for Enclosure of Oxide

Problems encountered in obtaining functionally adequate cladding components arise both from the properties of the cladding materials and from the fabrication behavior of the material. Neutron economy, high-temperature corrosion resistance, and low costs are extremely important requirements for the materials employed in large-scale power-producing reactors. Niobium and alloys of aluminum, iron, and zirconium have been considered. Zircaloy-2 has been the cladding material most intensively investigated for use in water-cooled reactors because it best meets the requirements of neutron economy and corrosion resistance. The cost of Zircaloy cladding has been relatively high. For example, estimated combined material and fabrication costs per 100 ft of 0.5-in.-diameter tubing purchased in comparable small experimental lots are \$8, \$70, and \$600 for M-388 (aluminum-1 wt. % nickel) alloy, stainless steel, and Zircaloy-2, respectively. Niobium tubing is not yet commercially available in the U. S., but it would be expected to cost approximately 10 times as much as the Zircaloy tubing if fabricated on an experimental basis. The development of fabrication processes for Zircaloy has been difficult, but thin-walled Zircaloy tubes with diameters up to approximately 0.5 in. are now routinely formed by extrusion. Tubing with diameters up to 1 in. has been produced satisfactorily by roll forming and welding of Zircaloy strip. Welded tubing has been produced³³ in which the welded zone reveals no evidence of any decrease in corrosion resistance. The roll forming and welding technique has also been extended to the fabrication of Zircaloy tubes having diameters as great as 3 in., but there have been problems in warping of these tubes. Drawing,

swaging, and metal-flowing techniques have been developed by which it appears to be possible to form these tubes to close tolerances.

Stainless-steel cladding has been considered for the Yankee Pressurized Water Reactor and other reactors because it is relatively inexpensive, easily fabricated, and has excellent corrosion resistance in high-temperature water. It is undesirable with respect to neutron economy. For example, a cladding of stainless steel (type 347) 0.005 in. thick will absorb approximately the same number of thermal neutrons as 0.020 in. of niobium, 0.080 in. of aluminum alloy (M-388), and 0.140 in. of Zircaloy-2.

In recent years aluminum alloys have been developed which resist the intergranular corrosion encountered with high-purity aluminum in high-temperature water.^{34,35} The UO_2 - ThO_2 pellets in the Borax IV fuel elements were enclosed in aluminum-alloy (M-388) cladding and irradiated at water-coolant temperatures up to approximately 260°C.^{36,37} Because of their neutron economy, ease of fabrication, and relatively low cost, these alloys are now being studied in a number of laboratories. Principal disadvantages are the high uniform corrosion rates and the low strength in high-temperature water coolant.

The cladding material of a fuel element must not react with the UO_2 core at the operating temperatures expected in the reactor. There is no evidence of reaction between UO_2 and aluminum,³⁸ Zircaloy-2,³⁹ or niobium⁴⁰ at temperatures of less than 400, 600, and 1000°C, respectively. Compacts of mixed UO_2 and stainless-steel (type 308) powders have been sintered at approximately 1200°C, apparently without reaction between the UO_2 and stainless steel.⁴¹

Spacing members in the form of ribs or spiders are necessary to ensure precise alignment of the metal-clad UO_2 components with respect to each other and to the reactor coolant channel. The geometry of the fuel element determines the type of spacing member. For a fuel assembly such as the PWR rod cluster, the short rods composing a bundle are welded into place in holes drilled through Zircaloy end plates as illustrated in Fig. 7. For fuel assemblies such as the nested tubular fuel element in Fig. 7, straight or spirally wound ribs extending the entire length of the fuel element are desirable. It is presumably desirable that the ribs be attached over the full length to avoid vibrations under operating conditions.

Thin-walled Zircaloy tubing having integral straight ribs has been produced on an experimental scale.⁴² Ultrasonic welding techniques have been developed for attaching either straight or spirally wound ribs to aluminum tubing,⁴³ but these techniques have not been so successful with other metals. A promising method for attaching ribs to these materials is a high-frequency resistance-welding process.⁴⁴ This process has been adapted very satisfactorily to the high-speed forming and welding of Zircaloy tubing and to the welding of spiral ribs to 1-in.-diameter tubing. A major advantage of this process is that the tubing is not heated sufficiently to cause warping or to affect its corrosion resistance. The heat-affected zone of a high-frequency Thermatool weld is compared with a conventional Heliarc weld in Fig. 9.

End fittings are necessary to align and support the fuel assembly in the reactor. They have usually been fabricated by machining from metal stock. Vacuum-casting techniques that have recently been applied to the fabrication of Zircaloy end fittings appear to provide a relatively simple, inexpensive method for forming complex fittings which are difficult and costly to fabricate by other methods.⁴⁵ Powder-metallurgy techniques also may be applicable.⁴⁶

3.2 Assembly of Fuel-element Components

Final assembly of a fuel element containing sintered UO_2 compacts involves (1) inserting the oxide pieces into the carefully tested and inspected cladding, (2) making the end closures, and (3) joining the metal-clad oxide components to the end fittings or hangers.

The clearances permissible between the oxide cores and the metal cladding affect the ease of assembly, particularly for the tubular fuel elements. The minimum allowable clearance between the oxide core and the metal cladding is dictated not only by the ease of assembly but also by the fact that the core of the fuel element is heated to a higher temperature, under irradiation, and expands more than does the cladding. As clearances are decreased, closer tolerances on the dimensions of both the core and the cladding components are required. This markedly increases cladding fabrication costs. The maximum clearance permissible is de-

Fig. 9—Heat-affected zones in welded zirconium.

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Fig. 10—Cross-sectional views of irradiated UO_2 fuel elements, illustrating how the core material is redistributed because of thermal fracture.

terminated principally by considerations involving the rate of heat transfer across the core-to-cladding interface.

The spatial relation between the core and cladding is drastically changed during irradiation because thermal stresses fracture the sintered oxide into many pieces. These pieces are far more stable on further irradiation, and, in either cylindrical or tubular fuel elements, they remain more or less tightly keyed together within the cladding, as illustrated in Fig. 10. Irradiation tests conducted to evaluate the necessity of close tolerances have led to the conclusion that such cracking effectively relocates part of the original annular gap to the hotter interior of the fuel material, where the enhanced radiative heat-transfer mechanism acts to increase the over-all heat-transfer rate. Calculations show that the effect on a helium-filled, 0.011-in. core-cladding gap in the maximum UO_2 core temperature is of less consequence than replacement of the helium of a 0.004-in. gap with steam as a result of a cladding defect or failure. Kisiel²⁸ has shown that no core melting occurs at a surface heat flux of 475,000 Btu/hr/sq ft in PWR type fuel rods assembled with a helium atmosphere and a cold diametral clearance of 0.004 in. Melting does occur when the atmosphere is steam and the as-assembled clearance is only 0.001 in.

In the fuel assemblies for the Borax IV experiment, heat transfer between the core and cladding is reported to be improved by filling the annulus with lead.³⁶ The lead bonding is obtained by simply lowering the aluminum (M-388) sheathing, containing UO_2 - ThO_2 pellets, into molten lead at 490 to 500°C.

The most common type of closure used in the manufacture of UO_2 -containing fuel elements is the fusion weld formed by an inert-gas-shielded arc. This weld is very satisfactory for all the cladding materials that have been considered. Such closures have satisfactory corrosion resistance when they are completed in an inert atmosphere, and they also possess the structural strength that is important in enclosures of massive fuel elements. Techniques for making fusion-welded closures of cylindrical Zircaloy-clad oxide fuel elements were developed in connection with production of the first loading for the PWR.¹¹ The procedure for making the final closure of the PWR type fuel rod involves (1) cleaning the metal components, (2) inserting the end plug into the pellet-loaded tube, (3) evacuating the fuel rod in a welding chamber, (4) filling

Fig. 11 — Cross-sectional view of zirconium tubing with a seam weld.

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the welding chamber with helium, and (5) rotating the fuel rod at 18 rpm in a collet chuck while making a single weld pass, using a thoriated tungsten electrode. Contact between the welding electrode and the fuel rod, or contamination of the weld area as revealed by a light-brown or blue film, is cause for rejection of the weld.

A very interesting diffusion type closure was developed for the aluminum-clad Borax IV fuel elements described above. The closure procedure consists of simultaneously heating and "pinching off" the ends of the aluminum cladding.

Resistance seam welding,⁴⁷ combined with a Heliarc fusion weld, is being developed as a method of obtaining a double closure for large fuel elements such as the nested tubular Plutonium Recycle Program Reactor assembly illustrated in Fig. 7. A cup formed from the cladding material is inserted into the end of the cladding tube, where it is welded into position by a resistance weld extending around the circumference at a short distance from the end of the fuel element. A fusion weld is then completed at the extreme end of the cup and cladding as illustrated in Fig. 11. The double closure is desirable because a minute pinhole or subsurface crack in a weld can destroy the usefulness of a relatively large quantity of fissionable material. Even more important, such defects could jeopardize the safety and continuity of reactor operation. The double closure has the further advantage that only one of the welds is subjected to stresses associated with supporting the fuel element in the reactor.

The closure of UO_2 elements by an electron-beam welding process has been investigated recently on a limited scale.⁴⁸ In this process the fuel-element assembly is placed in a vacuum box, and the high-intensity beam of electrons from a heated tungsten cathode is focused on the area to be welded. The kinetic energy of the electrons is converted into the heat necessary for forming the fusion weld.

Partial end closure of Zircaloy-clad oxide fuel rods by metal-spinning techniques has recently been investigated.¹ A number of other conceivable closure techniques, such as percussion welding, butt welding, spot welding, condenser discharge welding, and induction melting, have also been considered.⁴⁹

3.3 Nondestructive Testing

Defective fuel components and assemblies are detected by visual examination, measurement of dimensions, autoclaving in high-temperature water or steam, helium leak testing, X-ray examination, dye penetrants, and eddy-current and ultrasonic methods.

PWR fuel-rod clusters have been autoclaved in 750°F steam to detect inadequate corrosion resistance of the Zircaloy cladding, particularly in welded areas. Techniques have been developed for examining corrosion products on the surfaces of the corrosion-tested clusters with a Kollmorgen panoramic camera.¹

X-ray techniques have been effective in detecting holes, inclusions, and subsurface defects in cladding of PWR blanket-fuel-element rods. The feasibility of inspecting end closures by an X-ray photometer also has been investigated. Mass spectrometers have been employed in making helium leak tests. Flaws such as cracks and inclusions have been determined by eddy-current tests involving the fuel-element cladding materials and, to a limited extent, the end closures.¹

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Uranium Dioxide as a Reactor Fuel

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1 INTRODUCTION

The main attraction of uranium dioxide as a reactor fuel rests on its relative chemical inertness toward many possible coolant materials, including hydrogen, water, and CO_2 . It has a high melting point and is strong at temperatures up to 1000°C ; these properties can be exploited to produce fuel elements that could operate at high temperatures.

There are, of course, certain disadvantages in the use of uranium dioxide as a fuel, for example, since it is brittle and it cracks owing to thermal stresses, the strength of the fuel element must be largely supplied by the can. In this respect it differs from uranium metal which may itself provide the structural part of the fuel element up to about 500°C , the can merely serving to retain fission products. Since aluminum and magnesium are too soft above 400°C , they cannot be used to contain uranium dioxide fuel at can-surface temperatures above 400°C . The only metals of low neutron-capture cross section which might therefore be used for high-temperature service are zirconium and beryllium, both of which are expensive. This combined with the fairly high fabrication cost for ceramic fuel leads to high fuel costs. In addition, uranium dioxide has a poor thermal conductivity, particularly at temperatures above 1500°C , and, although this is somewhat offset by its high melting point, it does introduce a restriction in the design of fuel elements. In particular, to avoid center melting, the use of fuel elements of small diameter is required; this causes a further increase in the cost of fabrication of the fuel and requires a larger amount of canning material.

The cost of producing power in power reactors of present designs is largely controlled by capital costs so that it would be possible to produce power more cheaply if the rating of the reactor core and the fuel temperature were increased, even if such changes demanded a rather more costly fuel element. The use of uranium dioxide fuels is, therefore, a promising line of development in the attempt to obtain cheaper power, and such development is encouraged by the initial results obtained.

The work on uranium dioxide fuels so far published in the unclassified literature has mainly been on stoichiometric UO_2 ; this material differs in its properties in many ways from that of nonstoichiometric uranium dioxide and higher oxides formed when UO_2 powder is exposed to air. It is the purpose of this paper to describe the preparation, properties, and some aspects of the behavior under irradiation of nonstoichiometric uranium dioxide and to attempt to relate some of the changes observed under irradiation with the differences in physical and mechanical properties.

2 STRUCTURE OF URANIUM DIOXIDE

When higher oxides of uranium are reduced in hydrogen, the structure of the powder so prepared is stoichiometric $\text{UO}_{2.0}$, but, when the powder is exposed to air at room temperature,

the oxygen content increases by an amount that depends mainly on the particle size of the powder but also on the time of exposure. The structure of the material so produced is not an equilibrium structure and has not been investigated. Equilibrium structures are developed by holding, in the absence of air, at temperatures of 300°C and above. At about 300°C, oxides in the range UO_2 to U_4O_9 consist of mixtures of two phases having the compositions UO_2 and U_4O_9 . As the temperature is raised, the oxygen content of the UO_2 increases while the oxygen content of the U_4O_9 decreases. For example, UO_2 goes to $\text{UO}_{2.05}$ at 450°C and to $\text{UO}_{2.15}$ at 850°C.¹ At the sintering temperatures normally employed, it is believed that oxides in the range UO_2 to U_4O_9 consist of a single phase which, on cooling, will again break down into two phases based on UO_2 and U_4O_9 if the composition lies between these two extremes. UO_2 has a cubic calcium fluoride structure whereas U_4O_9 has a similar structure with the extra oxygen atoms in interstitial positions. U_4O_9 has a smaller lattice parameter than that of UO_2 . The equilibrium diagram for material with more oxygen than U_4O_9 is not well established and is not of great importance in the present context since all material after sintering contains less oxygen than U_4O_9 owing to loss of oxygen during sintering. Thus sintered specimens will consist either of stoichiometric UO_2 or two-phase mixtures of UO_2 and U_4O_9 . The custom has developed of calling the latter two-phase structure nonstoichiometric uranium dioxide. This nomenclature will be used in this paper; also the term uranium dioxide will be used to describe any powder produced by reduction to $\text{UO}_{2.0}$ followed by oxidation in air at room temperature. This is used both for convenience and because lack of knowledge of the nonequilibrium structures developed in this process precludes the use of any more-accurate description.

3 PREPARATION AND PROPERTIES OF URANIUM DIOXIDE POWDER

Uranium dioxide powder can be prepared by the reduction of a higher oxide such as UO_3 with hydrogen in the temperature range 500 to 800°C, and the powder particles obtained in this way are agglomerates of crystallites. The particle size and crystallite size of the uranium dioxide are functions of the characteristics of the higher oxide and of the reduction temperature;² the higher the reduction temperature the greater the particle size and crystallite size of the powder produced. As reduced, the composition is UO_2 .

Uranium dioxide powders will oxidize in air at low temperatures (18 to 100°C). Powders with particle sizes in the region of 1 μ will generally oxidize to compositions of about $\text{UO}_{2.02}$ after a 1-month exposure at room temperature. Smaller particle size preparations in the range of 0.1 μ particle size oxidize more rapidly and may heat up so violently that partial conversion to U_3O_8 occurs.

Several methods can be used to formulate the characteristics of uranium dioxide powders primarily for control purposes.

1. The surface area can be measured by nitrogen adsorption or by gas permeability methods. In relation to reactivity and its effect on subsequent sintering behavior, the former method, although more time consuming, gives an answer nearer the truth since the application of the Kozeny relation (on which the gas permeability method depends) to this type of fine, agglomerate powder is theoretically doubtful. Empirical correlations can, however, be obtained between nitrogen adsorption and gas permeability measurements on uranium dioxide powders and the rapid gas permeability method used for control of batches of powder.

2. Attempts have also been made to use differential thermal analysis curves obtained on heating uranium dioxide in air or oxygen to characterize the powder. Whereas general trends are apparent between the temperatures of the peaks on D.T.A. curves and the reactivity of the powder,³ there is a lack of quantitative agreement between different laboratories.

3. The oxide composition under standard storage times and conditions is a useful and quick way of indicating reactivity, and it is surprising that it is not used more widely for high surface area powders.

Generally, surface area determinations, preferably by nitrogen adsorption, and determination of the oxide composition and specific gravity afford suitable criteria for defining the characteristics of uranium dioxide powders.

4 FABRICATION OF SOLID URANIUM DIOXIDE

The main technique for preparing solid uranium dioxide from powder developed thus far is that of cold compacting followed by sintering in a controlled atmosphere. Alternative techniques of fabrication have been investigated with a view to reducing the costs of oxide fuel elements which are mainly concerned with the control of dimensions of the fuel pellets and selection of the canning material. Thus it has been shown that certain grades of uranium dioxide can be warm-pressed at 800°C using 10 Tsi pressure to bulk densities of around 10.5 g/cm³ to dimensional tolerances of less than 0.001 in. in diameter.⁴ This would allow greater dimensional tolerances on the can for a given clearance. This development of warm pressing, which it is believed can be automated, also offers a convenient method of producing uranium dioxide flat plates as opposed to cylindrical fuel elements. Fuel elements have also been made by packing powder in aluminum or stainless-steel tubes followed by drawing with additional swaging operations to densify the powder. In this way elements with uranium dioxide bulk densities of 9.0 to 9.5 g/cm³ have been made. Attempts are being made to increase the density still further.

It must be emphasized that the properties of material prepared by these relatively low-temperature deformation techniques remain to be evaluated.

5 PHYSICAL AND CHEMICAL PROPERTIES OF FABRICATED URANIUM DIOXIDE

The mechanical and thermal properties of sintered uranium dioxide have been described previously.⁴ The properties do not differ appreciably from those of other pure oxides such as magnesia but are inferior to those of sintered alumina.

No reaction in the solid state has been found over prolonged periods between solid uranium dioxide specimens and beryllium or stainless steel at 600 to 700°C. In wet and dry CO₂, the rate of oxidation⁵ of UO₂ is much slower than that of uranium metal in the temperature range 500 to 900°C. The compatibility of uranium dioxide with possible coolant gas and canning materials for gas cooled reactors is therefore favorable.

6 SINTERING OF NONSTOICHIOMETRIC URANIUM DIOXIDES AND HIGHER OXIDES OF URANIUM

The earliest work on the sintering of the oxides of uranium was carried out by Murray and Thackray⁶ when only two standard oxides were available, i.e., the American Mallinckrodt oxide UO_{2.04} and the British Springfields oxide UO_{2.14}. Pellets of the two oxides were cold compacted at 5 to 20 Tsi and sintered in argon over a range of temperatures. Densities of 10 g/cm³ were obtained for UO_{2.14} sintered at 1400°C. Under comparable conditions the Mallinckrodt oxide sintered to only about 8 g/cm³, although its green density was 6.2 g/cm³ compared with 4.7 g/cm³ for the Springfields UO_{2.14}. Oxidation of the UO_{2.04} to UO_{2.46} by heating in air at 300°C resulted in an improvement in its sintering properties, but it was still inferior to the Springfields UO_{2.14}.

When the Mallinckrodt oxide was sintered in hydrogen, the densities obtained showed little increase over the green density of the compact up to 1500°C.

The investigations of Alberman,⁷ Roberts,⁸ and Perio⁹ had shown that UO₂ of a sufficiently fine particle size would oxidize slowly at room temperature. Determinations by nitrogen adsorption of the surface areas of the powders, used in this first investigation, gave figures of about 6 m²/g for the UO_{2.14} and about 1 m²/g for the UO_{2.04}, this being the lower limit of the apparatus. Later microscopical measurements showed the particle size for the latter oxide to be about 2 μ.

More recent investigations have used oxides of compositions in the range UO_2 to U_3O_8 , and the effects of argon, nitrogen, hydrogen, carbon monoxide, and vacuum sintering atmospheres were studied both individually and combined. Cold-compacting pressures of 7 to 10 Tsi were used throughout these studies.

Argon and nitrogen atmospheres were found to give identical results. Oxides of compositions $\text{UO}_{2.08}$, $\text{UO}_{2.18}$, $\text{UO}_{2.23}$, $\text{UO}_{2.33}$, and U_3O_8 having surface areas of 2, 6, 6, 8, and 15 m^2/g , respectively, were sintered to densities above 10 g/cm^3 at 1200°C, the highest density achieved being 10.8 g/cm^3 for which the starting material was U_3O_8 .

During sintering in argon, there was a loss of oxygen from the pellets, e.g., after 2 hr at 1410°C, U_3O_8 became $\text{UO}_{2.26}$; $\text{UO}_{2.24}$, $\text{UO}_{2.19}$; $\text{UO}_{2.23}$, $\text{UO}_{2.14}$; and $\text{UO}_{2.08}$, $\text{UO}_{2.05}$. The weight loss during sintering could not be entirely accounted for by the loss of oxygen for material with oxygen content more than $\text{UO}_{2.25}$, indicating that uranium was also being lost by volatilization, as would have been anticipated from the work of Biltz and Muller,¹⁰ but the uranium loss also unexpectedly occurred for material in the range $\text{UO}_{2.08}$ to $\text{UO}_{2.23}$. Although too much reliance cannot be placed upon weight and composition determinations, deposits of uranium dioxide were found on portions of the sintering apparatus not in direct contact with the oxide pellet during sintering.

When zirconium and tantalum getters were placed near to, but not in contact with, pellets of $\text{UO}_{2.33}$ that were sintered in argon at 1450°C for 2 hr, densities of 9.4 g/cm^3 were obtained, and the pellets assayed $\text{UO}_{2.09}$. Identical pellets sintered under the same conditions but without getters assayed $\text{UO}_{2.19}$ and had a density of 10.2 g/cm^3 .

Dilatometric studies of the sintering process for $\text{UO}_{2.14}$ and $\text{UO}_{2.08}$ in argon and nitrogen showed that shrinkage was first apparent at 600°C and proceeded rapidly with further temperature rise, i.e., using a heating rate of 10°C/min, a density of 10 g/cm^3 was achieved by the time 1600°C was reached, and holding at this temperature for a further 2 hr raised the density to 10.4 g/cm^3 .

An experiment was carried out in which stoichiometric UO_2 of fine particle size was prepared by hydrogen reduction of UO_3 and handled under argon in a glove box to prevent oxidation. Pellets were then prepared from the stoichiometric material and sintered in argon at 1400°C for 2 hr. A separate batch of the stoichiometric powder was then exposed to the atmosphere and allowed to oxidize slowly. Portions were taken at regular intervals of time, analyzed for oxygen, and cold-compacted and sintered under constant conditions of time, temperature, and atmosphere. In this way a relation between sintered density and oxygen content was obtained. For stoichiometric material a density of 9.4 g/cm^3 was obtained, but for $\text{UO}_{2.04}$ the density of the sintered pellet was 10.1 g/cm^3 . Further increase of oxygen content caused little further increase of density.

Vacuum sintering of the powders $\text{UO}_{2.08}$ and $\text{UO}_{2.24}$ gave higher weight losses, oxygen losses, and slightly lower densities than the same powders sintered under the same conditions in argon. Thus, on sintering at 1410°C for 2 hr in argon, $\text{UO}_{2.24}$ goes to $\text{UO}_{2.14}$ of density 10.2 g/cm^3 with a weight loss of 0.6 per cent, whereas in vacuum $\text{UO}_{2.24}$ goes to $\text{UO}_{2.06}$ of density 9.95 g/cm^3 with a weight loss of about 6 per cent. The weight loss due to oxygen alone would be 1.03 per cent. Using identical conditions but sintering in an effusion cell with a small orifice, the weight loss of the specimen was reduced to 2 per cent, the density of the sintered pellet was 10.1 g/cm^3 , and the composition was $\text{UO}_{2.10}$. The loss from the cell could be accounted for by the loss of oxygen alone, a film of UO_2 being deposited on the coolest surface of the cell. During the melting of $\text{UO}_{2.2}$ in an argon arc furnace, deposits of material resembling UO_3 have been collected from the water-cooled hearth, suggesting that this may be the volatile phase. The volatile phase from the work of Ackerman appears unlikely to be UO_2 .

The use of hydrogen as a sintering atmosphere has a very deleterious effect upon the densities obtained for $\text{UO}_{2.08}$, $\text{UO}_{2.24}$, and $\text{UO}_{2.40}$. Sintering temperatures approximately 350°C higher were needed to achieve densities by sintering in hydrogen comparable with those for sintering in argon. The sintering behavior in hydrogen was very sensitive to moisture and oxygen content of the gas, and, when rigorous steps were taken to exclude these contaminants, the densities obtained were even lower than those indicated above. The final composition achieved depends on specimen size, time at temperature, and gas flow, but, for 2 hr at tem-

perature and specimens 0.5 in. in diameter above 1300°C, stoichiometric UO_2 is produced from starting materials $\text{UO}_{2.08}$ and $\text{UO}_{2.24}$. No loss of uranium could be detected visually when a hydrogen atmosphere was used during sintering.

When a fine nonstoichiometric oxide with a specific surface area of about $8 \text{ m}^2/\text{g}$ was oxidized to U_3O_8 and the resultant powder compacted and sintered in hydrogen for 4 hr at 1410°C, a stoichiometric pellet of density 10.43 g/cm^3 was obtained.

Dilatometric studies of the sintering of $\text{UO}_{2.14}$ and $\text{UO}_{2.08}$ in hydrogen showed that shrinkage did not occur below 800°C compared with 600°C for argon.

If dense pellets of nonstoichiometric oxides are reduced by hydrogen to stoichiometry at temperature of 1200°C, there is a decrease in density, e.g., $\text{UO}_{2.14}$ density goes to $\text{UO}_{2.00}$ density 10.0 g/cm^3 and $\text{UO}_{2.24}$ density 10.75 goes to $\text{UO}_{2.0}$ density 10.16 g/cm^3 . The decreases in density due to composition changes alone would be about 0.14 and 0.30 g/cm^3 , respectively, so there is an increase in porosity due to hydrogen reduction.

When cold-pressed pellets of $\text{UO}_{2.08}$ and $\text{UO}_{2.20}$ are heated in hydrogen to 700°C, held at this temperature to reduce the powder to $\text{UO}_{2.00}$, and then sintered in vacuum at 1400°C for 2 hr, slightly higher densities are obtained than when argon is used for the final sinter, e.g., $\text{UO}_{2.08}$ goes to $\text{UO}_{2.00}$ density, 9.85 g/cm^3 in vacuum, 9.15 in argon. If the hydrogen reduction step is omitted, the comparable figures are $\text{UO}_{2.08}$ and 10.35 g/cm^3 in vacuum, $\text{UO}_{2.09}$ and 10.60 g/cm^3 in argon. The comparable density for a complete sinter in hydrogen is 9.07 g/cm^3 .

Carbon monoxide has an effect similar to that of hydrogen on the sintering behavior of $\text{UO}_{2.88}$ and $\text{UO}_{2.08}$.

7 WARM COMPACTING OF NONSTOICHIOMETRIC URANIUM DIOXIDE

The relatively low sintering temperatures at which densities greater than 10 g/cm^3 could be obtained by sintering nonstoichiometric oxides in argon and the fact that sintering started at about 600°C indicated that the hot-compacting behavior of these oxides at about 800°C should be investigated. For two oxides, $\text{UO}_{2.08}$ and $\text{UO}_{2.20}$, it was found that, under 10 Tsi pressure at 800°C in a titanium carbide nickel-bonded die, densities of 9.9 and 10.6 g/cm^3 , respectively, were obtained. During this process the oxygen to uranium ratio remained constant to within ± 0.01 .

The addition of small amounts of metal powders to the nonstoichiometric oxides greatly modified their warm-compacting behavior. For a standard compacting pressure of 10 Tsi at 800°C using $\text{UO}_{2.08}$ powder, 2 wt. % iron reduced the density obtained to 6.5 g/cm^3 , whereas with $\text{UO}_{2.2}$ powder, 5 wt. % iron was needed to give a similar effect. The use of vacuum-degassed iron and uranium oxide powders produced no change in behavior. The iron additions quoted above produced the maximum depression of density on warm pressing. Using the $\text{UO}_{2.2}$ powder, it was found that 2 wt. % magnesium, 9 wt. % uranium, 7 wt. % tantalum, and 9 wt. % tungsten all reduced the density obtainable to about 6.5 g/cm^3 . Additions of nickel, molybdenum, copper, iron oxide, and alumina had no effect. Microscopical examination of sections of the oxide-metal powder mixtures showed that, where a low-density compact was obtained, there had been oxidation, to a varying extent, of the metal powder; when a high density was obtained, the metallic particles were unattacked. From an examination of the free energies of formation of the metal oxides at 800°C, it appears that metals whose oxides have free energies of formation in excess of approximately 40 kcal/mole at this temperature cause this depression of warm-pressed density by reducing the nonstoichiometric uranium dioxide to UO_2 .

8 HOT COMPACTING OF NONSTOICHIOMETRIC URANIUM DIOXIDE

Comparison¹¹ of the hot-compacting behavior of the Mallinckrodt and Springfields powders has proved that the latter material compacts to higher densities under the same pressure at lower temperatures than the former, e.g., 1400 compared to 1800°C. Large specimens of the nonstoichiometric powder cannot be prepared without cracking. Reaction of the graphite die with the oxide reduces the outer layers of oxide to stoichiometry, whereas the center remains

of nonstoichiometric composition, and the different compacting properties of the two compositions result in differential densification and subsequent cracking.

9 PROPERTIES OF NONSTOICHIOMETRIC DIOXIDES AT ELEVATED TEMPERATURES

Simple bend tests have been made at 800 and 1000°C using dense specimens of composition $\text{UO}_{2.14}$. A maximum fiber stress of 5000 psi was applied for 2 hr to specimens of section 0.12 by 0.07 in., the distance between supports being 0.75 in. In an argon atmosphere at 800°C, the specimens showed a permanent deflection of about 0.001 in. and, at 1000°C, 0.040 in. In a hydrogen atmosphere at 1000°C, there was no deflection. With specimens heated to 700°C and held for 2 hr in hydrogen and then stressed at 1000°C in argon, no deflection was observed.

10 DISCUSSION OF SINTERING BEHAVIOR

Differences in degree of nonstoichiometry need not be invoked to explain the difference in sintering behavior of Mallinckrodt and Springfields oxides, since this could be explained solely on the basis of difference in particle size. The improvement obtained by oxidation of the Mallinckrodt material to $\text{UO}_{2.48}$ could also be a result of decreased particle size, but no surface area data were available for this material.

These results are therefore poor evidence in favor of an effect of nonstoichiometry alone upon sintering behavior. Particle size and composition are interdependent for powders stored in air; the finer the particle size the higher the oxygen content. The experimental results for variation of sintered density with oxygen content, however, show that for a powder, the particle size of which remains sensibly constant, variation of the uranium to oxygen ratio between 2 and ~ 2.04 does appreciably affect the sintered density, i.e., it makes the difference between 9.3 and 10.2 g/cm³. It cannot be said that the particle size remained truly constant, for Roberts⁸ has shown that, when single-phase nonstoichiometric powders prepared by room-temperature oxidation are heated above 200°C to give the two-phase ($\alpha + \beta$) UO_2 structure, the surface area increases by about 20 per cent. Our experience of this transformation is that it is sluggish and that, at the heating rate normally employed in sintering, the specimens could very well remain single phase throughout the cycle. If such an increase in surface area occurred, then there is no obvious reason why its effect upon sintering should saturate at $\text{UO}_{2.04}$. Furthermore, the surface area of this particle powder was about 8 m²/g, and other results quoted for sintering of powders in argon showed that variation in surface area of 2 to 6 m²/g had little effect upon sintering behavior. It is, therefore, believed that deviation from stoichiometry does favorably influence sintering behavior of uranium dioxide; there are three possible ways in which the excess oxygen can operate to influence sintering. For the nonstoichiometric oxides there are clearly volatilization processes occurring during sintering in argon and vacuum, involving loss of oxygen and uranium oxide. The effect of sintering in vacuum where such processes are accentuated was slightly to reduce the densities obtained compared with argon; reduction of rate of evaporation slightly improved sintering. The behavior of the tantalum and zirconium getters on adversely affecting sintering in argon could also be explained by their upsetting the solid-vapor equilibrium and increasing the rate of volatilization as was observed. The improvement in sintering behavior of nonstoichiometric uranium dioxide cannot be attributed to the higher vapor pressure of the nonstoichiometric compared with the stoichiometric oxide. The reverse would appear to be true.

All the powders used in the investigations described were prepared by hydrogen reduction of a higher oxide. In studies of the sorption of reducing gases on UO_2 , Roberts¹² has shown that hydrogen will be chemisorbed or absorbed during this method of preparation. Desorption of this hydrogen as hydrogen from stoichiometric UO_2 is achieved only in vacuum at 800°C, but, if the powder is allowed to oxidize, the hydrogen will desorb as water vapor at 200°C. Calculations show that for the powders used the excess oxygen needed to ensure removal of the hydro-

gen as water vapor would raise the composition to $\text{UO}_{2.02}$ to $\text{UO}_{2.05}$. The basis of this argument is that chemisorbed or absorbed hydrogen adversely affects sintering behavior and the only function of oxygen in excess of stoichiometry is to ensure its removal. The poor sintering behavior in hydrogen follows naturally from this hypothesis. Further support for this point of view comes from the results of sintering hydrogen-reduced stoichiometric pellets in vacuum and in argon. Removal of hydrogen would be expected to occur more readily in vacuum than in argon, and so the pellets, as was observed, should sinter more readily in vacuum than in argon. However, these stoichiometric pellets still sintered as readily in vacuum as the non-stoichiometric material from which they were prepared.

The adverse effect of certain metal additions upon the warm-compacting behavior of the nonstoichiometric oxides also argues for a beneficial effect of departure from stoichiometry upon the densification mechanism. This again could be explained on the basis of the chemisorbed or absorbed hydrogen being the real offender and the excess oxygen merely providing a means for its ready removal at low temperatures. The implication is that the added metals remove the oxygen before the hydrogen can combine with it and desorb as water vapor at about 200°C . This is unlikely since the hydrogen would be uniformly distributed through the oxide, whereas the metal would be present as relatively widely spaced particles. When $\text{UO}_{2.20}$ powder that had been heated in vacuum at a temperature sufficient to remove the hydrogen as water vapor was mixed with 5 wt. % iron powder that had been degassed to remove residual hydrogen and warm-pressed, a density of only 6 g/cm^3 was achieved. The failure to density could not, however, be attributed to the presence of adsorbed hydrogen. It therefore appears that the hydrogen hypothesis is unlikely to be the true explanation for poor sintering.

Carbon monoxide has a similar deleterious effect upon sintering to hydrogen, but, since it is chemisorbed to only a minor extent, the counterpart of the hydrogen hypothesis cannot be advanced in this case. As it reduces nonstoichiometric oxides to UO_2 , the adverse effect of the carbon monoxide can be explained on the basis that extra oxygen in uranium dioxide in excess of stoichiometry will accelerate sintering processes.

Thus, considering all the experimental data, only part of the improved sintering properties of nonstoichiometric oxides can be attributed to removal of adsorbed or absorbed hydrogen. The effect upon the densification mechanisms of extra oxygen atoms in solution in UO_2 still remains to be discussed.

The mechanism of flow causing densification can be basically either vacancy diffusion or dislocation movement, both in warm compacting or in sintering.

In dealing with the warm-compacting process, the only mechanism so far advanced by which applied stress can effect material transfer via a diffusion mechanism is that described by Herring and Nabarro.¹³ The expression derived for the viscosity η of a solid consisting of equiaxed grains is

$$\eta = \frac{kTR^2}{4D\omega_0}$$

where k = Boltzmann's constant

T = absolute temperature

R = radius of the grains

ω_0 = atomic volume

D = diffusion coefficient

This viscosity is of Newtonian character.

The compacting behavior of glass at 600°C is similar to that of uranium dioxide at 800°C , and glass has a viscosity of about 10^9 poises at 600°C . Assuming we therefore require the nonstoichiometric uranium dioxide to exhibit a higher viscosity of 10^{10} poises, substitution of the appropriate values in the expression leads to a D value of about $10^{-12} \text{ cm}^2/\text{sec}$ for the uranium dioxide complex. Oxygen diffuses more rapidly in UO_2 than uranium, so it can be assumed that the rate of uranium diffusion will be the rate-determining step for the complex. Recent American determination of D for uranium¹⁴ in stoichiometric UO_2 at 1550 and 1750°C can be extrapolated to give a value of $D = 10^{-24} \text{ cm}^2/\text{sec}$ at 800°C . This is about 10^{10} too small to give

a viscosity of the right order to explain warm pressing. Considering the case for sintering in a similar manner using copper as an analogy, the disparity in extrapolated and required diffusion coefficients is about 10^6 . These calculations may be in error by several orders of magnitude, but, even so, it appears that a small amount of oxygen in excess of stoichiometry will have to raise the self-diffusion coefficient of uranium in uranium dioxide by at least five to six orders of magnitude to explain experimental observations of the effect of nonstoichiometry on the sintering, on the warm-compacting of powders, and on the creep properties of the bulk oxides.

It is difficult to propose a mechanism by which departure from stoichiometry could affect sintering, warm compacting, or creep if a plastic flow mechanism involving dislocation movement was responsible for deformation. Pratt¹⁵ has described the effects of the presence of point defects on the mechanical properties of ionic crystals. He has considered the effects likely to arise from appreciable differences in the energies of formation of positive and negative ion vacancies. The first result could be the formation of a surface charge of the same sign as the vacancy which is more readily formed. Also dislocation lines would carry a charge of similar sign which is screened by a cloud of oppositely charged vacancies which would help pinning of the dislocations. If, for nonstoichiometric uranium dioxide, the oxygen vacancies are formed more readily than metal vacancies, then there will be a negative surface charge and negatively charged dislocations pinned by uranium ion vacancies. Thus the mobility of the dislocation within the crystal would be determined by the mobility of the cation vacancies, i.e., the diffusion coefficient of uranium. The repulsive force between the dislocation lines and surface would hinder their breaking surface to effect plastic flow, but for nonstoichiometric UO_2 the presence of U^{+6} ions and their concentration at the surface could neutralize the surface charge and aid plastic flow in this manner. The determination of the diffusion coefficients for oxygen and uranium in nonstoichiometric oxides is thus the next step in elucidating their sintering, pressing, and creep behavior.

The abnormal physical properties of nonstoichiometric oxides must influence their irradiation behavior. The possible significance of a high vapor pressure will be discussed later in connection with the irradiation results. Low creep strength could give rise to bubbling phenomena in irradiated UO_{2+x} at temperatures not greatly in excess of 1000°C . The determining factor would probably be the surface temperature and temperature gradient, i.e., the thickness of material at temperatures below 1000°C available to act as a restraining can.

II BEHAVIOR UNDER IRRADIATION

The desire to use UO_2 at the maximum possible rating results in a design of fuel element in which the center temperature is near or even exceeds the melting point of UO_2 . The appearance of fuel elements containing stoichiometric UO_2 running under these conditions has been illustrated in a paper by Kisiel.¹⁶ In specimens in which the center temperature has exceeded the melting point, a hole appears surrounded by a region in which the grain size of the UO_2 has increased significantly during irradiation. A significant way in which nonstoichiometric uranium dioxide differs from stoichiometric UO_2 is that of greater volatility of the former. Results quoted above indicate that a considerable loss in weight can occur at temperatures exceeding 1100°C , thought to be due to the volatilization of a higher oxide of uranium, possibly UO_3 . Stoichiometric UO_2 does not volatilize at these temperatures. Temperatures to which the UO_2 is subjected during irradiation are of course much higher than 1100°C ; in fact at the center of the rod the melting point is often exceeded. In fuel elements containing nonstoichiometric uranium dioxide, distillation of UO_3 from the hotter center and condensation in the cooler parts of the fuel element is a process that might continue indefinitely since, on cooling, the higher oxide decomposes and the oxygen evolved can then recombine after diffusing to the hotter center of the fuel element. This process will differ in some aspects from formation of a hole by melting. Melting on irradiation will occur as soon as the specimen reaches full power, and there will be no long-term changes provided there is no long-term change in the thermal conductivity of the material. In contrast to this the distillation process will be time-dependent, probably governed by the rate of diffusion of UO_3 and oxygen in the vapor phase so

that the size of the hole would increase slowly during burn-up of the fuel. Examination of the microstructure of a section of a fuel element containing nonstoichiometric uranium dioxide indicates that the surface of the hole has a ragged appearance, quite unlike the surface of a sample of nonstoichiometric oxide that had been arc melted. After arc melting, a smooth surface is formed during freezing. It would thus appear that the hole in the center of a fuel element containing nonstoichiometric uranium dioxide is increased in size by the evaporation process.

The second difference between nonstoichiometric uranium dioxide and UO_2 is that the former sinters to densities of 9.5 to 10 g/cm³ at temperatures as low as 1450°C in an inert atmosphere, whereas $\text{UO}_{2.0}$ sinters only at 1750°C and above. Materials sintered at 1450°C will, therefore, undergo further structural changes when exposed to the higher operating temperatures in the fuel element. The thermal stresses imposed by the steep temperature gradient and the thermal shock occurring during start-up and close-down of the reactor cause cracking, usually in a radial direction, but much less frequently circumferential cracking occurs. Examples of such cracks can be seen on polished sections of fuel elements. Since the can will usually hold the cracked surfaces closely together, it is possible for them to resinter on subsequent running at the operating temperatures so that during the next shutdown a fresh series of cracks appear. It is likely that the fresh series of cracks would occur in places where there was already internal stress due to the presence of fission-product gases. The region in which the previous set of cracks had occurred would be depleted of fission-product gases, and, therefore, the fresh set of cracks would occur in different regions from previous cracks. In this way, after a sufficient number of shutdowns, most of the specimen will at some time or another have been within a few microns of the surface of a crack. The macrostructure of irradiated nonstoichiometric uranium dioxide pellets indicates the formation of a central hole and development of a radial fibrous texture extending right to the outer surface of the fuel. The microstructure of this irradiated material strongly suggests that a series of radial cracks has formed at various times during irradiation, many of which subsequently heal up to a greater or less degree. The healed cracks appear as a line of bubbles, some of which appear distinctly as a fairly widely spaced series of bridges across what may have been a crack, whereas in the others the identity of the line of bubbles is almost completely lost. In addition, there are some cracks that have not healed.

One of the mechanisms by which cracks in nonstoichiometric uranium dioxide heal is that of deposition of volatilized oxide on their cooler surfaces, but the main sintering mechanism is probably due to the enhanced diffusion rates in the solid rather than to vapor-phase transfer. The series of healed cracks gives the specimen a fibrous appearance when the macrostructure is viewed. An alternative explanation of the formation of the lines is that by some mechanism columnar grains were formed during irradiation and the porosity in the material diffuses to the grain boundaries. This suggestion does not explain why the lines of bubbles form structures ranging from what appear to be slightly bridged cracks to indefinite rows of bubbles.

Much of the difficulty in interpreting the behavior of the specimens described in this paper arises from uncertainty in the temperature distribution within the specimen. The oxide pellets were of rather uneven shape, and the width of the gap between the fuel and the can has a large influence on the temperature conditions prevailing. The possibility that the specimens melted completely while the can remained intact and that the fibrous appearance was due to formation of columnar crystals during subsequent solidification would appear, however, to be unlikely, especially since the heat rating of the specimens was low.

Nonstoichiometric uranium dioxide will creep at appreciable rates at 1000°C. It seems likely, therefore, that in specimens with low permeability the inert fission-product gases xenon and krypton developed at burn-ups of about 0.2 per cent of all metal atoms could cause swelling (of the type observed in metallic fuels) at temperatures above 1000°C. This behavior might, therefore, require lower temperatures of operation in high-density material than are possible in high-density stoichiometric UO_2 . On the other hand the mechanism of cracking and healing described above might be an efficient way of removing the fission-product gases from the fuel material. This mechanism could prevent the swelling that might otherwise arise from the low creep strength of nonstoichiometric uranium dioxide.

12 CONCLUSIONS

The above description indicates that there are large differences in the fabrication, properties, and irradiation behavior of uranium dioxide caused by changes in the oxygen content and particle size. In considering how changes in composition affect the choice of material for use in fuel, it is necessary to balance the increased ease of fabrication of the nonstoichiometric material against its properties, which to some extent suggest that it may not be quite so satisfactory as a fuel although there has as yet been by far too little work to lead to anything like a definite conclusion. Most of the adverse comments are of a speculative nature, and in the final analysis a choice of material must depend on the behavior of the materials during large-scale fuel-element testing.

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Properties of Uranium Dioxide*

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ABSTRACT

Information on the out-of-pile properties of UO_2 is reviewed. Methods of preparation and characterization of UO_2 powders are discussed. Results of experimental studies on the sintering process for UO_2 are treated phenomenologically, and mechanisms for sintering are suggested. Results of some physical measurements made on UO_2 are discussed; these include melting point, thermal conductivity, modulus of elasticity, modulus of rupture, and electrical and magnetic properties. The thermodynamic and kinetic aspects of the $\text{UO}_2\text{-O}_2$ and $\text{UO}_2\text{-H}_2\text{O}$ systems are examined, and measurements and interpretations of self-diffusion of uranium and oxygen in UO_2 are discussed.

1 INTRODUCTION

Those properties of UO_2 which were considered to be important in determining either its structure or performance as a bulk fuel in PWR Core 1 and for which insufficient data were available to permit satisfactory prediction of behavior or interpretation of test results are discussed in this paper. Information, therefore, obtained at Bettis in recent years and at cooperating laboratories is described with respect to its implications on the performance of UO_2 bulk fuel and compared with previous data. This paper is confined to out-of-pile experiments; another paper¹ describes the in-pile performance of bulk UO_2 .

Characterization of various methods of UO_2 powder preparation was undertaken primarily to permit detection and control of such properties as particle size, surface area, and density, which might affect the final properties and performance of the bulk UO_2 fuel. Such information was found to be primarily applicable to fabrication behavior of the powder. For the fabrication conditions employed in PWR Core 1 where a dense sintered body results, differences in initial powder characteristics primarily affected the rate at which the final structure was obtained and only to a minor degree the characteristics of the sintered body. Sinterability of UO_2 was studied, not with respect to development of a fabrication method which had been developed for PWR by Glatter et al.,^{2,3} but in order to characterize its physical structure and change with density so that operational behavior could be correlated with physical structure. Also, those physical properties were studied which affected performance capabilities (thermal conductivity, melting point, modulus of rupture, and elastic modulus) or gave information on defect structure (electrical and magnetic properties). The equilibrium and kinetic studies of the $\text{UO}_2\text{-U}_3\text{O}_8$ system were undertaken to permit reconciliation of corrosion properties as well as operational behavior of defected fuel elements; the water corrosion behavior is of obvious importance for the PWR application. Self-diffusion rate measurements were undertaken primarily to shed light on the related problem of fission gas release.

Thus the presentation will be limited to the present status of information considered important to the PWR application.

*This paper may also be identified as Report WAPD-184.

2 PHYSICAL CHARACTERISTICS OF UO_2 POWDER PREPARATION

Considerable evidence has been accumulated that the characteristics of UO_2 powders are determined largely by their preparative history. It has been found, for example, that the density, crystallite size, and surface area of a UO_2 preparation depend upon the density, crystallite size, and surface area of the substance from which it was prepared.⁴ Published data⁴⁻⁶ on the surface area, density, porosity, crystallite size, and microstructure of UO_2 show wide variation. A recent study,⁷ portions of which are summarized here, was undertaken at Bettis Plant in an attempt to ascertain relations between the preparation of UO_2 and its physical properties.

In this work,⁷ UO_2 powders having a wide range of physical properties were prepared by several methods. These included (1) hydrogen reduction of the higher uranium oxides (UO_3 , $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, $\text{UO}_3 \cdot \text{H}_2\text{O}$, and U_3O_8) at temperatures ranging from 500 to 1700°C; (2) steam and air oxidation of uranium hydride and uranium metal; and (3) conversion into UO_2 of precipitated U(VI) salts (ammonium diuranate, uranyl oxalate, and uranium peroxide) by direct hydrogen reduction or by hydrogen reduction after pyrolysis in air to U_3O_8 .

The prepared UO_2 powders were analyzed for total uranium, U(IV), U(VI), and water content. U(VI) was determined by a modification of a polarographic method of Tishkoff.⁸ Total uranium and U(IV) were determined volumetrically by titration with standard potassium dichromate. The moisture content was obtained by direct absorption in magnesium perchlorate. The analytical methods have been described in detail previously.⁹ By these procedures the O/U ratios of the powders were determined with an accuracy of ± 0.01 or better.

Densities of the various powder preparations were determined by both gas (helium) and liquid (CCl_4) displacement. Density data obtained by the displacement of a fluid that can penetrate all pores and capillaries of a solid down to molecular dimensions are termed "real" densities. "Closed pores," which are voids completely surrounded by the solid matrix and thus inaccessible to any fluid except by diffusion through the solid, are arbitrarily considered as part of the "real volume" of the material. The helium atom has a small molecular diameter which enables it to penetrate into very fine pores; in addition there is negligible adsorption of helium on solids at room temperature.¹⁰ Therefore, density obtained by helium displacement most closely conforms to the definition of "real" or "particle" density. Measurements obtained by liquid displacement are usually lower because of incomplete penetration of the pores of the solid by the liquid.¹⁰

This "real or particle" density should be distinguished from the "x-ray," "ideal," or "crystallite" density, which can be calculated from the size of the unit cell and the atomic weights of its constituents, assuming that all lattice points are occupied.

Helium density values obtained on the same material having volumes of 2 cm³ agreed to ± 0.5 per cent, the precision increasing with increasing sample size. Precision for the liquid density measurements was within ± 0.2 per cent.

Surface areas of the powder preparations were determined by volumetric measurement of the adsorption of nitrogen on UO_2 at liquid nitrogen temperatures. Apparatus and procedure used were similar to those previously described.¹¹ Surface area values were calculated by application of the BET equation to the experimental data.¹² Sample weights were generally 10 to 30 g. Ten minutes was allowed for pressure equilibration before readings were taken. Four experimental points at relative pressures between 0.05 and 0.3 were obtained for the BET plot. A standard technique of degassing the samples at 400°C for 4 to 6 hr at a maximum pressure of 10^{-5} mm Hg was adopted since it was shown that at lower temperatures (100 to 300°C) adsorbed gases were incompletely removed for reasonable degassing times. Chemical analyses showed that no oxidation occurred on degassing. Values obtained on samples treated in a similar manner agreed to ± 5 per cent.

Surface area measurements obtained by gas adsorption techniques measure the total area of a solid. Porous bodies possess besides their external (macroscopic) surface an internal (microscopic) surface due to tiny pores and cracks. The effective mean particle size can be calculated from specific surface areas measured by gas adsorption assuming that the particles

are smooth regular spheres. However, a particle with a broken surface or one containing large cracks will be measured as several smaller particles.

Surface areas, densities (CCl_4 and helium), and microstructure examinations of some of these powder preparations are shown in Tables 1 to 4 and Figs. 1 to 4. The powders were mounted in and impregnated with a room temperature setting plastic. Polished and polished-and-etched cross sections of individual particles were used for the observations. Important observations are summarized below.

Measured densities of powders prepared by steam oxidation procedures approach the theoretical density value, 10.97 g/cm^3 (see Table 1), showing that these powders consist of dense granules (no closed porosity) with varying amounts of small open pores. Microstructures of two of these preparations are shown in Figs. 2a and b and agree with the

Table 1—PROPERTIES OF UO_2 PREPARED BY STEAM OXIDATION METHODS

Method of preparation	Reaction conditions	O/U	Fluid density, g/cm^3		BET surface area, m^2/cm^3
			He	CCl_4	
High-pressure steam oxidation of uranium (NOH)	72-hr oxidation at 343°C and 2200 psig	1.97	10.92 ± 0.1	10.75	12.9
Controlled low-pressure steam oxidation of uranium	24-hr oxidation at 150°C at 3.5 to 7.5 psig; dried 8 hr <i>in vacuo</i> at 700°C	2.02	10.85 ± 0.1	10.91	2.4
Uncontrolled low-pressure steam oxidation of uranium	5-hr oxidation at 350°C at 3.5 to 7.5 psig; heated in hydrogen 5 hr at 900°C	2.03	10.92 ± 0.05	10.85	9.0
Steam oxidation of uranium from uranium hydride (NHOL)	4-hr oxidation at 400°C at 5 psig; heated in hydrogen 15 hr at 700°C	2.03	10.98 ± 0.1	10.67	22.6

conclusions from density and surface area measurements in showing coarse, dense particles. The crystallite size of these preparations, from x-ray line broadening measurements, was found to be very fine. The helium and liquid densities of UO_2 powders prepared by hydrogen reduction of the higher uranium oxides were considerably below the theoretical density and were in close agreement (see Table 2), indicating that these oxides contain little open porosity but an appreciable amount of closed porosity. Again the microstructures, a typical one of which is shown in Fig. 4a, agree with the measurements in showing coarse particle sizes but considerable isolated porosity. These powders as well as those listed in Tables 3 and 4 showed little line broadening on x-ray examination and hence a relatively coarse crystallite size. Those powder preparations which have densities above theoretical (11.0 to 11.3 g/cm^3) have high O/U ratios (see Tables 3 and 4). For many of the UO_2 powders prepared by precipitation methods the liquid densities were less than the helium values (see Table 3), suggesting that these powders have varying amounts of small, open pores. There is no correlation between density and BET surface area; a high surface area can be associated with either a high or a low density. As compared with powders produced by pyrolytic means or by metal oxidation, the particle sizes of chemically precipitated powders are quite small.

The UO_2 powders prepared both by steam oxidation and hydrogen reduction of the higher uranium oxides had relatively low total surfaces for the most part (see Tables 1 and 2). Surface areas of UO_2 made by hydrogen reduction of UO_3 showed a marked dependence on the temperature of reduction (see Fig. 1). A considerable amount of particle growth as well as coalescence of pores is observed with increase in reduction temperature for these preparations (see Fig. 3). Reduction in line broadening, indicating increasing crystallite size with increase in reduction temperature, was also noted, in agreement with the observations of Anderson et al.⁴ on UO_2 from reduced U_3O_8 .

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Fig. 1—BET surface area of UO_2 prepared from hydrogen reduction of UO_3 at various temperatures.

For powders made through ammonium diuranate precipitation, the U_3O_8 ignition temperature is important in determining the surface area of the UO_2 product. The higher the temperature of ignition the lower the surface area (see Table 4). There is no apparent relation in surface areas between the parent ammonium diuranate and the derivative UO_2 powder.

As would be expected, a comminution treatment, such as ball milling, increases the surface area of UO_2 appreciably. This increase in surface area for ball milled UO_3 is also retained upon reduction to UO_2 . The effect of ball milling on the microstructure of Mallinckrodt (MCW) oxide is shown in Figs. 4a and 4b and on measured surface areas in Table 2. The effect of ball milling, from Fig. 4c, appears to be primarily breakup of the agglomerates in Fig. 4a.

The work described above thus revealed that UO_2 powders could be prepared over a wide range in particle size and density. As will be discussed later, such variations had a large effect on sintering rates of compacted powders at elevated temperatures but a relatively minor effect on structure, at least at sintered densities above about 93 per cent of theoretical.

3 SINTERING CHARACTERISTICS OF UO_2

As is well known, UO_2 can be fabricated into finished shapes by a number of conventional powder-metallurgy techniques. The UO_2 can be cold pressed, either in a die or hydrostatically, slip cast, extruded, or hot pressed.^{2,3} All but the last of these methods must be followed by a sintering process to obtain high density and mechanical strength. Sintering of UO_2 compacts must be carried out in a hydrogen or inert atmosphere since UO_2 readily oxidizes in air.

Table 2—PROPERTIES OF UO_2 PREPARED BY REDUCTION OF HIGHER OXIDES
(NONCHEMICAL PRECIPITATION)

Method of preparation	Reaction conditions	O/U	Fluid densities, g/cm^3		BET surface area, m^2/cm^3
			He	CCl_4	
Hydrogen reduction of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$	6 hr at 850°C	2.01	10.25 ± 0.05	10.25	8.8
Hydrogen reduction of $\text{UO}_3 \cdot \text{H}_2\text{O}$ crystals grown hydrothermally in an autoclave	2 hr at 1700°C	2.01	10.34 ± 0.05	10.37	0.5
Mallinckrodt oxide as-received (UO_3 redn.)	4 hr at 815°C	2.02	10.16 ± 0.05	10.13	6.4
Wet ball-milled MCW oxide (MA)	4 hr at 815°C	2.10	10.28 ± 0.1		53.1
Air ignition of Mallinckrodt UO_2 to U_3O_8 ; hydrogen reduction to UO_2	24-hr oxidation at 800°C ; 15-hr reduction at 780°C	2.01	10.35 ± 0.1	10.32	5.4
Air ignition of high-pressure steam oxidized UO_2 to U_3O_8 ; hydrogen reduction to UO_2	24-hr oxidation at 800°C ; 15-hr reduction at 780°C	2.01	10.69 ± 0.1	10.67	5.4
Air pyrolysis of uranyl nitrate hexahydrate to UO_3 ; air ignition of UO_3 to U_3O_8 ; hydrogen reduction to UO_2	48-hr oxidation at 740°C ; 16-hr reduction at 800°C	2.02	10.03 ± 0.05	9.96	5.7
Air pyrolysis of uranium metal to U_3O_8 ; hydrogen reduction to UO_2	15-hr oxidation at 800°C ; 16-hr reduction at 800°C	2.01	10.02 ± 0.1	10.07	5.8
Hydried-air oxidized uranium; hydrogen re- duction of U_3O_8 to UO_2	24-hr oxidation at 740°C ; 16-hr reduction at 800°C	2.02	10.32 ± 0.15	10.46	9.4
MCW UO_3 wet ball-milled in dilute H_2SO_4 ; hydrogen re- duction of UO_3 to UO_2 (NURS)	16-hr reduction at 800°C	2.04	10.68		17.5

Table 3—PROPERTIES OF UO_2 PREPARED BY DIRECT REDUCTION
OF URANIUM PRECIPITATES

Source	Reaction conditions	O/U	Fluid density, g/cm^3		BET surface area, m^2/cm^3
			He	CCl_4	
Ammonium hydroxide precipitated diuranate	32 hr at $850\text{--}950^\circ\text{C}$	2.07	11.11 ± 0.2	10.81	37.4
Urea precipitated diuranate	16 hr at 800°C	2.08	10.74 ± 0.2	10.19	42.1
Ammonia precipitated diuranate	56 hr at 900°C	2.05		10.85	40.8
Ammonium carbonate precipitated diuranate	64 hr at 900°C	2.06		10.30	40.1
Uranium peroxide	56 hr at 900°C	2.08	11.00 ± 0.1	10.78	12.0
Uranyl oxalate	64 hr at 900°C	2.01	10.61 ± 0.2	10.61	7.3

A study of the sintering characteristics of UO_2 has been made at Bettis Plant by Padden and coworkers,¹³ and a brief summary of the results is listed below. This program was carried out in three stages, each with a particular objective. The first phase of this study was an attempt to determine the relative importance of the variables involved in cold pressing and sintering various UO_2 preparations. The second phase was a detailed study of the sintering

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Table 4—PROPERTIES OF UO_2 PREPARED BY REDUCTION OF U_3O_8 OBTAINED FROM URANIUM PRECIPITATES

Methods of preparation	Reduction conditions	O/U	Fluid density, g/cm ³		BET surface area, m ² /cm ³
			He	CCl_4	
Air ignition (500°C) of ammonium hydroxide precipitated diuranate to U_3O_8 ; hydrogen redn. to UO_2 (NAIR-1)	32 hr at 800°C	2.14	11.09 ± 0.15	10.77	59.9
Air ignition (800°C) of ammonium hydroxide precipitated diuranate to U_3O_8 ; hydrogen redn. to UO_2	25 hr at 900°C	2.02	10.61 ± 0.15	10.71	9.7
Air ignition (500°C) of urea precipitated diuranate to U_3O_8 ; hydrogen reduction to UO_2 (NAIR-2)	32 hr at 900–1050°C	2.11	11.34 ± 0.2	10.47	60.4
Air ignition (800°C) of urea precipitated diuranate to U_3O_8 ; hydrogen reduction to UO_2	40 hr at 900°C	2.01	10.55 ± 0.15	10.43	6.0
Air ignition (500°C) of ammonia precipitated diuranate to U_3O_8 ; hydrogen reduction to UO_2	80 hr at 900°C	2.04		10.46	58.0
Air ignition (500°C) ammonium carbonate precipitated diuranate to U_3O_8 ; hydrogen reduction to UO_2	110 hr at 900°C	2.05		10.30	36.2
Air ignition (1000°C) of ammonium carbonate precipitated diuranate to U_3O_8 ; hydrogen reduction to UO_2	16 hr at 900°C	2.02		10.46	14.1
Air ignition (500°C) of uranium peroxide to U_3O_8 ; hydrogen reduction to UO_2	56 hr at 900°C	2.02		10.44	11.9
Air ignition (500°C) of uranyl oxalate to U_3O_8 ; hydrogen reduction	62 hr at 900°C	2.03		10.68	30.4

characteristics of two main UO_2 preparations. The third phase, still in progress, is a study of the structure of the final compact and in particular of the changes in grain size and the size, shape, and spatial distribution of pores with sintering of one particular UO_2 powder preparation. Summarized below are important conclusions from this study. A definition of terms used in this discussion is first given.

A UO_2 compact, either as-pressed (referred to as "green") or pressed and sintered, contains open (connected) pores and closed (unconnected) pores. The total volume of a UO_2 compact can be considered to be the sum of the open pore volume (A), defined as the void volume accessible from the surface, the closed pore volume (B), defined as the void volume not accessible from the surface, and the theoretical UO_2 volume (C). The theoretical UO_2 volume (C) is determined from the weight of the compact and the theoretical density of UO_2 . The closed pore volume (B) is calculated from a measurement by liquid (CCl_4) displacement of the sum of volumes B and C. This measurement is based on the operational definition that a closed pore is one inaccessible to CCl_4 . The open pore volume (A) is calculated from the weight of water absorbed by the compact.

Porosity (open and closed) can be expressed as the ratio of the pore volumes (open or closed) to either the UO_2 volume or to the total compact volume. For example, in microscopic examination or lineal analysis it is preferable to express open and closed porosities

(a)

(b)

Fig. 2—Microstructure of UO_2 prepared by steam oxidation. (a) UO_2 prepared by high-pressure steam oxidation. (Magnification 250 $\times$.) (b) UO_2 prepared by low-pressure steam oxidation. Magnification 250 $\times$.)

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(a)

(b)

(c)

Fig. 3—Effect of reduction temperature on microstructure of UO_2 prepared from UO_3 . (a) Reduced at 1650°C . (Magnification $250\times$.) (b) Reduced at 480°C . (Magnification $250\times$.) (c) Reduced at 800°C . (Magnification $250\times$.)

(a)

(b)

(c)

Fig. 4—Microstructure of three UO_2 powder preparations. (a) As-received MCW UO_2 . (Magnification 150 $\times$.) (b) Nair powder. (Magnification 250 $\times$.) (c) Wet ball-milled. (Magnification 500 $\times$.)

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as $A/(A+B+C)$ and $B/(A+B+C)$ since these fractions together with the UO_2 volume fraction total 100 per cent. For changes of open and closed porosity with sintering, however, these expressions are not satisfactory. Since closed porosity changes little and open porosity changes considerably with sintering, it is more meaningful to express the porosities as A/C and B/C . The density of the compact calculated from these porosity measurements can be compared with the density measured pycnometrically by mercury displacement. These calculated and measured densities agree to within 0.5 per cent. The accuracy of these porosity and density measurements depends on the assumption that the open pores are penetrated by water and CCl_4 but not mercury at 1 atm pressure. Mercury, which does not wet UO_2 , will not enter pores smaller than 15μ at 15 psi, whereas microscopic examination and measurements by a high-pressure mercury porosimeter show that the open pores in a green UO_2 compact are smaller than 15μ (see below).

3.1 Factors Affecting Sinterability of UO_2

Mallinckrodt (MCW) UO_2 was the main UO_2 preparation studied since it was chosen as the reference oxide for PWR Core 1. The effect of various variables on pressing and sintering of this oxide was studied.

MCW oxide was used as-received, fractionated, and with the O/U ratio modified by reduction in H_2 or by oxidation in O_2 . Oxidation to O/U ratios of 2.11 and 2.17 had no apparent effect on the microstructure of the powders. The powders were cold pressed to various densities with a manually operated press using double acting rams in a stearic acid lubricated die. It was found that sieve particle size had no effect and excess oxygen had little effect on the pressed density attained with pressing pressure (see Table 5). It was observed, however, that the higher the O/U ratio, the greater was the tendency to form cracks during pressing. The pressures used ranged from 26,000 psi for compacts having pressed densities of 51 per cent of theoretical to 325,000 psi for compacts having pressed densities of 73 per cent of theoretical.

The effects of sieve-size fraction, as-pressed density, and O/U ratio on the density of MCW oxide pellets subsequently sintered in hydrogen at 1700 or 1750°C or in argon at 1550°C were investigated. Conclusions reached from this study are as follows:

1. The sieve-size fraction of MCW oxide has little influence on the sintered density provided that compacts made from various sieve fractions are pressed to comparable green densities (see Table 6).
2. The as-pressed density of MCW powder compacts determines the sintered density attained after prolonged sintering in hydrogen. The sintered density approaches a plateau asymptotically, and this plateau level is related to the as-pressed density (see Figs. 5 and 6).

Table 5 — PRESSING CHARACTERISTICS OF VARIOUS UO_2 POWDERS

Powder	O/U ratio	Density, % theoretical		
		189,000 psi	227,000 psi	265,000 psi
MCW as-received size distribution	2.02	67.1	69.3	70.9
MCW +325 sieve fraction	2.02	66.8	68.8	70.7
MCW -325 sieve fraction	2.02	67.3	69.3	71.4
MA	2.10	72.1		
MCW as-received and oxidized	2.11	65.9	67.6	69.6
MCW as-received and oxidized	2.17	65.2	67.1	69.3
NURS	2.04	63.0	65.7	68.3

Table 6—EFFECT OF SIEVE PARTICLE SIZE ON SINTERED DENSITY
(1750°C, H₂, 48 hr)

Powder	As-pressed density, % theoretical	Observed sintered density, % theoretical	Corrected* sintered density, % theoretical
MCW as-received	56.1	84.5	84.4
MCW +325 sieve fraction	55.9	84.4	84.5
MCW -325 sieve fraction	56.4	86.4	86.0
MCW wet ball-milled	57.9	97.4	

* Corrected for the difference in the as-pressed density.

Fig. 5—Sintering rates of UO₂ powders.

3. Oxygen in excess of stoichiometric UO₂ is not beneficial in attaining higher densities in either hydrogen or flowing argon atmosphere; oxygen in excess of UO_{2.02} is lost during sintering in both atmospheres (see Table 7). Note however that Thackray and Murray¹⁴ have found that high densities are attained under sintering atmosphere conditions such that the oxygen content is retained at relatively low sintering temperatures by use of high O/U ratio UO₂ powders.

Studies on the effects of ball milling on the sintering characteristics of MCW oxide were made. The major effects, which are the same regardless of the mill or grinding media used, are:

1. Higher sintered densities are attained.
2. Rate of sintering is increased.

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Fig. 6—Effect of as-pressed density on sintered density for long-time sintering (1700°C, H₂).

3. A more uniform grain structure in the sintered pellet is achieved.
4. The dependence of sintered density on as-pressed density is essentially eliminated.

The last condition can be used as a measure of the efficiency of a milling procedure. For example, it was found that wet milling is more efficient a process than dry milling. In the work referred to in this discussion the milling conditions that were used were the following: rubber-lined mill, $\frac{3}{8}$ -in.-diameter uranium balls (1500 g) as the grinding media, 64 ml H_2O /200 g UO_2 , and a 16-hr milling time.

3.2 Sintering Characteristics of Some UO_2 Powder Preparations

The pressing and sintering characteristics of seven different UO_2 powders were investigated. Shown in Tables 1, 2, and 4 are the powder histories, surface areas, and densities of these preparations. The observed sintering characteristics are presented in Table 8. These include:

1. The condition of the pellets after sintering.
2. The density attained with compacts which were pressed to 65 per cent theoretical density and sintered in H_2 at $1700^\circ C$ for 64 hr.
3. The relative dependence of sintered density on pressed density.
4. The density attained after sintering for 8 hr at $1700^\circ C$.
5. Relative rankings based on surface area, powder density, and fully sintered density.

The following observations can be made from these data:

1. There is some correlation between high sintered density attained by the compact and both high surface area and high density of the powder. However, the UO_2 powder produced by steam oxidation has poor sintering characteristics even when the powder is made with high surface area and density.
2. The powder preparations which have good sintering characteristics are (a) UO_2 made from ammonium diuranate (NAIR-2 and NAIR-1) and not milled, (b) ball-milled Mallinckrodt UO_2 (MA) and (c) UO_2 prepared from ball-milled UO_3 (NURS).
3. As-received Mallinckrodt oxide is markedly inferior to four of the powder types studied and ranks sixth in the group of seven powders.

3.3 Density, Porosity, and Grain Size Changes Associated with Sintering

Results of the experimental work discussed in the previous section showed that factors relating to UO_2 powder structure are most important in sintering of UO_2 . It was suspected that a powder of "ideal" sintering characteristics, i.e., one that sinters rapidly to high density, shows little dependence of sintered density on green density, and produces a more uniform grain structure in the sintered material, was one that had a high surface area, a high density, and either small particles ($<3 \mu$) or clustered particles that could easily be broken down uniformly during pressing to small particles (see Figs. 4b and 4c).

A series of experiments was made to test these observations by establishing differences in sintering characteristics between a hypothetical "ideal" powder and one that was not "ideal." Wet ball-milled (as representative of the former) and as-received MCW oxides were chosen for this comparison. Other than the ball-milling treatment, these two powders had the same preparation history. In some experiments, UO_2 made from ammonium diuranate* (referred to here as NAIR-1 powder) was also tested for purposes of comparison.

In the first series of experiments, measurements were made of the densities attained by these powder preparations at several temperatures for different as-pressed (green) densities. In the second series of experiments, measurements and microscopical observations were made of the changes in density and porosity with sintering time at two temperatures for the

* Ignition of aqueous ammonia precipitated diuranate to U_3O_8 at $500^\circ C$; hydrogen reduction to UO_2 at $800^\circ C$.

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Table 7—EFFECT OF O/U RATIO ON SINTERED DENSITY

Powder	O/U	Nominal pressed density, % T	Corrected* pressed density, % T	Observed sintered density, % T	Corrected* sintered density, % T
Hydrogen 16 hr at 1700°C					
MCW	2.02	70.1	70.0	94.2	94.1
Reduced					
MCW	2.03	69.6	69.5	93.8	94.0
As-received		69.4	69.3	93.6	93.9
MCW	2.11	69.4	69.0	92.9	93.3
Oxidized					
MCW	2.17	70.0	69.3	92.3	92.6
Oxidized					
Hydrogen 64 hr at 1700°C					
MCW	2.02	69.8	69.7	95.8	95.9
Reduced					
MCW	2.03	69.0	68.9	95.6	96.0
As-received		69.2	69.1	95.5	95.8
MCW	2.11	69.3	68.8	94.8	95.3
Oxidized					
MCW	2.17	69.9	69.2	94.0	94.3
Oxidized					
Argon 10 hr at 1550°C					
MCW	2.02	69.7	69.6	92.6	92.7
Reduced					
MCW	2.03	68.9	68.8	91.3	91.8
As-received					
MCW	2.11	69.3	68.9	91.3	91.8
Oxidized		69.6	69.2		91.6
MCW	2.17	69.8	69.1	91.2	91.6
Oxidized		69.9	69.2		91.5

* The pressed density is corrected for the excess oxygen. The sintered density is corrected for both the excess oxygen and the difference in the as-pressed density from 69.8 per cent theoretical.

powder preparations pressed at two green densities. Supplementary experiments were made on the measurement of changes in grain size with sintering and on the distribution of pores in sintered pellets.

Results of these measurements and observations are shown in Figs. 5 to 17.

(a) *Effects of As-pressed Density on Sintered Density.* As-received MCW UO_2 and wet ball-milled MCW UO_2 powder (MA) were pressed to various green densities and sintered in hydrogen at 1700°C for various times between 72 and 240 hr. The sintering curves and the residual open porosities after sintering for 240 hr are shown in Fig. 6. The as-polished and the polished-and-etched microstructures of the group sintered for 240 hr are shown in Figs. 7 to 9. As can be seen from Fig. 6, the green density of as-received MCW powder compacts strongly influences the sintered density, whereas the green density of ball-milled powder compacts has very little effect on the sintered density. Sintered density still increases significantly in all cases after 152 hr at 1700°C. There are marked differences between the microstructures of compacts sintered from as-received MCW powder and from wet ball-milled powder. The former are heterogeneous both with respect to the spatial porosity distribution and grain size, whereas the latter have uniform structures throughout (Figs. 7 to 9).

Table 8—SINTERING CHARACTERISTICS OF UO_2 POWDERS

Powder*	Compact condition after sintering (based on pressed density)		Highest sintered density (64 hr 1700°C H_2)	Density reached in 8 hr in H_2 at 1700°C		Dependence of sintered density on pressed density	Relative rank based on	
			65% TDG	Pressed density	Sintered density		Surface area	Density
NURS	Good	55%						
	Slight	65%						
	Cracks		98.9% T	57.5% T	96.4% T	Slight	5	5
NAIR-2	Good	55%						
	Good	65%	98.7% T	55.3% T	95.4% T	Slight	1-2	1-2
MA	Good	55%						
	Good	65%	98.1% T	55.1% T	96.4% T	None	3	6
NAIR-1	Bad	55% T						
	Cracked	65% T	97.9% T	55.1% T	96.8% T	Slight	1-2	1-2
NHOL	Cracks	55% T						
	Good	65% T	94.7% T	55.3% T	79.2% T	Marked	4	3
MCW	Good	55% T						
As-received	Good	65% T	92.7% T	55.0% T	78.5% T	Medium	7	7
NOH	Flaky	55% T						
	Good	65% T	79.2% T	55.2% T	58.1% T	Marked	6	4

* See Tables 1, 2, and 4.

(b) *Changes in Porosity and Density with Sintered Density.* In Figs. 5 and 6 are shown the gross differences in the sintering rates of the three powder preparations at 1700°C. Similar differences were observed at 1500°C. Compacts were cold pressed to 65 per cent of theoretical density and sintered for various times. At intervals, compacts were removed from the furnace and measurements were made of sintered density and open and closed porosity. Since all of the compacts were cold pressed to essentially the same density, the total porosity in the compacts was the same initially for all three powders. Relative changes in the open and closed porosities are plotted as a function of sintered density in Figs. 10 to 12. It can be seen from Figs. 10 to 12 that

1. The shape of the curves for all these powders is the same when the powders are pressed to a density of 65 per cent of theoretical.
2. Initially, the closed porosity is constant for all powders.
3. The main mode of densification is the decrease in the amount of open porosity.
4. For a given density, the relative amounts of open and closed porosity are the same for each powder whether sintered at 1500 or 1700°C.
5. Each curve shows a rise in the closed porosity when the open porosity approaches zero in the range of density of 90 to 95 per cent theoretical.

The main difference in the powders is in the length of time required to reach identical conditions. For example, the time required to reach the density corresponding to the maximum point of the closed porosity curve decreases from 152 hr for MCW oxide to 7 hr for NAIR powder and only 1 hr for ball-milled powder. However, when MCW oxide is pressed to a density of 60 per cent theoretical or less, there is still residual open porosity after 240 hr at 1700°C, whereas ball-milled powder pressed to a density of only 55 per cent theoretical reaches zero open porosity and maximum closed porosity in approximately 1 hr. Porosity changes in the NAIR powder compacts are intermediate in nature between the other two.

It may be noted that for all three powders the curves for open porosity versus density, if extrapolated linearly, show zero open porosity at 95 to 97 per cent theoretical density. The more precipitous decrease at 91 to 93 per cent and the increase in closed porosity may be related either to a more rapid disappearance of pores as they decrease in size and hence a true "pinching-off" of primarily open porosity or to the difficulty of measuring access of

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(a)

(b)

Fig. 7—Effect of as-pressed density on microstructure; MCW UO_2 sintered 240 hr in H_2 at 1700°C . (a) Left and right: 82.7 per cent TDS; 51.7 per cent TDG; 15.1 per cent OP/comp. vol. (Magnification 250 $\times$.) (b) Left and right: 87.0 per cent TDS; 55.2 per cent TDG; 10.2 per cent OP/comp. vol. (Magnification 250 $\times$.)

Fig. 8—Effect of as-pressed density on microstructure: MCW UO_2 sintered 240 hr in H_2 at 1700°C . (a) Left and right: 88.4 per cent TDS; 58.6 per cent TDG; 7.8 per cent OP/comp. vol. (Magnification 250 $\times$.) (b) Left and right: 93.9 per cent TDS; 65 per cent TDG; 0.0 per cent OP/comp. vol. (Magnification 250 $\times$.)

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(a)

(b)

Fig. 9—Effect of as-pressed density on microstructure: wet ball-milled MCW UO_2 (MA powder) sintered 240 hr in H_2 at 1700°C . (a) Left and right: 99.5 per cent TDS; 54.2 per cent TDG; 0.0 per cent OP/comp. (Magnification $250\times$.) (b) 99.7 per cent TDS; 66.3 per cent TDG; 0.0 per cent OP/comp. (Magnification $250\times$.)

Fig. 10— Porosity as a function of density.

water to pores of small dimension. If the linear extrapolation to 95 to 97 per cent density is valid, a marked change should be noted in surface area at such densities; this point will be further discussed. Note also that the grain size of wet ball-milled powder compacts increases only to a minor extent at densities up to about 96 per cent of theoretical and then increases rapidly as densification proceeds.

(c) *Mercury Porosimetry Measurements.* Pore size and distribution of pressed and sintered UO₂ compacts were measured by high pressure mercury porosimetry at Bettis Plant. This technique is based upon the relation given by Washburn,¹⁵

$$d = \frac{-4\gamma \cos \theta}{p}$$

where d = diameter of a pore which can be entered by mercury under pressure p

γ = surface tension of mercury

θ = angle of contact between mercury and the porous UO₂

p = absolute pressure

The surface tension of mercury was assumed to be a constant 480 dynes/cm. The contact angle between UO₂ and mercury was assumed to be 140°C. (This is the accepted value for most materials.) The basic problem is that of measuring the volume of mercury which is absorbed by a porous solid under a known pressure. A pore size distribution curve may be constructed from the volume measurement and the pore diameter which is obtained from the above equation.

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Representative pore size distribution curves for the powders and compacts investigated are shown in Figs. 12 to 16 for the three powders investigated and for a representative sintered powder (MCW ball milled). A wide variation in pore size distribution was also found in the compacts, pressed to comparable green densities, and is due to the differences in the parent powders. Small particles are capable of packing together tightly, thereby yielding a compact having pores of small and uniform size; thus, at comparable green densities, ball-milled MCW oxide yields a much more uniform distribution of sizes than does as-received MCW oxide.

Increase in green density was found to result in a decrease in the average pore size and a narrowing of the size range of pores. This finding is interpreted to mean that densification due to cold pressing occurs primarily through the progressive compression of the larger pores. Particles surrounding small pores are wedged together tightly and are thereby able to resist compacting forces.

The effect of sintering on the pore size distribution curves is shown in Figs. 15 and 16. These measurements were made on compacts sintered in H_2 at $1500^\circ C$. The pore size distribution measurements (Figs. 15 and 16) corresponding to the sintering curves (Figs. 10 to 12) indicate a direct correlation between sintering rate and pore size. The powder having the highest sintering rate (ball-milled MCW) contains the largest volume of small pores. The other two materials contain pores of larger diameter and their sintering rates are correspondingly lower. Pore size distribution charts show that for MCW as-received and NAIR compacts the average pore diameter increases with sintering time at least for sintering times up to 16 hr. Disappearance of small pores is accompanied by formation of pores which are larger than those present in the original compact. The pores in ball-milled MCW oxide

Fig. 11—Porosity as a function of density.

exhibited a somewhat different behavior; the formation of larger pores occurred only during the first 20 min of sintering. Extending the sintering time resulted in a uniform shrinkage of all pores. This observation is similar to the observation of formation of large pores at the expense of small pores in copper compacts by Rhines, Birchenall, and Hughes.¹⁶

(d) *Grain Size Measurements.* In some metal and ceramic systems, isothermal grain growth is related to time by the expression $D = Kt^n$, where D is the mean grain diameter, K is a temperature dependent constant, t is the time, and n is an exponent characteristic of the material. If grain growth in UO_2 follows this relation, a plot of the logarithm of the mean grain diameter versus the logarithm of time should give a straight line having a slope n . Grain sizes were measured from light micrographs of polished and etched sections of wet ball-milled MCW oxide compacts that were sintered at 1500 and 1700°C. Approximately 100 grains were used to determine the mean grain diameter of each compact. Data (shown in Fig. 17) fall reasonably close to a straight line having a slope of 0.67, at least up to grain diameters of 10 μ , indicating that the relation $D = Kt^n$ describes grain growth during the isothermal sintering (1500 and 1700°C) of this oxide.

At longer sintering times at 1700°C, note that the value of n decreases to much less than the value of 0.67. Padden has also heated pellets of MCW UO_2 previously sintered to a grain size of 6.2 μ at 1700°C to higher temperatures and obtained the following variation of grain size with heating time and temperature.

Temp., °C	Time, min	Pore grain size, μ
1700	As-sintered	6.2
2000	15	13.04
2200	15	18.8
2415	15	41.6
2300	4½	19
2300	9	28
2300	19	16.8
2300	38	24.02

Fig. 12—Porosity and grain size as a function of density.

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Padden correlated the above data on the basis of an index $n = 0.1$; the variations of K with temperature for these data were assumed to follow an Arrhenius plot, and an activation energy of 23,000 cal/mole applied. However, for the data presented in Fig. 17 where an index $n = 0.67$ applies, the activation energy was 59,000 cal/mole. Note, by comparing Figs. 12 and 17, that the sintering time at 1700°C at which deviation occurs from the relation $D = Kt^{0.67}$ is about 10 hr, corresponding to a density of about 97 per cent of theoretical. From the discussion above, this is about the density at which the open porosity extrapolates to zero. The significance of these relations will be discussed later.

(e) *Microscopic Examination of Sintered Compacts.* Explanation of the dissimilarity in some of the sintering characteristics of as-received and wet ball-milled MCW UO_2 can be made from the microscopic observations (Figs. 7 to 9) and the mercury porosimeter data (Figs. 13 to 16) for compacts sintered from these powders. The differences in the effect of green density, the amount of residual open porosity after prolonged sintering, the sintered compact grain size distribution, and the residual porosity size and spatial distribution can all be attributed to the type of shrinkage involved. As-received MCW powder compacts shrink nonuniformly on a microscale, but the ball-milled powder compacts shrink uniformly. This dissimilarity in the mode of shrinkage is the result of the difference in the porosity size and spatial distribution existing in the as-pressed compact; the latter in turn is the result of the powder particle structure.

From the micrographs (Figs. 7 to 9) it can be seen that in sintered MCW powder compacts there are areas which have sintered to high density and large grain size, whereas other areas contain numerous pores, have lower density, and have smaller grain size. Frequently, the high density areas are surrounded by a ring of pores more or less outlining the high density areas. These effects are more pronounced the lower the green density of the MCW powder compacts prior to sintering and are absent in ball-milled powder compacts which had green densities as low as 54.2 per cent of theoretical prior to sintering. Note by comparison of Fig. 4a with Figs. 7 and 8 that the original powder particle size can still be distinguished in pressed and sintered compacts and that the high density, large grain size regions can be identified with the original particles.

Fig. 13—Effect of powder preparation on the pore size distribution of UO_2 compacted to 65 per cent of theoretical density.

Fig. 14—Effect of powder preparation on the pore size distribution of UO_2 compacted to 65 per cent of theoretical density.

Fig. 15—Effect of sintering time at 1500°C in hydrogen on the pore volume distribution of MCW ball-milled UO_2 .

If it is assumed that these local areas of high density in the as-pressed compacts of Mallinckrodt powder are areas which potentially sinter faster than the surrounding matrix and that such a condition is absent in ball-milled powder compacts, the microscopic observations and the porosimetry data can be explained. During the initial sintering of Mallinckrodt powder compacts, the high density areas existing in the green compacts sinter faster than the

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Fig. 16—Effect of sintering time at $1500^\circ C$ in hydrogen on the pore volume distribution of MCW ball-milled UO_2 .

Fig. 17—Rate of grain growth.

surrounding matrix and thus pull away from the matrix in which they are set, either leaving a ring of pores or enlarging the pores in the immediate vicinity. Since these high density areas contain fewer pores than the surrounding matrix, grain growth would not be inhibited as much in these areas as in the low density matrix and so nonuniform grain growth would result. Thus, during the initial stages of sintering, the pore size distribution would become broader, that is, would shift toward the larger pore sizes, and would become more heterogeneously distributed in the compact. Thereafter, as the sintering rate of the high density areas slows down, the matrix might continue to shrink, tending to fill in the pore space around the high density areas and thus cause a reversal in the porosity distribution shift, that is, cause a shift toward the smaller pore sizes (see Figs. 15 and 16). If, however, the as-pressed compact is very heterogeneous, as might be the case in low density Mallinckrodt compacts, the initial increase in pore size, the existing heterogeneous spatial distribution of the pores, and the nonuniformity of grain growth may not be overcome by subsequent sintering. Thus, even after prolonged sintering at high temperature, considerable amounts of residual porosity heterogeneously distributed and a nonuniform grain size distribution would remain. It would also be expected that the extent of this effect would be related to the green density. On the other hand, as-pressed ball-milled powder compacts with a uniform distribution of porosity, even at low green density, would sinter uniformly and with uniform grain growth. After prolonged sintering, compacts of uniform distribution and grain size would result, and little or no effect of green density would be observed.

3.4 Pore Structure

Additional information on the changes in pore structure and distribution associated with sintering of UO_2 was obtained by T. R. Padden by electron microscopy. This study was made on ball-milled MCW oxide compacts taken from those that were sintered at either 1500 or 1700°C in the studies discussed above.

As-fractured surfaces from mechanically cleaved compacts were used in this work in order to avoid distortion of the size and shape of the pores that could result from polishing. As will be shown later (see Fig. 18), fracture at room temperature proceeds both at grain boundaries and transgranularly. Thus certain of the surfaces in Figs. 19 to 23 may be grain boundary surfaces and others intracrystalline surfaces. These cannot be distinguished in the figures.

A chromium-backed replica technique was developed¹⁷ for this investigation. In this technique, as-fractured pellets with the pores exposed are replicated with carbon, which is backed with an evaporated chromium film containing numerous holes or windows. The composite film is etch released and manipulated without additional backing. Subsequent dissolution of the chromium is unnecessary.

The results of this study are shown in Figs. 19 to 23 and are summarized below. It can be seen from Fig. 12 that data at both temperatures follow essentially the same curves. No difference was observed in the microstructures from comparable compacts pressed to the same density from the same powder and sintered to the same density at these two temperatures (1500 and 1700°C). Comparison is therefore made on the basis of density and not sintering temperature.

Referring to Figs. 19 to 23, Fig. 19a is an electron micrograph made from a replica of wet ball-milled MCW UO_2 powder. Figure 19b, made from an as-fractured compact surface, shows that at a density of 81.4 per cent of theoretical there are two classes of pores: large irregular pores apparently located on the grain boundaries and small regularly shaped pores usually observed in clusters inside the grains. At a density of 90.9 per cent theoretical (Fig. 20a) the microstructure is qualitatively the same as that observed at a density of 81.4 per cent of theoretical (Fig. 19b). Pronounced changes in pore structure occur in the density range from 91 to 98 per cent theoretical. At a density of 94.4 per cent theoretical the large irregular pores have already begun to spheroidize (Fig. 20b), and some of the pores exhibit well developed planes on their surfaces. When a density of 97.6 per cent of theoretical is reached (see Figs. 21a and 21b), the majority of the pores show well developed planes and

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(a)

(b)

Fig. 18—Transgranular and intergranular fracture in wet ball-milled MCW UO_2 . 98.9 per cent TD. (Magnification 500 x.)

Fig. 19—(a) Wet ball-milled MCW UO_2 powder. Carbon replica of particles. (Magnification 6800 $\times$.) (b) As-fractured ball-milled MCW UO_2 compact sintered to 81.4 per cent TD. (Magnification 6500 $\times$.)

Fig. 20—(a) As-fractured ball-milled MCW UO_2 compact sintered to 90.9 per cent TD. (Magnification 6700 $\times$.) (b) As-fractured ball-milled MCW UO_2 compact sintered to 94.4 per cent TD. (Magnification 2600 $\times$.)

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Fig. 21 — (a) As-fractured ball-milled MCW UO_2 compact sintered to 97.6 per cent TD. (Magnification 6800x.) (b) Different area from same sample as (a). (Magnification 7100x.)

Fig. 22 — (a) As-fractured ball-milled MCW UO_2 compact sintered to 98.8 per cent TD. (Magnification 6800x.) (b) As-fractured ball-milled MCW UO_2 compact sintered to 98.8 per cent TD. (Magnification 6500x.)

(a)

(b)

Fig. 23—(a) As-fractured ball-milled MCW UO_2 compact sintered to 98.7 per cent TD. (Magnification 13,300 $\times$.) (b) As-fractured ball-milled MCW UO_2 compact sintered to 98.7 per cent TD. (Magnification 32,000 $\times$.)

fairly regular geometry and some exhibit very pronounced growth steps. Occasional clusters of small pores are still present. When this density is reached, it is apparent that at least some of the large pores have the symmetry of a truncated octahedron; i.e., a polyhedron bounded by the $\{111\}$ and the $\{100\}$ planes.

In Figs. 22a and 22b, made from compacts having densities of 98.8 per cent of theoretical, the pores show very well developed truncated octahedral symmetry. There is also a variation in pore shape with pore size. The smaller pores are in general bounded by planes only, whereas the larger pores are bounded by both planes and curved surfaces. These smaller pores probably originated from the large pore class because they are still larger than the pores in the clusters observed at lower density. Figures 23a and 23b show that at least some of the larger pores in the high density compacts are bounded by both spherical surfaces containing symmetrically positioned concentric growth steps and well developed planes having the symmetrical arrangement of a truncated octahedron.

The angles were measured between the planes and the centers of the concentric growth steps observed on the pores in Fig. 23a. From these measurements, the truncated octahedron symmetry was verified; that is, the planes observed in the pores are the $\{111\}$ and the $\{100\}$ planes, and it was also determined that the centers of the concentric growth steps are along the $\{110\}$ directions. These steps appear to be the edges of $\{110\}$ planes. If it is assumed that these edges tend to conform to the curvature of the sphere, a height difference of approximately 50 Å between steps is obtained. Apparently the symmetry observed for UO_2 pores is somewhat analogous to the symmetry associated with crystal growth. The main difference is, of course, that in the case of a pore it is the symmetry of the surface of a cavity in a solid that is related to the crystallographic structure of the solid, whereas in the case of a crystal it is the symmetry of the surface of the crystal of the solid itself. The crystallographic unit cell of UO_2 has the fluorite structure and should have the idiomorphic crystal growth pattern of fluorite. According to Winchell,¹⁸ CaF_2 is isometric hexoctahedral; the crystals are usually cubic, octahedral, and sometimes dodecahedral. It is not too surprising, therefore, that the cube and octahedron symmetry and planes, the $\{100\}$ and $\{111\}$ planes, respectively, are observed in pores in UO_2 .

3.5 Effective Surface Area of Sintered UO_2

The BET method¹² of measurement of specific surface area of a solid by low temperature gas adsorption should, in principle, provide a measure of total accessible surface of the solid. For a sintered material, for example, high density UO_2 , the extent of open porosity should be measurable by both gas adsorption and water pickup.

Surface area measurements made at Bettis Plant by krypton or butane gas adsorption on hydrogen sintered oxide compacts are listed in Table 9. It appears from the data that significant amounts of connected porosity persist in high density UO_2 even though water absorption measurements indicate the absence of connected voids. These data may be reconciled with the extrapolations made in Figs. 10 to 12 of open porosity versus density by assuming that the apparent open porosity measured by water absorption becomes increasingly in error as the size and amount of the pores decrease. The extrapolations in Figs. 10 to 12 show that open porosity should be negligible at densities above about 97 per cent of theoretical, but that significant interconnected surface could persist below such densities. The data in Table 9 are entirely consistent with this hypothesis. Note that Eichenberg et al.¹ make considerable use of these data in explaining fission gas release from irradiated UO_2 .

3.6 Steam Sintering of UO_2

The effect of steam on the sintering of UO_2 was investigated at Armour Research Foundation,¹⁹ Corning Glass Works,²⁰ and Bettis Plant.¹³ Summaries of the information obtained from these studies are shown in Tables 10 to 12 and Figs. 24 and 26.

In the ARF work, MCW oxide, ball-milled* and cold pressed at 30 tsi, was sintered in both oxidizing and reducing atmospheres at temperatures up to 1500°C. It can be seen from

*The -325 sieve size fraction was wet-milled in a glass mill with flint pebbles.

Fig. 24—Density and O/U ratio changes of UO_2 pellets as a function of sintering time, temperature, and atmosphere.

Fig. 25 — Equilibrium oxygen pressures extrapolated as a function of reciprocal temperature.

Fig. 26 — Variation of densification rate of UO₂ as a function of temperature.

the results (shown in Table 10) that steam aids in densification but only when hydrogen is used for cooling from the soaking temperature of 1500°C. Pure steam however, is not necessary since an inert wet gas leads to high densification. Although wet hydrogen appears to be better than dry, the presence of hydrogen diminishes the effectiveness of steam. The effect of steam is also decreased when used in the cooling part of the sintering cycle. Results of various soaking times and temperature (shown in Table 11) indicate that the optimum temperature for introducing steam is about 1400°C and that the optimum soaking period is about 2 hr at 1400°C or 1 hr at 1500°C.

An explanation for the densification caused by exposure to steam was suggested by Armour Research Foundation. The formation of hydroxyl and oxygen free radicals from the dissociation of steam could penetrate the UO_2 lattice, oxidizing U^{4+} to higher oxidation states, creating a defect structure, and thereby promoting the mobility of the lattice ions.

In the Corning Glass Works study, it was found that UO_2 pellets having a density of 96.5 per cent of theoretical could be made by firing in steam for only 4 hr at temperatures as low as 1300°C. Hydrogen was not eliminated, however, since a 1200°C exposure to hydrogen for 2 hr was found to be necessary. Ball-milled* MCW oxide was also used in this investigation.

It was found that hydrogen is necessary in the presintering atmosphere but not in the postsintering atmosphere. Oxygen picked up during the steam-sintering process is retained if cooling is done in steam. It was found that the steam-cooled pellets consisted of two cubic phases,† UO_2 and U_4O_9 , and had O/U ratios of about 2.19. If cooling is done in H_2 rather than steam, however, the resulting O/U ratio is 2.03 and only a single UO_2 phase shows up by x-ray analysis.

These facts were interpreted by the Corning workers to mean that the reaction

is driven to the right in flowing steam, subject to the tendency of the UO_{2+x} to dissociate according to the reaction

Since reaction 1 is faster than reaction 2, UO_2 is oxidized in flowing steam. In flowing hydrogen, on the other hand, reaction 2 is rapidly driven to the right toward nearly stoichiometric UO_2 .

Additional studies were made at Bettis Plant¹³ on the effect of steam on the sintering of UO_2 . Two different powder preparations were used: as-received MCW oxide and wet ball-milled MCW UO_2 . Two groups of pellets with green densities of 55 and 65 per cent of theoretical were pressed from each powder. Two pellets of each powder preparation and green density combination were sintered in each cycle.

The steam sintering cycle suggested by Corning Glass Works was chosen for further study. Results obtained for this cycle (shown in Column A of Table 12) were comparable to those reported by Corning. By substituting argon for steam in this cycle (see Column B of Table 12), the importance of steam in producing high density material at these low temperatures was confirmed. It is evident from the data in Column C of Table 12 that the hydrogen soak period is a necessary part of the cycle.

Since it was established that both hydrogen and steam atmospheres are apparently essential, an experiment was made to determine the portions of the cycle in which sintering took place. This was accomplished by sintering to certain points in the cycle and subsequently cooling in the atmosphere which was present at the time at which the cycle was interrupted. Results of these measurements are shown in Fig. 24. The lower curve shows the time-temperature-atmosphere conditions, and the upper curves represent the sintered densities and O/U ratios corresponding to points on the lower curve. It can be seen that densification during steam sintering occurs during the heating periods to 1200°C and between 1200 and

*Ball milling was done dry in a Borundum mill using Borundum grinding cylinders for 16 hr.

†The phases were distinguishable by x-ray analysis but not by low-power microscopic observation.

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Table 9—SURFACE AREAS, POROSITIES, AND DENSITIES OF SINTERED UO_2 COMPACTS

Type of sample	Treatment	Density, % theoretical	Open porosity,* %	BET surface area, cm^2/g	Roughness† factor	Adsorbate
MCW oxide pellets	Centerless and end ground	93.1–93.8	1.3–2.2	46 ± 10	70	Butane
MCW ball-milled UO_2 pellets	As-sintered	98.9	0	1.3 ± 0.6	2	Butane
MCW ball-milled UO_2 pellets	As-sintered	94.4–94.8	0	3.3 ± 0.7	4.4	Ethane
MCW ball-milled UO_2 pellets	As-sintered	98.0	0	1.9 ± 0.9	3	Butane
MCW ball-milled UO_2 plates	As-sintered	96.6	0.6	4.8 ± 1.2	12	Butane
MCW ball-milled UO_2 pellets	Hand-ground	94.5	0	11.4 ± 2	15	Butane
Steam oxidized UO_2 pellets	As-sintered	70		5180		Krypton
MCW oxide pellet	As-sintered	89		257		Krypton
MCW oxide pellet	As-sintered	94.3		76.7		Krypton
MCW oxide pellet	As-sintered	96.5		37.5		Nitrogen

* As measured by water absorption.

† Ratio of BET area to geometrical area.

Table 10—EFFECT OF ATMOSPHERE ON SINTERING OF UO_2

Atmosphere*	Sintered density, % theoretical	O/U ratio
H_2 only	81.2	2.00
Air 1400–1500°C†	86.9	2.00
Steam 1400–1500°C†	97.7	2.01
Steam only	8.22	2.10
98 H_2 + 2 H_2O only	85.8	2.00
84 H_2 + 16 H_2O only	85.8	2.00
62 H_2 + 38 H_2O only	88.4	2.01
98 He + 2 H_2O 1400–1500°C†	97.3	2.00
43 He + 57 H_2O 1400–1500°C†	97.7	2.00
98 He + 2 H_2O only	86.3	2.09
98 N_2 + 2 H_2O 1400–1500°C†	95.6	2.01
98 N_2 + 2 H_2O only	82.9	2.11

* Soaking time 1 hr at 1500°C in indicated atmosphere.

† H_2 up to 1400°C and down from 1500°C.

1400°C, and during the “soak” period at 1400°C. No densification was observed during the 2-hr soak at 1200°C in hydrogen. Metallographic examination of a pellet that had been sintered to an O/U ratio of 2.19 revealed the presence of a second phase, identified by x-ray diffraction analysis as U_4O_9 , in confirmation of the Corning work.

That uranium oxides of composition near $\text{UO}_{2.19}$ are attained by steam sintering is in agreement with an extrapolation from data on oxygen pressures in equilibrium with uranium oxides (see Sec. 5). Such an extrapolation is shown in Fig. 25. At approximately 1400°C, the O_2 pressure in equilibrium with $\text{UO}_{2.19}$ is estimated to be approximately 2.2×10^{-4} atm (0.17 mm Hg). A calculation of the equilibrium oxygen pressure from the reported value²¹ for the dissociation of water at 1705°K (1432°C) gives a value of 5.10×10^{-4} atm (0.39 mm Hg), equivalent to an estimated O/U ratio from the plot (Fig. 25) of 2.21.

The reasons for formation of a higher oxide ($O/U = 2.19$) and the presence of U_4O_9 upon steam sintering can be explained. UO_2 is oxidized, and at these temperatures (about 1400°C) oxygen is soluble in the nonstoichiometric UO_{2+x} lattice. U_4O_9 is not stable above 1167°C (reference 22), but upon cooling, this second phase, now stable, appears. With cooling in hydrogen after steam sintering, U_4O_9 is reduced to UO_2 .

Some other highly significant effects were noted in this study. The grain sizes of compacts sintered in steam to the same density as those in hydrogen were the same size even if the former were performed at 1400°C and the latter at 1700°C . This is additional confirmation of the observation made previously that grain size depends primarily on sintered density and hence on grain structure. Another significant observation is plotted in Fig. 26, in which the activation energies for sintering in steam are compared with those for hydrogen sintering. For

$$\alpha = \frac{\text{density at time} - \text{green density}}{\text{theoretical density} - \text{green density}} = 0.5$$

the activation energy for steam sintered MCW as-received powder is 30,500 cal/mole, and that for hydrogen sintered powder is 76,000 cal/mole.

3.7 Sintering Mechanism of UO_2

From the data presented above, a mechanism for the sintering of UO_2 has been postulated and is presented below. From the data presented in Table 2, it is clear that the initial particles of the oxides used in these sintering studies contain both open and closed porosity. On cold-pressing into compacts, additional open porosity is formed between the powder particles. It is postulated that two mechanisms operate simultaneously to remove the open and closed porosity, the one either a viscous or plastic flow²³ or evaporation and condensation²⁴ mechanism and the other a bulk diffusion mechanism.²⁵ As will be shown later, at sintering temperatures of 1700°C or below, the diffusion rate of oxygen ions in UO_2 is many orders of magnitude greater than that of uranium ions and has an activation energy of about 30,000 cal/mole. The operative diffusion rate in UO_2 will therefore be sensitive to the excess oxygen content. In steam sintering, because of the UO_2 - O_2 equilibria described below, a high concentration of excess and mobile oxygen ions is present (about 0.19 mole fraction), and hence the diffusion rate is expected to be quite high. In hydrogen sintering, on the other hand, the concentration of excess oxygen is vanishingly small, and only that oxygen ion mobility will be noted which corresponds to the thermodynamic equilibrium amount of disorder in oxygen ion

Table 11—OPTIMUM TIME AND TEMPERATURE FOR STEAM SINTERING*

Temperature† range of steam, $^\circ\text{C}$	Soaking time, hr	As-pressed density, % theoretical	Sintered density, % theoretical
1200–1500	1.0	59.3	87.2
1300–1500	1.0	59.3	95.3
1400–1500	1.0	62.0	96.3
1200	2.0	62.0	77.4
1300	2.0	61.5	91.8
1400	2.0	60.1	96.9
1400	1.0	62.0	90.4
1400	0.5	62.0	85.7
1400–1500	2.0	60.1	96.8
1400–1500	1.0	60.1	96.6
1400–1500	0.5	62.0	93.6

* Milling time 8 hr.

† H_2 to indicated temperature and on cooling.

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Table 12 — EFFECT OF ATMOSPHERE, POWDER PREPARATION, AND GREEN DENSITY ON THE SINTERED DENSITY OF UO_2 COMPACTS

Temperature, °C	Atmosphere			
	A	B	C	
25–300	Argon	Argon	Argon	
300–1200	Steam	Argon	Steam	
2 hr soak at 1200	Hydrogen	Hydrogen	Steam	
1200–1400	Steam	Argon	Steam	
1 hr soak at 1400	Steam	Argon	Steam	
1400–600	Steam	Argon	Steam	
600–25	Argon	Argon	Argon	

Powder preparation	Green density, % theoretical	Sintered density, % theoretical		
		A*	B†	C*
MCW as-received	55	76.9	61.6	68.2
MCW as-received	65	88.5	76.2	77.5
MCW ball-milled	55	93.8	71.5	78.2
MCW ball-milled	65	96.4	83.4	77.4

* Densities were corrected for final O/U ratio (2.19 by analysis).

† Final O/U ratio was 2.00.

lattice. Thus, in hydrogen sintering, other sintering mechanisms will predominate over the diffusional mechanism. Of the other proposed mechanisms, it is unlikely that the evaporation-condensation model will explain the data in light of the observed activation energy for hydrogen sintering of 76,000 cal/mole, whereas the evaporation model predicts an activation energy equal to the heat of vaporization or 137,000 cal/mole.²⁴ It is therefore likely that in steam sintering densification occurs by oxygen ion diffusion with an activation energy of 30,000 cal/mole, whereas in hydrogen sintering a plastic or viscous flow model is applicable with the activation energy for flow being about 76,000 cal/mole.

Additional light is shed on these mechanisms by consideration of the grain size variations discussed above and shown in Fig. 17. It has been shown that the grain size of UO_2 is controlled by its density. This is rather unexpected behavior since it has repeatedly been shown for many systems²⁶ that grain boundaries absorb pores by acting as sinks for vacancies; thus in microexamination it is often noted that the area around grain boundaries is pore-free and that the pores are concentrated in grain centers. Almost the opposite behavior is noted in UO_2 , where the pores prefer to segregate at grain boundaries. This is shown in low density compacts in Fig. 7 and in high density compacts in Fig. 27. As will be noted in Fig. 28, closed pores in high density compacts intersect grain boundaries with no apparent pore distortion, the pore having that shape in each grain which it would assume were it in the grain center. This would indicate that grain boundaries in UO_2 do not act as sinks for vacancies, but rather that pores act as anchoring points for grain boundaries since the latter cannot move without first changing the pore shape. This anchoring action is similar to that proposed for grain boundaries in iron by Van Vlack,²⁷ except that not only will grain boundary movement be inhibited by curvature required in grain boundaries to enter the pores at the proper interface angle (such curvature can be perceived by close examination of Fig. 27) but also by the energy required to change pore shape. Thus the growth of grains will be controlled by that activation energy which controls the disappearance of pores. For the initial stages of sintering in H_2 or steam, respectively, as shown above, the activation energy is 76,000 and 30,000 cal/mole, respectively, whereas during the stage when closed pores only remain, the activation energy for grain growth is 23,000 cal/mole, implying that closed pores sinter out at a rate controlled by oxygen ion diffusion.

4 PHYSICAL PROPERTIES OF UO_2

Summaries of many of the physical properties of UO_2 have been presented in the literature.^{6,28} Some recent data, not generally available, are summarized below.

4.1 Melting Point

Some of the earlier values of the melting point of UO_2 are those of Ruff and Goecke²⁹ (2176°C) and of Friederick and Sitting³⁰ (2500 to 2600°C). Recent determinations include Lambertson and Mueller's³¹ value of $2878 \pm 22^\circ\text{C}$ and Ackermann's³² value of $2407 \pm 19^\circ\text{C}$. The latest determination, a value of $2760 \pm 30^\circ\text{C}$ by Wisnyi and Pijanowski,³³ was made in hydrogen, argon, and helium atmospheres. In this method, a small tungsten ribbon furnace heating element in the shape of a "V" was used as the container and also provided for black body conditions (emissivity approximately 0.95). The UO_2 that was used was Mallinckrodt (MCW) oxide having a lattice constant of $5.472 \pm 0.005 \text{ \AA}$ as determined by x-ray diffraction analysis. Lattice parameters, measured before and after melting in the various atmospheres, agreed to within the experimental error $\pm 0.0005 \text{ \AA}$, indicating that no impurities were picked up to this order of precision. Also, differences in melting point greater than the experimental error, $\pm 30^\circ\text{C}$, were not observed for any of the atmosphere conditions. The effect of small amounts of impurities on the melting point of UO_2 is not known, but the work previously cited indicates that such effects might be large.

4.2 Thermal Conductivity

Two separate determinations of the thermal conductivity of UO_2 as a function of temperature have been made. In the earlier work of Kingery et al.³⁴ the measurement was made with a comparative linear flow apparatus on a 1-in. cube sample of UO_2 cast from a suspension and fired at 1980°C *in vacuo* to a theoretical density of 73.3 per cent. In the more recent work carried out at the Armour Research Foundation³⁵ a radial heat flow method was used. Disks of UO_2 , 3 in. in diameter, were made by cold pressing MCW oxide at 20 tsi and sintering to a

Fig. 27—Increase in grain size with resintering of MCW UO_2 resintered at 2415°C for 15 min. Average grain size 41.6. (Magnification $250\times$)

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Fig. 28—Electron micrograph of wet ball-milled MCW UO_2 . 97.6 per cent TD. (Magnification 26,700 $\times$.)

density of 74.5 per cent of theoretical in a hydrogen-steam cycle.* Results of these two independent measurements together with data extrapolated to a theoretical density of 95 per cent are shown graphically in Fig. 29.

It may be noted that the two measurements agree to within about 0.002 cal/sec-°C-cm or 33 per cent; in general such agreement is quite good for so difficult a measurement, particularly since two different sources of oxide and fabrication methods were employed. It should be noted that the Armour results were obtained on cracked samples; it is expected, therefore, that these results should be low and that the Kingery data are more accurate material values. The application of these data to the in-pile behavior of UO_2 is discussed by Eichenberg et al.¹

4.3 Modulus of Elasticity

The value for Young's modulus of elasticity of 20°C for UO_2 has been reported to be 25×10^6 psi.³⁶ A recent determination of the modulus of elasticity of UO_2 as a function of temperature has been made at the National Bureau of Standards (NBS).³⁷ Measurements were made by a dynamic method *in vacuo* ($< 1 \mu$ Hg) over the temperature range 25 to 825°C. Specimens were fabricated to a density of approximately 93 per cent of theoretical from UO_2 made from ammonia-precipitated diuranate. As can be seen from Fig. 30, the modulus of elasticity values were found to decrease, but not linearly, with increasing temperature.

4.4 Modulus of Rupture

Determinations of the modulus of rupture of sintered UO_2 have been made at NBS³⁸ and at Corning Glass Works.³⁹ In the NBS work, arc-fused (Norton Co.) uranium dioxide, ball-milled (porcelain mill, alumina balls, 99.5 per cent ethyl alcohol) and fractionated, was pressed at 10,000 psi in a hardened steel mold, hydrostatically repressed at 45,000 psi and

Fig. 29—Thermal conductivity as a function of temperature.

*Heating was done first in hydrogen to a temperature of 1400°C. The hydrogen was then replaced with steam, and the temperature was increased to 1500°C and held at this temperature for 2 hr. Cooling to room temperature was done in a hydrogen atmosphere (see Sec. 3.6).

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Fig. 30 — Modulus of elasticity versus temperature *in vacuo*.

sintered in an atmosphere of static argon in an inductively heated graphite susceptor furnace (2000°C). Measurements on specimens were obtained in a helium atmosphere at room temperature, 400, 700, and 1000°C by the flexure method. Increments of stress were 1000 psi applied at 20-sec intervals. Stress was applied to the specimen at approximately the quarter points, and the modulus of rupture was calculated from the formula

$$MR = \frac{3 PA}{bd^2}$$

where MR = modulus of rupture, psi

P = applied load in pounds at fracture

A = distance from a support point to the closed load point — approximately $\frac{1}{4}$ span

b = breadth of specimen at point of rupture, in.

d = depth of specimen at point of rupture, in.

In the Corning Glass Works, MCW oxide was used. After a dry ball-milling operation (Borundum mill, Borundum grinding cylinders), specimens were formed by pressing in a hardened steel die at 6400 psi and hydrostatically repressing at 40,000 psi. Sintering was carried out in a molybdenum-wound hydrogen atmosphere furnace at temperatures from 1500 to 1750°C. The fired dimensions of test bars were approximately 0.250 by 0.520 by 4.250 in. For the standard modulus of rupture bar, the thickness and width dimensions were reduced to 0.240 and 0.515 in., respectively, by grinding with #400 grit Al₂O₃. The edges of the surface to be placed in tension in the bending test were beveled approximately $\frac{1}{32}$ in. and buffed.

A method similar to that used by NBS was employed in the work done by Corning Glass Works except that a symmetrical two point loading was used. Room temperature measurements were made in air. Measurements at 500 and 1000°C were made in a static atmosphere consisting of 20 per cent hydrogen—80 per cent helium.

Results of these two determinations are shown graphically in Fig. 31. The points for the NBS data are averages of 3 to 6 measurements; the curves for the Corning Glass Works work

Fig. 31—Modulus of rupture as a function of temperature.

are composites of various data, discussed below. The modulus of rupture shows a decrease with increase in particle size and hence, from Sec. 3, with decrease in sintered density, and an increase with increase in testing temperature. The rate of increase in strength with temperature decreases as the particle size increases and as the sintered density decreases.

The points on the curves for the Corning Glass Works measurements represent mean modulus of rupture values for specimens fired at 1750 $^{\circ}\text{C}$ for various times. A trend to higher strength values at 1000 $^{\circ}\text{C}$ was observed, in agreement with the NBS work. If the modulus of rupture is plotted against sintering time, it appears that for sintering times over 1 hr, a general decrease in the modulus of rupture values occurs. The effect of sintering temperature on the modulus of rupture (measured at room temperature) when the sintering time is kept constant at 20 hr is shown in Fig. 32. This time was chosen because high density could be obtained at temperatures as low as 1500 $^{\circ}\text{C}$. This curve shows that maximum strength seems to occur at a 1550 $^{\circ}\text{C}$ sintering temperature and that maximum strength does not coincide with maximum density.

The existence of the maximum in this curve implies that two competing mechanisms are affecting the strength properties. As sintering proceeds up to 96 to 97 per cent theoretical density, as explained in Sec. 3, open porosity continuously decreases; decrease in this quantity would be anticipated to increase strength. Beyond 96 to 97 per cent, the porosity consists primarily of more or less rounded isolated pores (Figs. 21 and 22) which would be expected to have but a minor effect on mechanical properties. As further increase in density occurs, grain growth sets in. As shown in Fig. 18, Padden has found that room temperature fracture in UO_2 occurs at least partially at grain boundaries. Therefore with increased sintering time, as grain growth occurs, grain boundary fracture can occur more readily and hence decrease in modulus of rupture properties would be encountered. Increase in modulus of rupture with increase in temperature is a common phenomenon in brittle materials, arising from an increase of the ability of the material to deform with increasing temperature rather than to fracture.

The effect of specimen surface treatment on modulus of rupture was also investigated.

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Specimens that were sintered at 1750°C for 1 hr were tested with different surface finishes, as follows: (1) as-sintered, (2) ground with #400 grit Al_2O_3 , (3) ground with A.O. #303-1/2, and (4) fine grinding and polishing with cerium oxide. Mean modulus of rupture values are shown in Table 13. An apparent increase in room temperature strength resulted from grinding the "as-sintered" surface, indicating that smoother surfaces produced strength increases at this temperature. This observation would seem to support the belief that most failures occurring in brittle materials initiate at minute or submicroscopic flaws in the surface. However, this theory is not supported by the data since the polished specimen showed a lower strength at room temperature. Of particular interest is the fact that the A.O. #303-1/2 ground and the polished bars could not be heated without breaking. The fact that the polished bars showed the greatest tendency to shatter indicates that thermal shock resistance of these bodies is markedly affected by surface finishing operations.

Fig. 32 — Modulus of rupture and sintered density as a function of sintering temperature.

Table 13 — MEAN MODULUS OF RUPTURE OF UO_2 SPECIMENS
(Sintered at 1750°C for 1 hr at various temperatures and surface conditions)

Test temperature, °C	Mean modulus of rupture, psi			
	As-sintered	#400 Al_2O_3	A.O. 303-1/2	Cerium oxide
Room temperature	12,500	14,850 14,800 13,900	15,800	14,700
500	13,400	16,150 12,950	*	*
1000	12,800	14,500	*	*

* Specimen failed spontaneously during heating of the testing apparatus.

4.5 Electrical Properties

The electrical conductivity of the oxides of uranium has been studied by many investigators and the results of their work have been summarized by Meyer⁴⁰ and by Katz and Rabinowitch.⁶ Recent studies on the electrical conductivity and thermoelectric power of uranium oxides in the UO_2 - U_3O_7 range at temperatures between 27 and 400°C were carried out at Battelle Memorial Institute.⁴¹

In most of the earlier investigations only one or two specimens were studied and the purity and excess oxygen content were not known. The type of conductivity (electron or positive hole) was not determined nor was the possibility of the existence of several phases considered. In the later Battelle work, attempts were made to consider these factors.

All specimens studied by BMI were prepared from MCW oxide and were hydrostatically pressed at 50 tsi (without a binder) into cylindrical rods about $\frac{1}{4}$ by 4 in. These rods were sintered in a hydrogen atmosphere at 1650 or 2050°C for 1 hr. Specimens for electrical measurements were cut from the rods either before or after sintering. Conductivity measurements made as a function of O/U ratio were done on unsintered rods.

Metallic impurity content of these materials was low—a few ppm at most—from spectrographic analysis. The O/U ratios were calculated from the weight gain on ignition of the UO_2 powder to U_3O_8 . After the electrical measurements were completed on a particular sample, phases present were determined by x-ray techniques in most cases.

Electrical conductivity, measured by the probe technique* was converted to "corrected" conductivity (σ_c) by the expression⁴²

$$\sigma_c = \left(\frac{1 + P}{1 - P^{2/3}} \right) \sigma_m$$

where P represents the volume pore fraction of the specimen and σ_m is the measured conductivity. Conductivities were referred to the theoretical density of UO_2 because the excess oxygen was determined on a weight per cent basis, whereas the conductivity depends on the number of carriers per unit volume. This correction made it possible to compare the conductivity of specimens of different densities. As pointed out by the BMI workers, a quantitative interpretation of the data should be made with caution because of the effects of grain boundaries.

The thermoelectric power, Q, was determined by establishing a thermal gradient along the specimen and measuring the thermal emf generated. The thermal gradient was produced by contacting one end of the specimen with a heat source and the other end with a heat sink.

Conclusions reached by Willardson et al.⁴¹ on the electrical properties of uranium oxides are summarized as follows:

1. UO_{2+x} behaves as a metal-deficit (as oxygen excess) semiconductor (p type), U_4O_9 -y as a metal-excess semiconductor (n type), and U_3O_7 -z as a metal-excess semiconductor.
2. An energy of about 0.4 ev is required to free a positive carrier from the interstitial oxygen in UO_{2+x} . In U_4O_9 or U_3O_7 the energy required to free an electron from the hexavalent uranium varied from 0.4 ev at high carrier concentrations to 0.9 ev at lower concentrations.
3. Considerable differences in the electrical conductivity values at high temperatures (250 to 400°C) were observed for a specimen of UO_2 which sintered to high density (95 per cent of theoretical) as compared with a specimen which sintered to low density (79 per cent of theoretical); the low density specimen had higher values of electrical conductivity but showed an anomalous decrease with temperature at 400°C. This anomaly was attributed to a possible nitrogen impurity in the low density specimen.
4. No evidence was found for the existence of UO_{2-x} , although Meyer⁴⁰ reported UO_2 to be an amphoteric semiconductor. Measurements on a specimen with an O/U ratio of 1.96 showed p type conductivity; therefore the specimen was UO_{2+x} plus a second phase. All n type conductivity could be attributed to the presence of U_4O_9 -y or U_3O_7 -z.

*The potential drop between two probes positioned at points within the specimen is compared with the potential drop across a standard resistor.

5. An anomalous behavior of the thermoelectric power of sintered specimens was observed: i.e., thermoelectric power increased with increasing conductivity. This anomaly was explained by the presence of U_3O_{7-z} at the lower temperatures and the decrease in its relative amount as the temperature is increased. See Sec. 7 for conductivity due to oxygen ions.

4.6 Magnetic Properties

A magnetic analysis of nonstoichiometric uranium oxides has been recently carried out between 2 and 300°K by Arrott and Goldman.⁴³ Earlier work on UO_2 included that of Dawson and Lister,⁴⁴ Trzebiatowski and Selwood,⁴⁵ and Arrott and Goldman.⁴⁶ In this recent work of Arrott and Goldman,⁴³ magnetic susceptibility measurements were made from liquid helium to room temperature using a null method of magnetic detection.⁴⁷ Magnetic isotherms were obtained at room temperature, liquid nitrogen temperature, and liquid helium temperature. Magnetization was measured at intermediate temperatures at a fixed field.

Fig. 33—Susceptibility as a function of O/U ratio at different temperatures.

Cold-pressed uranium oxide specimens (prepared at Bettis) of varying O/U ratios were studied. Powders used as source materials were: (1) UO_2 prepared by steam oxidation of uranium metal, having an O/U ratio of 1.97, and (2) MCW oxide, both in the as-received state (U/O ratio = 2.03) and after oxidation in air to various O/U ratios. The oxidized powders were not annealed but were used as-oxidized in making the compacts; as a result, it is likely that inhomogeneous oxidation may have occurred and nonequilibrium phases were present.

A plot of the susceptibility at different temperatures as a function of O/U ratio (see Fig. 33) showed, according to the authors, that in the samples examined the two-phase region extends from O/U ratios of 2.31 to 2.44. This result is conditioned, however, by the fact that the measurements were made on unannealed specimens, as mentioned above. A comparison of the data obtained by Arrott and Goldman⁴³ with that of Dawson and Lister⁴⁴ is shown in Fig. 34. Arrott and Goldman attribute the discrepancies between the two results for the region $2.0 < \text{O/U} < 2.3$ to concentration differences.

The inverse susceptibility should vary with temperature by the relation $1/\chi = (T/C) + \delta$, where δ , the interaction term, is expected to increase with excess oxygen content if oxygen ions enter interstitial positions, but remain independent of composition if metal ion vacancies form. From the variation of δ shown below, it was concluded that excess oxygen content was accommodated by interstitial occupancy.

O/U	δ ($T > 150$)	δ ($T < 150$)
2.03		189
2.10	187.7	169
2.20	219.6	194
2.30	305.6	255

4.7 Neutron Diffraction

In an attempt to determine the position of the added oxygen atoms in UO_{2+x} , samples of UO_2 and $\text{UO}_{2.25}$ were examined by neutron diffraction.⁴⁸ The results indicate that the excess oxygen enters the UO_2 lattice at definite positions and is not distributed at random. An apparent superlattice is formed which is based on a unit cell formed from the normal UO_2 cell. The superlattice reflections cannot be uniquely indexed by a simple doubling or tripling of the UO_2 cell.

5 UO_2 - U_3O_8 SYSTEM

5.1 UO_2 - U_3O_8 Equilibria

Phase relations in the uranium-oxygen system in the composition range UO_2 - U_3O_8 have been studied by many investigators.⁴⁹⁻⁵¹ An excellent summary of the earlier work was given by Katz and Rabinowitch,⁶ and work subsequent to that review was brought up to date by Gronvold.⁵⁰ Gronvold investigated the system at temperatures up to 1000°C using high temperature x-ray diffraction techniques. At the higher temperatures, he found three stable phases: UO_2 , U_4O_9 , and U_3O_8 , each existing over a range of composition. At temperatures near 1000°C, the α -cubic structure is stable up to a composition of $\text{UO}_{2.20}$; the U_4O_9 phase has a stability range of $\text{UO}_{2.24}$ - $\text{UO}_{2.26}$; and the U_3O_8 phase extends to below $\text{UO}_{2.60}$.

Biltz and Muller⁴⁹ measured equilibrium pressures of oxygen over uranium oxides in the range U_3O_8 to $\text{UO}_{2.20}$ at temperatures up to 1160°C using the tensimetric method. Their pressure measurements indicated that the U_3O_8 phase existed down to a composition of $\text{UO}_{2.61}$ and that a two phase region existed below that composition. Below $\text{UO}_{2.60}$, however, the data of Biltz and Muller are very sparse.

Two recent investigations of the equilibrium conditions in the composition range UO_2 - U_3O_8 at temperatures near 1000°C are discussed in this paper. Blackburn²² studied the uranium oxides at temperatures of 950 to 1150°C using the Knudsen effusion method in conjunction with a vacuum microbalance. Equilibrium oxygen pressures were determined, and thermodynamic data were calculated for oxides of compositions $\text{UO}_{2.15}$ to U_3O_8 . Phase

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Fig. 34 — Room temperature susceptibility as a function of O/U ratio.

boundaries were delineated, and thermodynamic properties of the system were calculated. Blackburn did not study the system below $\text{UO}_{2.15}$; the technique he used was not applicable below this composition because of the low equilibrium oxygen pressures. Aronson and Belle⁵² at Bettis Plant studied the uranium oxides in the region $\text{UO}_{2.01}$ - $\text{UO}_{2.20}$ at temperatures of 1150 to 1350°K by a solid state electrochemical technique developed by Kiukkola and Wagner.⁵³ Thermodynamic data were obtained and equilibrium pressures of oxygen were calculated.

Blackburn's delineation of the phase boundaries is in good agreement with the work of Gronvold (see Fig. 35) except in one region and represents an extension of the phase information from 950 to 1150°C. At 1000°C, Blackburn locates the boundary of the UO_{2+x} phase at $\text{UO}_{2.195}$ and the boundaries of the U_4O_{9+x} phase at 2.235 and 2.258. This lower limit for the U_3O_{8-x} phase differs from that of Gronvold. Blackburn considers this phase to be $\text{U}_5\text{O}_{13+x}$ and suggests that this phase is supported by some x-ray evidence.⁵¹ According to Blackburn the composition of the phase boundary is approximately $\text{UO}_{2.61}$, in agreement with Biltz and Muller, and is constant with temperature. Gronvold's data indicate that the composition of the phase boundary is $\text{UO}_{2.55}$ at 500 to 750°C. Since it is unlikely that the composition of the boundary would increase to $\text{UO}_{2.61}$ at 850°C, the lowest temperature of Blackburn's measure-

Fig. 35—Phase diagram for uranium oxides from UO_2 to U_5O_{13} .

ments in this region, Blackburn believes that Gronvold's data in this region are in error. He suggests that the error may be due to an erroneous calculation of the oxide composition.

Blackburn obtained thermodynamic equations for the regions he studied. In the UO_{2+x} region, the following equations were obtained on the assumption that the partial molar free energy, enthalpy, and entropy are quadratic functions of composition.

$$\Delta \bar{F} = -93,000 - 57,000x + 1,410,000x^2 + 32.5T + 57xT - 800x^2T$$

$$\Delta \bar{H} = -93,700 - 57,000x + 1,410,000x^2$$

$$\Delta \bar{S} = -32.5 - 57x + 800x^2$$

where $\Delta \bar{F}$, $\Delta \bar{H}$, and $\Delta \bar{S}$ are the partial molar free energy, enthalpy, and entropy of solution of 1 mole of oxygen in UO_{2+x} , respectively, and x is the number of gram atoms of oxygen added to a mole of UO_2 to form UO_{2+x} .

The integral free energy, heat, and entropy of solution per gram atom of uranium are, respectively,

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$$\Delta F = \frac{x}{1+x} (-46,800 - 14,000x + 240,000x^2 + 16.2T + 14xT - 130x^2T)$$

$$\Delta H = \frac{x}{1+x} (-46,800 - 14,000x + 240,000x^2)$$

$$\Delta S = \frac{x}{1+x} (-16.2 - 14x + 130x^2)$$

Blackburn states that these expressions are valid between 1200 and 1400°K and at compositions above $\text{UO}_{2.15}$. The free energy of formation of U_4O_9 from UO_{2+x} per gram atom of uranium is, according to Blackburn, $\Delta F = (0.125 - x/2) (-123,400 + 69.9T)$.

Aronson and Belle⁵² studied the region $\text{UO}_{2.01}$ - $\text{UO}_{2.20}$ using emf cells of the type Fe, FeO |(ZrO₂, CaO)| UO_{2+x} , Pt, where x varied from 0.01 to 0.20. The iron-iron oxide (wüstite) mixture was prepared from Fe₂O₃ and Fe powders.⁵³ A mixture of these powders was annealed in an evacuated sealed quartz bulb for three days at 1000°C. The powder was ground, reannealed and reground, and pressed into cylindrical pellets about 0.1 in. in height and 0.4 in. in diameter. A solid solution of 15 at. % CaO in ZrO₂ was prepared by mixing together nitric acid solutions of CaCO₃ and zirconyl nitrate. The mixture was evaporated to dryness, decomposed at 500°C, and fired overnight at 1000°C and at 1200°C. The powder was pressed into pellets about 0.1 in. in height, which were sintered overnight in air at 1400°C. X-ray diffraction patterns of the pellets showed the presence of a single phase fluorite structure.⁵⁴

The various compositions of uranium oxide were prepared in two ways. UO_2 was oxidized in oxygen at about 200°C to the desired composition and annealed in an evacuated bulb at 800°C for two weeks. Other compositions were obtained by mixing U_3O_8 and UO_2 in the proper proportions and annealing in evacuated bulbs at 1000°C for two weeks. Both methods gave comparable results. The powders were pressed into pellets about 0.1 in. in height.

The three pellets were placed one upon the other and clamped between two Vycor rods. The flat ends of the rods in contact with the Fe-FeO and UO_{2+x} pellets were covered with pieces of platinum foil which were attached to platinum wires, thus making electrical contact. This assembly was inserted into a Vycor tube placed in a tube furnace. An inert atmosphere was maintained around the pellets by flowing a slow stream of helium or argon gas under slight pressure through the tube. The emf readings were taken with a potentiometer at 50°C intervals from about 1150 to 1350°K. The temperature was measured by a Pt, Pt-10 per cent Rh thermocouple positioned adjacent to the top pellet. Measurements were taken at increasing and decreasing temperatures; the emf values obtained in this way agreed to ± 4 mv.

The compositions of the uranium oxide pellets were determined both before and after the measurements by chemical analyses for U(IV) and U(VI). The compositions did not change noticeably during the experiments; i.e., O/U ratios before and after the emf measurements agreed to within ± 0.005 , the limit of the experimental error.

The free energy change for the cell is related to the voltage by the simple relation, $\Delta F = -nFE$, where n is the number of electrons involved, F is the Faraday number, and E is the voltage. The free energy change for the cell is the sum of free energy changes occurring in both of the half cells. The free energies of formation of wüstite (FeO) have been determined by other workers. The compilation of Richardson and Jeffes⁵⁵ was used. The partial molar free energy of solution of oxygen in UO_{2+x} , $\Delta \bar{F}_{\text{O}_2}$, is obtained by subtracting the free energy change for the decomposition of wüstite from the total free energy change of the cell. The partial molar entropy of solution of oxygen in UO_{2+x} , $\Delta \bar{S}_{\text{O}_2}$, is calculated from the relation $\partial \Delta \bar{F} / \partial T = \Delta \bar{S}$. The partial molar enthalpy of solution of oxygen in UO_{2+x} , $\Delta \bar{H}_{\text{O}_2}$, is obtained from the relation $\Delta \bar{H}_{\text{O}_2} = \Delta \bar{F}_{\text{O}_2} + T \Delta \bar{S}_{\text{O}_2}$. The pressure of oxygen in equilibrium with UO_{2+x} is calculated from the relation $\Delta \bar{F}_{\text{O}_2} = RT \ln p_{\text{O}_2}$.

To establish the validity of the method, the emf's of the cell Fe, FeO|(ZrO₂, CaO)|Ni, NiO were determined at temperatures 800 to 1100°C. The free energies of formation of NiO calculated from the emf measurements were in agreement with reported values.

The emf of the cells employing uranium oxide was found to vary linearly with temperature (see Figs. 36 and 37) over the range 1150 to 1350°K, indicating that the partial molar

Fig. 36—Emf versus temperature of cells Fe, FeO[(ZrO₂ + CaO)]UO_{2+x}, Pt.

free energy of solution of oxygen in UO_{2+x} is a linear function of temperature. A break in the emf-temperature curve occurred with pellets of composition UO_{2.20}; this break occurred at about 930°C and indicated a phase transformation. Presumably two phases are present below this temperature. This observed phase change is in agreement with the work of Gronvold⁴⁹ and Blackburn.²²

Partial molar free energies, entropies, and enthalpies of solution of oxygen in UO_{2+x} were calculated from the data. The enthalpy and entropy increased negatively with increase in oxygen content but the values are too scattered to indicate the nature of the dependence. Equilibrium pressures of oxygen were calculated, and the following empirical equation was found to fit the data:

$$\text{Pressure (in atmospheres)} = 76 \exp \frac{(-33,000)}{T(^{\circ}\text{K})} \exp \frac{(31x)}{1-x}$$

Comparison of the pressure values calculated from Blackburn's equation with those calculated from the above equation (see Fig. 38) shows good agreement down to a composition of UO_{2.10} and fair agreement to UO_{2.05}.

Aronson and Belle⁵¹ considered their data in the light of the theoretical discussions of nonstoichiometry in binary crystals by Lacher,⁵⁶ Anderson,⁵⁷ and Rees.⁵⁸ These workers

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Fig. 37 — Emf versus temperature of cells Fe, FeO[(ZrO₂ + CaO)]UO_{2+x}, Pt.

found that experimental data, primarily on metal hydrides, fit a modified form of the Langmuir equation, in which attraction between defects, interstitial ions or holes in the lattice, precipitates a new phase. The data on UO₂ show no agreement with the theoretical equations and indicate that attractive forces between defects do not affect the pressure-composition isotherms. The appearance of the U₄O₉ phase does not seem to be a direct consequence of the grouping of interstitial ions but probably occurs when the UO₂ phase with interstitial ions becomes unstable with regard to a new structure with a rearranged oxygen lattice.

5.2 Kinetics of Oxidation of UO₂

A number of investigations on the kinetics of oxidation of UO₂ at various temperature ranges have been carried out.^{59,66,69} Differences of opinion still exist on the mechanism of the low temperature (100 to 360°C) oxidation of UO₂. Roberts⁵⁹ found that at -183°C, oxygen is chemisorbed on the oxide surface. Anderson et al.⁶⁰ found that at temperatures of -130 to 50°C, the amount of oxygen absorbed increases with the logarithm of time and probably involves the penetration of oxygen ions into interstitial positions in the oxide lattice several layers deep. At high temperatures (100 to 180°C), Alberman and Anderson⁶¹ and Anderson et al.⁶⁰ found that in air at atmospheric pressure and in oxygen at pressures of 10⁻³ to 48 cm

Fig. 38—Pressures of oxygen in equilibrium with UO_{2+x} .

Hg, uranium dioxide is oxidized to either a tetragonal oxide of composition $UO_{2.30}$ - $UO_{2.38}$ or a cubic oxide of composition $UO_{2.25}$. The rate data for this temperature range were explained by Alberman and Anderson on the basis of an assumed mechanism in which the rate determining step was the diffusion of oxygen into interstitial positions in the UO_2 lattice. They assumed that oxygen is randomly distributed until the average composition reaches $UO_{2.25}$ where an ordering takes place succeeded by formation of two tetragonal phases at higher concentrations. Perio, in his study on the oxidation of uranium dioxide in air at 120°C (references 62 and 63), agreed with Alberman and Anderson⁶¹ that the oxidation reaction corresponds generally to a reaction controlled by diffusion but differed with them on the interpretation. Perio maintained that the reaction proceeds by formation of a new, nonstoichiometric phase, a hypothesis which Alberman and Anderson discussed but which they rejected because it was at variance with their x-ray data. Aronson et al.⁶⁴ concluded from their study that the oxidation of UO_2 to U_3O_8 in dry air and oxygen at temperatures of 160 to 350°C proceeds by a two-step reaction. In the first step the tetragonal oxide of composition $UO_{2.34 \pm 0.03}$ is formed. In the second step this tetragonal phase is converted to orthorhombic U_3O_8 by a process of nucleation and growth.

It was concluded by these workers that the mechanism for the first stage of the reaction was similar to that suggested by Alberman and Anderson, namely, that oxidation occurs by diffusion through the nonstoichiometric phase UO_{2+x} without the appearance of a second phase. In all of this work, oxidation studies were carried out on UO_2 in powder form. In work reported by Blackburn et al.⁶⁵ and by Weissbart et al.⁶⁶ oxidation studies were carried out at 120 to 280°C on sintered UO_2 pellets as well as on UO_2 powder. These workers concluded that oxidation of uranium dioxide at these temperatures results in the immediate formation of a surface tetragonal U_3O_7 phase around the UO_2 particle. Further reaction occurs by the diffusion of oxygen through the new oxide to form additional U_3O_7 at the U_3O_7 - UO_2 interface. This process continues until the UO_2 particle is converted to U_3O_7 .

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The assumption that oxidation occurs by diffusion of oxygen into the UO_{2+x} phase is supported by two main lines of evidence: (1) good agreement between the kinetic data and the diffusion equation for the suggested model and (2) absence of x-ray spectra for a second oxide phase. Another contributing piece of evidence is the absence of a significant increase in the surface area, i.e., the formation of a second phase should lead to a "breakup" of the large particles with a corresponding increase in the surface area. As pointed out by Alberman and Anderson⁶¹ and by Aronson et al.⁶⁴ discrimination between the two mechanisms—diffusion through UO_2 or diffusion through a second phase—is not possible on the basis of rate data alone. Observation of the other distinguishing criteria were made by Alberman and Anderson⁶¹ and by Aronson et al.⁶⁴ For example, the English workers did not detect a second phase at 180°C until the composition of their compounds had reached $\text{UO}_{2.25}$. Similarly, in the work of Aronson et al.,⁶⁴ for oxidation at 230°C, only the α -cubic (fluorite) structure of uranium dioxide was observed up to an O/U ratio of 2.16. At this composition, a tetragonal phase appeared, which increased in quantity with increasing oxygen content. The cubic phase co-existent with the tetragonal phase decreased in quantity with increasing oxygen content. These authors maintained that if an increasingly thick layer of stoichiometric oxide U_3O_7 were forming around stoichiometric $\text{UO}_{2.00}$ during the course of the reaction, one would expect that the tetragonal phase would appear at O/U ratios of 2.03 to 2.06 when more than 10 per cent of product would be present. Their work showed, however, that the tetragonal phase did not appear until the reaction was 30 to 50 per cent complete.

On the other hand, Weissbart et al.⁶⁶ present evidence for the immediate formation of a U_3O_7 phase on the UO_2 particle from the appearance of many sharp lines in the x-ray pattern at a composition $\text{UO}_{2.06}$ for sintered pellets oxidized at 250°C. For powder specimens oxidized at 150 and 200°C, lines of U_3O_7 were not observed, however, until the composition $\text{UO}_{2.11}$ was reached. The fact that U_3O_7 was not easily observed below $\text{UO}_{2.06}$ and the discrepancy noted for the appearance of U_3O_7 for pellet and powder samples was explained on the basis of the particle size of the UO_2 preparation. These authors concluded that the lack of x-ray evidence for formation of U_3O_7 may be due in part to the limitation of the x-ray method in observing layers of U_3O_7 below thickness values of 900 to 1000 Å.

The other criterion—lack of evidence for surface area changes—was supported by Alberman and Anderson⁶¹ and by Aronson et al.⁶⁴ but not by Weissbart et al.⁶⁶ Alberman and Anderson found no significant changes in surface area upon oxidation. In the work of Aronson et al., surface area measurements on samples oxidized to $\text{UO}_{2.35}$ at 277°C and to $\text{UO}_{2.34}$ at 230°C were 0.72 and 0.61 m²/g, respectively, as compared with 0.60 m²/g for the starting material, indicating that oxidation did not cause appreciable particle breakdown. Blackburn et al.⁶⁵ suggest that the slight difference between the UO_2 cell and the tetragonal U_3O_7 cell may not be enough to break up the crystals with consequent increase in surface area.

Weissbart et al.⁶⁶ present additional but inclusive evidence from density measurements for the mechanism involving the immediate formation of the tetragonal U_3O_7 phase. These measurements were made on powder specimens oxidized at 200°C to compositions in the range of $\text{UO}_{2.04}$ to $\text{UO}_{2.27}$ using a differential gas displacement method.* The results of these measurements show a linear increase in density with oxygen concentration that is near to that calculated for the formation of U_3O_7 and indicate that the mechanism based on the immediate formation of the second phase U_3O_7 gives the best agreement with the data. The fact that the measurements gave consistently higher densities than either diffusion model was interpreted by the authors to be due to decreases in porosity of the structure as oxidation proceeds.

Still further evidence for the second phase formation hypothesis was suggested by Weissbart et al.⁶⁶ from their measurements of the lattice parameter of αUO_2 over the composition range $\text{UO}_{2.00}$ to $\text{UO}_{2.30}$. Their results show that the a_0 parameter is independent of the oxide composition over the range studied (see below). If oxygen dissolves in the αUO_{2+x} phase (as believed by Alberman and Anderson⁶¹ and by Aronson et al.⁶⁴), these authors maintain that a contraction of the a_0 parameter should occur in direct proportion to the amount

*The difference in volume between a sample of known density and of unknown density was obtained by measuring the buoyancy as a function of gas pressure.

of oxygen dissolved. Such a lattice contraction was not observed. However, this argument can not be used a priori to conclude that oxygen does not dissolve in the UO_2 lattice at these oxidation temperatures. It is assumed that Vegard's law directly applies to UO_{2+x} , and this is still an assumption, not an independent observation. Moreover, Vegard's law presumes equilibrium, and it is unsafe to apply equilibria conditions to a kinetic process. The work of Aronson et al.⁶⁴ and of Alberman and Anderson⁶¹ also show that the lattice parameter remains essentially constant with oxidation.

From a study of the magnetic susceptibilities of the uranium oxides in the composition range UO_2 - U_3O_8 at temperatures of 2 to 300°K, Arrott and Goldman⁴³ (see Sec. 4.6) conclude that when oxygen is added to UO_2 the anion lattice is undisturbed and oxygen enters into interstitial positions. Willardson et al.⁴¹ (see Sec. 4.5), in a study of the electrical properties of uranium oxides, reported the phases UO_{2+x} , U_4O_9 , and U_3O_7 . At 200°C, oxygen is soluble in UO_2 up to a composition of $\text{UO}_{2.06}$. At higher O/U values U_4O_9 appeared, and the two phase region UO_{2+x} U_4O_9 exists up to an O/U ratio of 2.24.

Final resolution of these discrepancies in the assumed mechanism still await further work.

On the assumption of oxygen diffusion through the nonstoichiometric phase UO_{2+x} without the appearance of a second phase, both Alberman and Anderson⁶¹ and Aronson et al.⁶⁴ used the diffusion equation

$$C = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-\pi^2 n^2 D t / a^2)$$

to derive oxygen diffusion coefficients. The expression obtained by Aronson et al. for the oxygen diffusion coefficient over the temperature range 160 to 350°C was $D = 5.5 \times 10^{-3} \exp[-(26,300 \pm 1500)/RT]$. This value for the activation energy (26.3 ± 1.5 kcal/mole) is in good agreement with the value obtained by Alberman and Anderson⁶¹ (27 kcal/mole) for air oxidation and with the value obtained by Anderson et al.⁵⁹ (18 to 27 kcal/mole) for oxygen oxidation. It also compares favorably with the activation energy obtained (29.7 ± 2.3 kcal/mole) from oxygen self-diffusion kinetic studies reported in Sec. 7 of this paper (see discussion in Sec. 7). On the assumption that UO_2 oxidizes by formation of tetragonal U_3O_7 surface phase at a rate controlled by diffusion of oxygen or uranium ions through U_3O_7 , Blackburn et al.⁶⁵ found that the heat of activation for this reaction was 21.7 kcal/mole. The rate of advance of the tetragonal phase was given by

$$x^2 = 7.69 \times 10^{-5} t \exp(21,670/RT)$$

where x is thickness of U_3O_7 formed in centimeters and t is the time in seconds.

Data obtained by Aronson et al.⁶⁴ on the second stage in the oxidation of uranium dioxide (oxidation of $\text{UO}_{2.34 \pm 0.03}$ to U_3O_8) showed sigmoidal rate curves characteristic of an autocatalytic reaction (see Fig. 39). These authors interpreted the reaction as one proceeding by a process of nucleation and growth. A semiquantitative treatment of the data was made using the discussion given by Johnson and Mehl⁶⁷ on grain boundary nucleation in metallurgical transformations. Growth constants and rates of nucleation were calculated. An activation energy for growth was estimated to be 35 kcal/mole.

Indirect support for the postulate that oxidation occurs by diffusion into the UO_2 particles rather than by formation of an external skin of U_3O_7 is afforded by the observations shown in Fig. 39. If a U_3O_7 coating formed on each particle immediately, it is not clear why U_3O_8 should also not form immediately; in other words, if U_3O_7 forms in the manner predicted by equilibrium considerations, it then must be assumed that the formation of U_3O_8 is governed by nonequilibrium considerations and must await complete conversion of the particle to U_3O_7 before its growth begins. It appears more reasonable to assume that both phenomena are governed by nonequilibrium conditions. Further indirect evidence is afforded by the observation that the activation energy for oxygen diffusion calculated on the assumption that oxygen is diffusing interstitially into UO_2 agrees well with that found later for the self-diffusion of

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Fig. 39 — Experimental rate curves for the oxidation of UO_2 .

oxygen ions in UO_2 , namely, 26,300 and 29,700 cal/mole, respectively. Final evidence is afforded by the observation of Anderson, Roberts, and Harper⁶⁰ on the effect of oxygen pressure on the oxidation of UO_2 particles. The oxidation rate was found to vary continuously with pressure, increasing strongly with increasing pressure. If an external film of relatively fixed composition were formed on each particle, the oxidation rate should vary either discontinuously with oxygen pressure or quite slowly. These results imply a surface concentration proportional to the oxygen pressure. In this connection, Bloem and Kröger⁶⁸ report that Cu and Ni ions can penetrate PbS at temperatures at which self-diffusion is negligible via interstitial sites; similarly the low-temperature oxidation of UO_2 may occur by a similar interstitial process wherein the interaction with lattice ions is negligible.

5.3 Stable Nonequilibrium Structures in the Uranium Oxides

There is much evidence in the literature to indicate that nonequilibrium structures of some degree of stability occur in uranium oxides of composition above UO_2 . It is probably a major cause of the differences reported on the oxidation of UO_2 at low temperatures (120 to 350°C) (see above). Thus, Hering and Perio⁶⁹ and Perio⁶² oxidized a UO_2 powder to compositions above $\text{UO}_{2.3}$ at 120°C without the appearance of a new phase and observed a marked decrease in the lattice parameter with increase in oxygen content. In oxidations of UO_2 powders to compositions between $\text{UO}_{2.10}$ and $\text{UO}_{2.23}$, Alberman and Anderson,⁶¹ Aronson et al.,⁶⁴ and Weissbart et al.⁶⁶ observed no new phase and no appreciable change in lattice parameter. The disappearance of the tetragonal phase formed on oxidation with subsequent annealing, noted by many workers, is another indication of a nonequilibrium phase. These studies indicate that the nature of the oxidized material depends on the properties of the individual UO_2 preparation and on the oxidation conditions.

Some recent work at Bettis Plant⁷⁰ indicates that discrepancies also exist in observations of oxidized UO_2 powders which have been well annealed. In this work, MCW oxide was reduced in H_2 and oxidized in oxygen to various compositions up to $\text{UO}_{2.25}$. These preparations were then annealed for one, two, and three weeks at 700, 350, and 200°C, respectively. The samples were cooled to room temperature in sealed evacuated Vycor tubes. No significant

effect of the annealing temperature was observed. Two phases, α and β cubic UO_2 , were present at compositions of $\text{UO}_{2.10}$ to $\text{UO}_{2.23}$ (Table 14), in agreement with the high temperature x-ray data of Gronvold.⁴⁹ For compositions below $\text{UO}_{2.10}$, however, results were obtained which are different from those of Gronvold. It can be seen from Table 14 that only one phase is present at a composition of $\text{UO}_{2.07}$ at all three temperatures and that there is little lattice contraction. These results differ from those of Gronvold in two respects: Gronvold found two phases to be present in samples of composition $\text{UO}_{2.05}$ and above when cooled to room temperature; at the higher temperatures where the α cubic structure of UO_2 is stable over an extended composition range, he found that the lattice parameter decreases with increase in oxygen content.

A calculation of the lattice constants for $\text{UO}_{2.00}$ and $\text{UO}_{2.10}$ at 700°C from Gronvold's equation⁴⁹ for the temperature dependence of the lattice constant shows that the change in a_0 is approximately 0.001 Å per 0.01 units in O/U ratio. This value of Gronvold's for the decrease in lattice parameter with O/U ratio is approximately three times that observed by Aronson and Clayton⁷⁰ (see Table 14).

It is possible that slow rates of phase transformation may be responsible for the non-appearance of a second phase in the samples of composition $\text{UO}_{2.07}$. The rate of disproportionation of α cubic $\text{UO}_{2.07}$ into U_4O_9 and UO_2 may be very slow at temperatures of 200 and 350°C, the annealing temperatures of some of the samples. According to Gronvold, only the α cubic phase would be present in $\text{UO}_{2.07}$ at 700°C, the third annealing temperature. The β phase might not appear on quenching from 700°C to room temperature in air but may appear on slow cooling. For example, Gronvold cooled his samples from 1000°C to room temperature in stages over a period of two months.

This discussion points up an important conclusion. The very real possibility of equilibrium structures must be considered in presenting arguments from x-ray data to support conclusions regarding phase relations and oxidation mechanisms.

Table 14—IDENTITY OF PHASES PRESENT AND LATTICE PARAMETERS IN URANIUM OXIDES

O/U ratio	X-ray analyses				Lattice parameter, Å
	A	B	C	D	
2.01	α	α		α	5.4701 ± 0.0013^B 5.4695 ± 0.0013^D
2.02	α		α	α	5.4689 ± 0.0009^C
2.03			α		
2.04	α	α		α	
2.05					
2.07	α	α	α	α	5.4666 ± 0.0013^B 5.4681 ± 0.0016^C 5.4678 ± 0.0015^D
2.10		α, β			
2.11	α		α, β	α, β	
2.14		α, β			
2.15	$\alpha, \text{U}_3\text{O}_7$			α, β	
2.16			α, β		
2.19	$\alpha, \text{U}_3\text{O}_7$	α, β	α, β	α, β	
2.23	$\alpha, \text{U}_3\text{O}_7$	α, β	β	β	
2.25	$\alpha, \text{U}_3\text{O}_7$	β	β	β	5.4401 ± 0.0025^B 5.4408 ± 0.0015^C 5.4393 ± 0.0017^D

^AAs-prepared powder.

^BAnnealed *in vacuo* for three weeks at 200°C.

^CAnnealed *in vacuo* for two weeks at 350°C.

^DAnnealed *in vacuo* for one week at 700°C.

5.4 Kinetics of Reduction of U_4O_9 and U_3O_8

The reduction of U_4O_9 powders to UO_2 in hydrogen is being studied at Bettis Plant⁷¹ at temperatures of 400 to 600°C and pressures of 20 to 500 mm Hg. Three U_4O_9 powders of different specific surfaces have been used, including MCW UO_2 oxidized to $UO_{2.25}$ in oxygen and annealed at 800°C. Typical rate curves are shown in Fig. 40 for MCW powder at 100 mm Hg hydrogen pressure.

Samples of MCW U_4O_9 were partially reduced at 470°C, and the phases present were identified by x-ray diffraction. The partially reduced samples were mixtures of two phases: α cubic UO_2 and β cubic U_4O_9 . The relative amount of the α cubic phase increased with decrease in O/U ratio.

The rate was found to be proportional to the 0.6 to 0.8 power of the pressure. This strong pressure dependence indicates that the rate controlling process occurs at the surface of the powder particles and that internal phase transformations and diffusion processes are therefore relatively rapid. It is possible that the rate shown in Fig. 40 results from the complete early reduction of the finer particles in the particle aggregate. Rate constants have been determined on the assumption of a constant rate of surface reaction. Plots of log rate constant against $1/T$ give straight lines, and activation energies of 22 to 28 kcal/mole have been calculated for the three powders.

The reduction of U_3O_8 to UO_2 in hydrogen was studied at temperatures of 500 to 700°C at pressures of 100 mm Hg using MCW oxidized to U_3O_8 at 800°C in air as the starting material. Some rate curves are shown in Fig. 41. X-ray information shown in Fig. 42 shows that there is a change in the lattice parameter of the product phase with extent of reduction. The lattice parameter varies from a value close to that for U_4O_9 in the first stages of the reaction to a value corresponding to the lattice of UO_2 at the end of the reaction. It is believed that the reaction occurs in two stages: U_3O_8 is reduced to U_4O_9 , which is subsequently reduced to UO_2 . The reason for the gradual transition of lattice parameter with average composition in the middle portion of the reaction is not clear.

Fig. 40 — Reduction of U_4O_9 (made from MCW UO_2) by hydrogen.

Fig. 41—Rates of reduction of U_3O_8 to UO_2 in hydrogen. Fig. 42—Lattice constants of products formed during reduction of U_3O_8 to UO_2 in H_2 at 500 and 600°C.

Surface area measurements made on the U_3O_8 powders that had been reduced to UO_2 at 700, 600, and 500°C gave values for the specific surface of 0.37, 0.40, and 0.64 m^2/g , respectively, as compared with a value of 0.33 m^2/g for the original U_3O_8 powder. It is seen that an increasing amount of breakdown occurs as the reaction temperature is lowered. Greater particle breakdown probably occurs at the lower temperatures because mobility is lower in

solids, and strains resulting from the phase transformation are less easily annealed out. The breakdown on reduction of U_3O_8 is in contrast with the reduction of U_4O_9 where little breakdown was noticed.

Assuming, as in the case of U_4O_9 , that the reaction is surface controlled, reaction rate constants have been obtained. A plot of log rate constant against $1/T$ gives an activation energy of 25 kcal/mole for the over-all reduction process.

6 STABILITY OF UO_2 IN WATER

6.1 Corrosion of Compacted UO_2

Failure of sintered UO_2 exposed to high temperature water could be chemical or mechanical. Failure could be caused by the chemical reaction of the oxide with water or dissolved oxygen. Mechanical breakdown such as erosion of the solid surface due to the abrasive action of water on the solid could also occur. A summary of results obtained from a corrosion study made at Bettis Plant by Aronson⁷¹ is presented below.

In order to determine the stability of compacted UO_2 in water, compacts were exposed to 650°F degassed water and 750°F degassed steam maintained under the following conditions:

1. Water, 650°F, $<0.05 \text{ cm}^3 \text{ O}_2/\text{kg}$, $<0.3 \text{ cm}^3 \text{ H}_2/\text{kg}$, pH 6 to 8 for 343 days.
2. Water, 650°F, $<0.05 \text{ cm}^3 \text{ O}_2/\text{kg}$, $<0.3 \text{ cm}^3 \text{ H}_2/\text{kg}$, pH 10.2 to 10.8 (LiOH) for 316 days.
3. Steam, 750°F, inlet water containing $<0.05 \text{ cm}^3 \text{ O}_2/\text{kg}$ for 302 days.

In the tests at 650°F, the water was pumped continuously through the autoclaves at a slow rate to maintain the specified conditions. The compacts tested in steam were first exposed to "static" steam at 1500 psi for 128 days. They were then exposed for 174 days in an autoclave provided with a slow continuous flow of fresh degassed steam at 1500 psi.

The specimens tested consisted of cold-pressed UO_2 , cold-pressed and sintered UO_2 , and hot-pressed UO_2 . The powder used for fabricating most of the pellets was as-received (MCW) Mallinckrodt oxide. Some of the pellets were made from powder prepared by the low pressure and high pressure steam oxidation methods. Compacts were cold-pressed to 65 to 70 per cent of theoretical density and were sintered in hydrogen at 1700 to 1750°C to 92 to 93 per cent of theoretical density. Hot pressing was performed at 1700°C, and densities of 90 to 95 per cent were attained. Some of the powder used to fabricate the pressed and sintered pellets had polyvinyl alcohol or sterotex added to it prior to pressing as binding and lubricating agents. The cold-pressed and sintered pellets were cylinders of 0.4 in. in diameter and length and weighed about 5 g; the hot-pressed pellets were approximately twice as large. The pellets were placed in Zircaloy-2 containers 0.75 in. in diameter and height and were dried after exposure by heating at 70°C *in vacuo* for 12 hr.

One of the objectives of the testing program was to determine weight gains due to oxidation. Weight gains resulting from chemical reaction could not be determined directly by weighing pellets before and after exposure because of weight losses on the pellets due to erosion or fracture. Therefore the Zircaloy-2 containers with their total contents were weighed after each exposure. The weight gains due to oxidation of the Zircaloy-2 containers were corrected by determining weight gains on empty Zircaloy-2 cups exposed to the same conditions.

Some of the compacts, especially among those that had been hot pressed, fractured during the course of the experiments. It is likely that this breakdown, which occurred at least partially during handling, was due to poor fabrication, resulting in structurally weak compacts or to inclusions of carbon from the graphite die. Data on these compacts are not included in this summary.

The only observable change in the exposed compacts was a slight dulling of the surfaces. A number of compacts were polished and etched and compared with unexposed compacts similarly treated. Microscopic observation showed no change in the internal structure of the compacts exposed to any of the conditions. Chemical analyses of exposed samples are shown in Table 15. The percentages of U(VI) and water are very low, indicating that little if any oxidation or water absorption occurred. Weight changes (shown in Table 16) were very low

Table 15—CHEMICAL ANALYSES OF UO_2 COMPACTS EXPOSED TO HIGH TEMPERATURE WATER

Specimen type	Test condition	% U(VI)	% H_2O
A*	Degassed steam, 750° F	0.64	0.09
A		0.50	0.06
A		0.27	0.01
B†		0.43	0.07
A	Degassed water, 650° F	0.08	0.06
A		0.06	0.08
A		0.25	0.05
B		0.31	0.10
A	Degassed water, 650° F,	0.11	0.06
A	pH 10.5	0.25	0.03
A		0.25	0.07
B		0.05	0.06

* Cold pressed and sintered.

† Hot pressed.

Table 16—STABILITY OF UO_2 COMPACTS IN HIGH TEMPERATURE WATER

Test condition	Specimen type	Number of specimens	Exposure time, days	Av. fractional weight change	Av. deviation
Degassed water 650° F	Cold pressed and sintered	14	343	+0.0003	±0.0004
	Hot pressed	5		-0.0020	±0.0017
Degassed water, 650° F; pH 10.5	Cold pressed and sintered	11	316	+0.0002	±0.0005
	Hot pressed	6		-0.0028	±0.0029
Degassed steam 750° F	Cold pressed and sintered	14	302*	-0.0004	±0.0006
	Hot pressed	4		-0.0042	±0.0031

* This includes 128 days in a "static" test and 174 days in a "dynamic" steam system.

for the cold-pressed and sintered pellets; the hot-pressed specimens showed small weight losses, indicating that loss of surface material occurred.

Several UO_2 pressed compacts and several specimens that had been pressed and sintered were tested in 650° F water containing 1 to 3 $\text{cm}^3 \text{O}_2/\text{kg}$. A greenish yellow loose scale of higher oxide ($> \text{UO}_{2.80}$) formed on the surface. The sintered and green compacts lost approximately 15 per cent of their weight after exposure of only eight days.

Three primary conclusions can be drawn from this work.

1. UO_2 compacts are stable to oxidation over long periods in degassed water and steam at neutral and high pH.
2. UO_2 compacts are resistant to erosion under the same conditions.
3. Exposure to water containing oxygen causes the formation of a surface scale of higher oxide.

6.2 Kinetics of Oxidation of UO_2 in Water

Thermodynamic calculations have been made⁷² on the stability of UO_2 in degassed water from a consideration of the partial pressure of oxygen to be expected from the equilibria:

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1. $\text{U}_3\text{O}_8 (\text{c}) = 3\text{UO}_2 (\text{c}) + \text{O}_2 (\text{g})$
2. $\text{UO}_3 (\text{c}) = \text{UO}_2 (\text{c}) + \frac{1}{2}\text{O}_2 (\text{g})$
3. $\text{H}_2\text{O} (\text{l}) = \text{H}_2 (\text{g}) + \frac{1}{2}\text{O}_2 (\text{g})$
4. $\text{H}_2\text{O} (\text{g}) = \text{H}_2 (\text{g}) + \frac{1}{2}\text{O}_2 (\text{g})$

The following conclusions were reached concerning the stability of UO_2 in water:

1. UO_2 will react with completely degassed water or steam to form U_3O_8 below 2700°F or UO_3 below 1800°F.
2. In water containing 1 cm³ H_2 /liter, UO_2 will not react to form U_3O_8 or UO_3 if there is no excess oxygen in the water.
3. Oxygen impurities in the water, if present in detectable amounts, will react with UO_2 to form U_3O_8 or UO_3 provided that the water contains a sufficiently small concentration of hydrogen.

The free energy data on which the calculations were based are questionable. It is also possible that other reactions occur in water, for example, the formation of hydrates,⁶ which would alter the free energy considerations. These facts obviously limit the applicability of the conclusions drawn. It should also be noted that the conclusions concern equilibrium conditions and are not concerned with the rates at which equilibrium is approached. For example, a mixture of several cubic centimeters per kilogram each of oxygen and hydrogen can easily be maintained in water up to the critical temperature, each gas independently reacting with oxide, although at equilibrium the two gases would have combined to form water which would react much more slowly with the oxide.

The object of the work carried out at Bettis Plant by Aronson⁷¹ was to obtain kinetic data on the oxidation of UO_2 in degassed water and in water containing oxygen, as well as to determine phase changes occurring in the oxide as a result of the reactions. Powder samples were primarily used since it was felt that data obtained on powders of known composition, density, and specific surface would be of more general applicability and would have more validity than data obtained on oxide samples that had undergone additional fabrication processes.

The uranium oxide powder samples that were used in these studies were MCW oxide reduced in hydrogen at 800°C to an O/U ratio of 2.02. Powders were exposed to degassed water and to water containing 25 cm³ O_2 /kg at temperatures of 87 to 177°C. The experiments were made in stainless steel containers having sintered porous bottoms. A very thin layer of oxide powder was placed in each container. Water was forced upward through the bottom of the container by pumping. Fully homogeneous oxidation was obtained by this method. The water was checked periodically for constant temperature, oxygen content, pH, and resistivity. Samples of oxidized powders were analyzed chemically and by x-ray diffraction.

The rate data are shown in Fig. 43. Three samples were taken for analysis in each case. The average deviations are shown by the vertical lines through the points corresponding to average values of the composition. The squares in the data at 104 and 177°C correspond to data obtained in a second run at these temperatures.

X-ray analysis of the partially oxidized samples indicates increasing amounts of a new phase with increase in oxidation. The new phase was identified as $\text{UO}_2 \cdot 0.8\text{H}_2\text{O}$ by comparing $\sin^2\theta$ values obtained from the diffraction patterns with values given for known UO_3 hydrates by Dawson et al.⁷³ (see Table 17). In a study of the effect of water on UO_3 , Dawson et al.⁷³ found $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ to be present at 170°C, in agreement with the data presented here. The increase in water content of the samples with degree of oxidation (see Table 18) also indicates that the trioxide formed was approximately a monohydrate.

The UO_2 powder exposed to degassed water (<0.05 cm³ O_2 /kg) did not oxidize or hydrate. Thus water itself will not react with UO_2 at low temperatures even though a reaction is thermodynamically possible. In this connection, the effect of oxygen pressure on the reaction rate of UO_2 discussed previously is probably controlling.

It thus appears that oxidation occurs by the joint reaction of water and oxygen with UO_2 , and $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ is the direct product. The activation energy, based on the rate curves, is low,

Fig. 43—Oxidation of UO₂ in water containing oxygen.Table 17—COMPARISON OF $\sin^2 \theta$ VALUES OBTAINED IN THE OXIDATION OF UO₂ IN WATER WITH CALCULATED VALUES OF DAWSON ET AL. ON UO₃·0.8H₂O

Index h k l	$\sin^2 \theta$			
	UO ₃ ·0.8H ₂ O (ref. 73)	104°C	127°C	177°C
2 0 0	0.0227	0.241	0.0241	0.0239
0 2 0	0.0500	0.0514	0.0521	0.0521
1 1 1	0.0506			
2 2 0	0.0727	0.0751	0.0751	0.0741
4 0 0	0.0909	0.0934	0.0934	0.0934
3 1 1	0.0961	0.0976	0.0986	0.0976
0 0 2	0.1297	0.1308	0.1308	0.1308
4 2 0	0.1409	0.1440	0.1440	0.1428
1 3 1	0.1506			0.1502
2 0 2	0.1524	0.1527	0.1539	0.1539
5 1 1	0.1869	0.1799	0.1813	0.1826
3 3 1	0.1960	0.1894	0.1908	0.1894
0 4 0	0.2000	0.2005	0.1991	0.2005
2 2 0	0.2024	0.2075	0.2089	0.2075
6 0 0	0.2045			
4 0 2	0.2206	0.2219	0.2219	0.2233
2 4 0	0.2227			
6 2 0	0.2545	0.2576	0.2591	0.2576

5 to 10 kcal/mole. Although the data are insufficient to postulate a mechanism, the oxidation of UO_2 by oxygen dissolved in water is very different from that in air.

6.3 Reduction of U_3O_8 and UO_3 in Water

Some experiments were performed on the reduction of U_3O_8 and UO_3 powders in 650°F degassed water to which was added 100 cm^3 H_2 /kg. The final product of the reduction reactions was uranium dioxide. The only new phases detected by x-ray diffraction during the reduction were the β cubic phase of U_4O_9 and the α cubic phase of UO_2 . There was no evidence for hydrate formations from either x-ray or chemical analyses.

7 SELF-DIFFUSION KINETICS

Investigation of the self-diffusion of oxygen and uranium in UO_2 and nonstoichiometric uranium oxides is in progress at Bettis Plant. Preliminary results⁷⁴ on the first phase of this study, the measurement of oxygen and uranium self-diffusion coefficients in nearly stoichiometric UO_2 ($\text{UO}_{2.00}$ - $\text{UO}_{2.01}$), are summarized below.

7.1 Self-diffusion of Oxygen in UO_2

The standard diffusion couple sectioning technique was tried but abandoned because of experimental uncertainties in the analyses for O^{18} - O^{16} content by solid emission mass spectrographic techniques. The method of solid-gas isotopic exchange, however, was found to be suitable.

Experiments were carried out using the exchange between O^{18} labeled UO_2 and a limited amount of CO_2 gas of natural O^{18} concentration. This method of solid-gas isotopic exchange is applicable for diffusion coefficient measurements when the surface exchange reaction between gas and solid is rapid compared with the diffusion of the exchanging ion into the lattice. Solutions to the diffusion equation for various solid-gas isotopic exchange experiments have been derived by Carman and Haul.⁷⁵ The diffusion equation solution appropriate for the present experiments and for particles of spherical shape is the following:

$$1 - \frac{W}{W_\infty} = \sum_{n=1}^{\infty} \frac{6\lambda(1+\lambda)}{9(1+\lambda) + \lambda^2 q_n^2} \exp - q_n^2 \frac{Dt}{a^2} \quad (1)$$

where W = total amount exchanged in time t

W_∞ = total amount exchanged in time $t = \infty$

λ = effective volume ratio (the ratio of the number of moles of exchanging specie in the gas to the number of moles of exchanging specie in solid)

q_n = nonzero positive roots of $\tan q = \frac{3q}{(3 + \lambda q^2)}$

D = diffusion coefficient (cm^2/sec)

t = time

a = average particle radius

This equation is applicable for small values of $1 - (W/W_\infty)$, i.e., for long times. For shorter times the following equation is used:

$$1 - \frac{W}{W_\infty} = (1 + \lambda) \left[\frac{\gamma_1}{\gamma_1 + \gamma_2} \text{eerfc} \frac{3\gamma_1}{\lambda} \sqrt{\tau} + \frac{\gamma_2}{\gamma_1 + \gamma_2} \text{eerfc} \frac{-3\gamma_2}{\lambda} \sqrt{\tau} \right] - \lambda \quad (2)$$

where $\text{eerfc} \equiv \exp x^2 \text{erfc} x$ and $\tau = Dt/a^2$.

The exchange data are analyzed in the following manner: For each experiment, a plot of $1 - (W/W_\infty)$ vs τ is made for the particular λ value of the experiment. In the case of UO_2 and CO_2 exchange, λ is simply the ratio of the moles of CO_2 to moles of UO_2 . It has been found

that usually only Eq. 2 need be used for this calculation. Then, from the experimental data, $1 - (W/W_\infty)$ is evaluated from the relation

$$1 - \frac{W}{W_\infty} = \frac{P - P_\infty}{P_2 - P_\infty}$$

where p = the amount O^{18} in CO_2 at time t

P_∞ = the amount O^{18} in CO_2 at time $t = \infty$

P_2 = is the amount O^{18} initially present in the CO_2

The determination of P_∞ can be done experimentally or from the relation

$$\lambda = \frac{P_\infty - P_1}{P_2 - P_\infty}$$

where P_1 is the amount of O^{18} initially present in the solid. For each experimental value of $1 - (W/W_\infty)$ a value of τ is obtained from the original plot of $1 - (W/W_\infty)$ vs τ . These τ values are in turn plotted against the corresponding time. Since $\tau = Dt/a^2$, this plot should be a straight line of slope D/a^2 passing through the origin. By knowing the average spherical radius of the particles, the diffusion coefficient is then calculated.

The solutions to the diffusion equation used here require that a constant and limited supply of gas be in contact with the solid. It is also assumed that at all times equilibrium exists between the surface of the solid and the gas and there is no concentration gradient within the gas. Two experimental approaches have been used in trying to satisfy these conditions. In the first, the apparatus consisted of a fused silica reaction tube to which a freeze out bulb and two 6 in., 3 mm diam. pyrex sample tubes were attached. A ball joint was also included so that the whole unit could be attached to a gas filling system and assembled. When at temperature, the unit could then be filled with CO_2 and sealed off. Immediately after sealing a timer was started, and at various intervals, $3/4$ -in. to 1-in. lengths of the sampling tube were sealed off the 3-mm sampling tubes. There were some major experimental difficulties encountered with this method. First, it was observed that diffusion of the CO_2^{18} through the reaction tube and into the sampling tubes was not sufficiently rapid to warrant the assumptions of no concentration gradient in the gas and equilibrium between the surface of the solid and the gas. This condition was improved somewhat by momentarily freezing and then warming the CO_2 immediately before a sample was sealed off. The other difficulty with this apparatus was the inability to quickly introduce the measured quantity of CO_2 into the combustion tube before the gas could come in contact with the UO_2 ; hence the selection of the starting time of the experiment was somewhat arbitrary. Also, results at the highest temperatures were so erratic as to indicate that the apparatus was not sensitive enough to the rapid changes of the gas composition.

Table 18 — INCREASE IN WATER CONTENT WITH DEGREE OF OXIDATION

Temp., °C	Comp.	Exposure time, days	Per cent water	H_2O/UO_3
177	2.02	0	0.045	
	2.02	4	0.09	
	2.42	2	2.1	0.95
	2.57	4	2.8	0.92
	2.67	6	3.2	0.89
	2.85	8	3.6	0.80
	2.17	4	0.80	0.91
127	2.25	8	1.3	0.98
	2.40	12	2.2	1.06
	2.52	16	2.4	0.87

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At the end of the experiment the CO_2 remaining in the system was sealed off in the freeze out bulb and weighed. The λ value of the experiment was calculated from these data. This λ figure is reliable only if the total amount of CO_2 withdrawn for analysis is small compared to the total CO_2 introduced. In these experiments the amount of CO_2 removed was kept to within 1 per cent of the total CO_2 .

A second apparatus was designed and constructed in order to eliminate some of the difficulties encountered in the earlier experiments. This apparatus is based on a "race track" type of design, where the gas is continuously circulating by convection around the UO_2 sample. A sample of gas can be removed from the gas flow path quickly and sent into a sampling system external from the gas flow system. Thus the problem of the gas diffusing and becoming equilibrated in long narrow tubes was eliminated. Also, the system was so designed that the introduction of CO_2 with the sample at temperature is efficiently accomplished. There is, however, with an apparatus of this type, the consideration of a large concentration gradient within the gas flow system. Thus a sample withdrawn might in no way be representative of the actual O^{18} concentration in the solid. Preliminary experiments with the new apparatus showed that after the initial 3 to 4 min the equilibration of the gas was rapid compared with the change of O^{18} concentration of the gas.

The uranium dioxide, enriched in O^{18} , used in these experiments was prepared by the high pressure steam oxidation of uranium metal foil in the presence of O^{18} enriched water. The preparation is carried out in an autoclave at 340°C and a steam pressure of about 2200 psig. Pressure and temperature are maintained for about 24 hr. After preparation, the uranium dioxide is dried, screened through a 120 mesh screen and annealed in a hydrogen atmosphere for 15 hr at 900°C .

Chemical, mass spectrometric, and x-ray diffraction analyses and density, surface area, and particle size distribution measurements were made on the powder. These results are discussed below.

The analysis of the gas samples is made with a Consolidated Electric Corp. Model 21-610 mass spectrometer. The spectrometer is equipped with a glass inlet system to which a device is attached for breaking the small glass sample tubes. The analyses are accomplished by comparing the intensity of the mass 46 peak ($\text{C}^{12}\text{O}^{16}\text{O}^{18}$) to the mass 44 peak ($\text{C}^{12}\text{O}^{16}\text{O}^{16}$). In natural CO_2 this ratio is 0.00400, calculated from the abundances of the various carbon and oxygen isotopes.

For the oxygen isotopic analysis of UO_2 , a CO_2 - UO_2 equilibration method is used. Advantage is made of the relation, previously presented,

$$\lambda = \frac{P_\infty - P_1}{P_2 - P_\infty}$$

In this equation P_1 is to be measured. It is the amount of O^{18} initially present in the solid. By making λ very small P_1 becomes nearly equal to P_∞ , which is the final composition of the gas. Thus P_1 can be determined by a measurement of P_∞ .

Chemical and x-ray analysis of the powder after annealing showed that the UO_2 consisted of the single cubic α phase of O/U ratio 2.004. The density, measured by liquid displacement, is 10.8 g/cm^3 , and the surface area, by nitrogen adsorption methods, is $0.26 \text{ m}^2/\text{g}$. An average spherical particle radius calculated from the density and surface area measurements is about 1.1μ .

The amount of O^{18} initially present in the UO_2 was measured using the method discussed above. The λ value of the experiment was adjusted to between 0.001 and 0.01 and the exchange reaction performed at about 700°C for 8 hr to ensure completion. The measured peak ratio for $\text{C}^{12}\text{O}^{16}\text{O}^{18}$ to $\text{C}^{12}\text{O}^{16}\text{O}^{16}$ was 0.0280, an enrichment of seven times over the natural O^{18} concentration in the CO_2 .

It was first necessary to confirm the assumption that the reaction being studied was diffusion controlled and not controlled by a surface exchange reaction. If the rate controlling step is a simple surface exchange reaction, the reaction can be analyzed by using first order kinetics. Thus a plot of $\log W/W_\infty$ vs time (W/W_∞ being the extent of the reaction) should

Fig. 44—Extent of exchange reaction as a function of time.

be linear. A few of the experiments are plotted in such a manner in Fig. 44. The deviation from the linearity is apparent. It can be concluded then that a first order kinetic reaction is not rate controlling. Typical plots of the data analyzed with the diffusion equations are shown in Fig. 45. The linear nature of the curves supports the assumption that diffusion of oxygen through the UO_2 is rate controlling.

It is seen that curve b in Fig. 45 is a better straight line than curve a. Curve b was obtained with the flowing gas apparatus, whereas curve a was obtained with the static system. This improvement was noted for all experiments performed on the flowing gas system. However, in both cases the plots do not intersect the origin as theory predicts they should. Possible reasons for this are: (1) the approximation of particle sphericity is inexact; (2) there are possible errors in t ; and (3) D may vary with concentration.

Experiments were performed using both the static and flowing systems in the temperature range 450 to 850°C. The diffusion coefficients calculated from the data are based on an average spherical particle radius of 1μ . The results are shown in Table 19; some experiments are marked to indicate those done in the static gas system.

In Fig. 46 the data from which the activation energy is calculated are plotted as $\log D$ vs $1/T$. The results of the three high temperature experiments made with the static system are not included because of the large amount of scatter obtained. Consequently the temperature range included in this plot is from 450 to 600°C. A least squares calculation of the data gave an activation energy of 29.7 ± 2.3 kcal/mole. The variation of the diffusion coefficient with temperature can be represented by the equation $D = 2.6 \times 10^{-5} \exp(-29,700/RT)$. This value for the activation energy for the self-diffusion of oxygen in UO_2 is in fair agreement with that obtained (26.3 ± 1.5 kcal/mole) for the diffusion of oxygen in UO_2 from kinetic studies of the oxidation of UO_2 in the temperature range 160 to 350°C (reference 64). The D_0 values differ somewhat— 2.6×10^{-5} in this work as compared with 5.5×10^{-3} obtained from the oxidation kinetics work.

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Fig. 45 — $\tau(Dt/a^2)$ as a function of time for two diffusion experiments.

It should be noted that the exchange reaction was carried out in CO_2 . Note also that analysis of the UO_2 powder after the exchange showed no change in O/U ratio, at least within the experimental error (see Table 19). The $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ equilibrium would predict that oxygen pressures of 10^{-6} and 10^{-7} atom should exist at 850 and 450°C, respectively, the temperature limits of the exchange experiments. Also, from an examination of Fig. 38, one would infer that, if $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ equilibrium were attained, considerable oxidation of the UO_2 would occur. That this was not observed is indication of the absence of equilibrium condition for this exchange reaction. Thus, as previously reported,⁶⁰ it is likely that the very low rate of oxidation of UO_2 at low oxygen pressure prevents attainment of equilibrium in the powders for the times used.

Although the activation energies obtained from the two oxygen diffusion studies—the CO_2 - UO_2 exchange reaction and the low temperature oxidation reaction—agree to within the experimental errors, the preexponential terms (the D_0 values) differ. The ratio of these D_0 values (D_0 for exchange to D_0 for oxidation) is approximately 0.005. It is interesting to note that the ratio of the excess mobile oxygen anions is, for exchange to oxidation, 0.004/0.34 or 0.012; of course, this ratio will vary considerably with the absolute error in O/U ratio, ± 0.004 . On the assumption that the preexponential term is temperature independent, this

Table 19—SELF-DIFFUSION COEFFICIENTS OF OXYGEN IN UO_2

Temp., °C	Diffusion coefficient, $\text{cm}^2/\text{sec} \times 10^{13}$	O/U ratio† after exchange reaction
445	0.21*	2.002
465	0.40	2.003
497	1.8	2.001
517	1.8	2.007
522	2.7*	2.007
535	1.4*	2.013
540	1.9	2.002
571	5.5	2.001
600	6.8*	2.005
603	14	2.002
650	1.3*	2.002
686	6.5*	2.004
855	11.5*	2.000

* Experiments performed in static gas system.

† O/U ratio of starting material was 2.004 ± 0.004 .

Fig. 46—Variation of diffusion coefficient with temperature.

agreement in the D_0 ratio with the ratio of excess mobile oxygen anions is as expected since D_0 should be proportional to the number of excess mobile oxygen ions, n_i (see below). The mechanisms for the two diffusion sections may thus differ in this respect: in the exchange reactions there is exchange of oxygen in lattice positions primarily, whereas in the oxidation

reactions there is movement of interstitial oxygen ions and the interaction with lattice ions is negligible.

An estimate of the ionic conductivity (that due to oxygen ions) can be made from the oxygen self-diffusion data using the Nernst-Einstein relation,

$$\sigma_i = \frac{n_i Z^2 e^2}{kT} D_i$$

where σ_i = ionic conductivity

n_i = number of excess mobile oxygen ions per cubic centimeter

Ze = charge of oxygen ions

D_i = self-diffusion coefficient of oxygen ions

k = Boltzmann's constant

T = absolute temperature

For a temperature of 500°C (773°K), the value for D_i is 1.0×10^{-13} cm²/sec; n_i for O/U ratio = 2.004 is approximately 1×10^{20} atoms/cm³. The ionic conductivity due to oxygen ions is calculated to be approximately 9.6×10^{-11} ohm⁻¹cm⁻¹. From the measurements of Willardson et al.⁴¹ the electrical conductivity measured at 500°C for sintered UO₂ (O/U ratio approximately 2.000) is 0.1 ohm⁻¹cm⁻¹, indicating that electrical conductivity in UO₂ is essentially electronic. This is as expected from the BMI measurements since no change in electrical conductivity with time was observed. The transference number, t_i , the ratio of the calculated ionic conductivity to the measured total conductivity, is approximately 1×10^{-9} .

7.2 Self-diffusion of Uranium in UO₂

The self-diffusion of uranium (U⁴⁺) in nearly stoichiometric UO₂ is being determined⁷⁶ by the conventional method involving sectioning and analysis of diffusion annealed couples. Diffusion couples are prepared from sintered high density natural UO₂ pellets upon which a thin layer of UO₂ enriched in U²³⁵ is vacuum deposited. Diffusion in these couples takes place during a high temperature anneal. The conditions of this experiment approximate that of a semi-infinite solid, extending from $x = 0$ to $x = \infty$ with an instantaneous source of diffusing media at $x = 0$. After annealing, sections from the diffusion couples surfaces are obtained by grinding with 600 mesh SiC abrasive powder on a glass plate. Uniform layers of UO₂ as thin as 0.0005 cm can be removed. The UO₂ is separated from the SiC carbide by dissolving it in concentrated nitric acid. Isotopic analyses for U²³⁵ and U²³⁸ are made mass spectrometrically.

For the boundary conditions employed in these experiments, the solution to the diffusion equation,

$$C = \frac{C_0}{\sqrt{\pi Dt}} e^{-x^2/4Dt}$$

or $\log C = -0.1086x^2/Dt + \log k$, shows that a plot of log concentration against diffusion distance squared ($\log C$ vs x^2) is a straight line. In all the experiments that have been carried out to date this has not been observed. What is observed is that the absolute value of the slope of the curve becomes smaller for increasing values of x^2 (see Fig. 47). This implies that the diffusing material is moved a greater distance than that predicted by the solution for the diffusion equation. A diffusion coefficient calculated from such a curve by fitting the best straight line through the distribution results in a value which is too small near the original surface and too large at greater diffusion depths.

Diffusion coefficients have been calculated from similar nonlinear distributions when reasons for the anomalous behavior were known. For example, deviations in slope have been shown to be due to slight changes in the stoichiometric composition of the lattice.⁷⁷ In the case of UO₂ since all diffusion anneals take place in a hydrogen atmosphere, it appears that there would be no consistent compositional variation throughout the diffusion couple. The deviation from linearity can be attributed to contributions from grain boundary and/or surface

Fig. 47—Surface and/or grain boundary diffusion and lattice diffusion for $U^{235}O_2$ - $U^{238}O_2$ diffusion couple annealed at 1615°C.

diffusion, as was done by Slifkin et al.⁷⁸ in a study of self-diffusion in silver. From an analysis of Fischer,⁷⁹ they were able to separate the grain boundary contribution from lattice diffusion. At high temperatures the relation between $\log C$ and x^2 was found by Slifkin et al.⁷⁸ to be linear, indicating that only volume diffusion processes are present. From the plot of $\log$ concentration versus diffusion distance squared (shown in Fig. 47) it can be noted that contributions from both grain boundary (or surface) and volume diffusion are present.

The temperature region where grain boundary diffusion effects appear to confound those of volume diffusion seems to be around $0.7 T_m$. This is in the region where diffusion measurements have been made on UO_2 . If it is assumed that two effects, grain boundary and volume diffusion, are present in UO_2 , then a volume diffusion coefficient can be calculated from the $\log C$ vs x^2 plot using the points near the original surface. This has been done for diffusion anneals carried out at temperatures from 1410 to 1750°C. Diffusion coefficients calculated from these experiments are listed in Table 20, and an activation energy between 90 and 125 kcal/mole was estimated.

This value for the activation energy is 3 to 4 times greater than that observed for oxygen self-diffusion.

An estimate of the surface and grain boundary diffusion coefficients was made from a diffusion couple annealed at 1730°C, using the method developed by Fischer.⁷⁹ From a plot of $\log C$ versus penetration distance, a grain boundary and surface diffusion coefficient was estimated to be 8×10^{-11} cm²/sec, which is about 30 times the value obtained for the bulk diffusion coefficient.

Extension of these measurements to higher temperatures and use of UO_2 depleted in U^{235} to permit better concentration gradients is being carried out by Auskern at Bettis Plant.⁷⁸

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Table 20 — SELF-DIFFUSION COEFFICIENTS OF URANIUM IN UO_2

Temp., °C	Diffusion coefficient, $\text{cm}^2/\text{sec} \times 10^{13}$
1410	0.6–1.3
1590	3
1607	6
1677	6
1712	6
1730	25
1750	43

8 CONCLUSIONS

Characterization studies of various methods of UO_2 powder preparation showed that although powder properties such as particle size, surface area, and density of a UO_2 powder can vary over a wide range depending upon method of preparation, these properties can be controlled through judicious choice of variables in the preparation procedure. These variations in physical properties have a large effect on rates of sintering of compacted powder at elevated temperatures but a relatively minor effect on the structure of high density UO_2 .

Some conclusions that can be made from the information obtained from sintering studies on UO_2 are the following:

1. The characteristics for a powder to sinter rapidly to high density, to show little dependence of sintered density on green density, and to produce a uniform grain structure in the sintered material are high surface area, high density, and either small particle size or a clustered particle size easily broken down uniformly to a small particle size.
2. These properties can be achieved by a comminution process such as ball milling.
3. Densification due to cold pressing occurs primarily through the progressive compression of the larger pores.
4. Main mode of densification in the early stages of sintering is the decrease in the amount of open porosity, and the main difference among various powder preparations is in the length of time required to reach the stage of nonconnected porosity.
5. Sintering in hydrogen probably occurs through a plastic or viscous flow mechanism, whereas densification in steam sintering occurs by oxygen ion diffusion.
6. Grain size is controlled by the density of UO_2 .

Results of studies on the physical properties of UO_2 can be summarized as follows:

1. The melting point of UO_2 is $2760 \pm 30^\circ\text{C}$.
2. As expected, modulus of rupture of UO_2 increases with increase in temperature, whereas modulus of elasticity decreases with increase in temperature.
3. UO_2 is an electronic conductor; an estimate from self-diffusion data shows that the ionic contribution is small.
4. Magnetic susceptibility measurements indicate that, in high O/U ratio UO_2 , the excess oxygen content is accommodated by interstitial occupancy.
5. Neutron diffraction measurements indicate that excess oxygen enters the UO_2 lattice at definite positions and is not distributed at random.

Extensions of phase equilibria studies for the UO_2 - U_3O_8 system showed little changes from the recent phase diagram presented by Gronvold. These differences are in the location of the boundary of the UO_{2+x} phase and U_4O_{9+x} phase. Partial molar free energies, entropies, and enthalpies of oxygen in UO_{2+x} at temperatures of 1100 to 1350°K were obtained. It was found that the partial molar free energy of solution of oxygen in UO_{2+x} is a linear function of temperature.

Oxidation of UO_2 in the temperature range 120 to 350°C proceeds by a diffusion mechanism whereby oxygen ions diffuse into interstitial positions in the UO_2 lattice. These measurements

are in agreement with diffusion data from CO_2 - UO_2 exchange reactions. The reduction of U_4O_9 and U_3O_8 to UO_2 is a surface controlled reaction.

As revealed from self-diffusion kinetic measurements, the mobility of oxygen anions is much greater than that of uranium cations in UO_2 ; the activation energy for oxygen diffusion is 29.7 kcal/mole as compared with a value of 90 to 125 kcal/mole for uranium diffusion.

If properly fabricated, high density UO_2 is stable to oxidation over long periods of time in degassed water and steam at neutral and high pH. In the presence of dissolved oxygen, however, UO_2 reacts to form a hydrated oxide $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$.

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Thermal Conductivity of Uranium Dioxide

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The thermal conductivity of UO_2 , an early product sintered in a carbon furnace, has been measured up to 1800°C in connection with the high rate of heat transfer. This temperature is the average between two thermocouples in the radial heat-flow direction.

The thermocouples used were the tungsten-molybdenum combination in the inner hottest positions and platinum-platinum/rhodium in the outer hole. Insulation for the thermocouples was made of MgO , which limited the temperature to about 2200°C , which is the melting point of the $\text{UO}_2\text{-MgO}$. We have successfully tried ThO_2 as an insulator for the continued experiments.

Figure 1 shows the UO_2 cylinders, 15 mm in diameter and 20 mm in length, with the three positions for thermocouples at different radii. The tungsten heating rod is positioned in the

Fig. 1— UO_2 cylinders used in the heat-transfer and cycling experiment.

large central hole. The cylinders are not grained, and the waist is a few tenths of a millimeter. Figure 2 shows the cylinders assembled for the first run.

The UO_2 cylinders were fitted into an aluminum canning tube and put in a water loop, which kept the surface at about 50°C . The maximum surface heat rating in run 5 was 17 watts/ cm^2 at 2200°C on the inner thermocouple. The assembly after this run is shown in Fig. 3. The

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Fig. 2—Five UO_2 cylinders mounted on a tungsten wire (run 1).

Fig. 3— UO_2 cylinder assembly cycled to a maximum center temperature of 1800°C with the surface cooled by water (run 5).

Fig. 4—Close-up of the UO_2 cylinders (run 5).

outer layer of the UO_2 cylinders was granulated and was collected on the paper. Close to the tungsten rod the UO_2 was crystalline with large grain size. In the boundary between these regions there was a layer of soft or powdery UO_2 . Spectroscopical analysis showed this powder to be still crystalline. Figure 4 shows a close-up of the same assembly. In the middle the tungsten wire can be seen.

Before presenting the results of the measurements, it is of interest to discuss the thermal conductivity values found in the literature. In Fig. 5, curve 3 is taken from Kingery¹ and Tebo² for a density of 8.0 g/cm^3 , and curve 4 is from Hedge³ for a density of 8.17 g/cm^3 . Kingery has extrapolated his values to theoretical density by assuming the dependence to be a linear function of the density, as shown in curve 2. However, using the formula by Loeb⁴ but substituting for the radiation term the thermal conductivity of the gas in the pores, the formula shown for curve 5 is obtained. By taking into account that, for a crystalline material, the heat-transfer coefficient should be inversely proportional to the absolute temperature, curve 1 is obtained for the theoretical density and curve 5 is obtained for a density of 10.0 g/cm^3 .

Figure 6 shows our results for a typical series of temperature cycling runs. After only three cycles the heat-transfer coefficient broke down to $0.007 \text{ watt/cm}^2/\text{C}$. The large drop in the heat conductivity can be explained if the UO_2 becomes powdered as a result of the very large temperature gradient; this will be discussed later. The last cycle was run up to an average temperature of 1800°C . It is of interest to note that the heat conductivity increases when the temperature increases to the sintering temperature. The thermal conductivities at the theoretical density and at 10.0 g/cm^3 are also shown in Fig. 6.

The very pronounced oscillations of the values as a function of temperature are not understood but may be explained by the formation of cracks. These oscillations also appeared in all the measurements with other UO_2 cylinders. The maximum error in the measured heat-transfer coefficient is calculated to be 35 per cent.

UO_2 cylinders of the same quality as those used in the previous experiment were irradiated in the research reactor R1 at a flux of $1.8 \times 10^{12} \text{ neutrons/cm}^2$. Thermocouples were mounted in holes in the cylinders, one in the center and one close to the surface, so that the radial heat flux produced by the fission could be used. The heat losses to the ends were minimized by using two equal UO_2 cylinders at each end of the test cylinder. The cylinders were contained in an aluminum canning tube. A flux monitor mounted close to the sample was made of a small uranium metal cylinder insulated by asbestos. The temperature drop from the uranium over the asbestos was measured by thermocouples and calibrated, even during operation, by an electric heater in the uranium. The temperature during operation was thought to be held at 350°C by means of air cooling and an electric heater. However, the heater failed, and therefore the temperature constancy was not so good as would be desired.

Figure 7 shows the thermal conductivity as a function of the neutron dose. The rapid breakdown of thermal conductivity which occurred was unexpected; therefore an irregular start-up of the reactor was allowed for, conditioned by other experiments. The first point is thus at $2.2 \times 10^{15} \text{ neutrons/cm}^2$, where the thermal conductivity had dropped to about one-third of the value that unirradiated UO_2 is assumed to have at 350°C . At $10^{18} \text{ neutrons/cm}^2$ the thermal conductivity had dropped to $0.005 \text{ watt/cm}^2/\text{C}$. The later increase to about $0.007 \text{ watt/cm}^2/\text{C}$ is not understood. The thermocouples were checked, and they gave the same readings as before the start.

The large fluctuations as a function of irradiation (Fig. 7) are also not understood. An attempt to explain the fluctuations with the varying temperature is made in Fig. 8, but no correlation is observed. The large drop in thermal conductivity to about $0.007 \text{ watt/cm}^2/\text{C}$ in this case can be explained if the UO_2 becomes powdered by the concentrated heat release from the fission products. The measurements will be repeated with better sintered UO_2 as described in the paper by Kiessling and Runfors.

An investigation of the thermal conductivity in powders has been made in order to explain the large drop in thermal conductivity of sintered UO_2 just described. Using the basic idea of Jacob,⁵ the formula given in Fig. 9 is obtained. In this formula the $\sqrt{2}$ is a geometrical factor,

(Text continues on page 525.)

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Fig. 5— Thermal conductivity of sintered UO_2 as a function of temperature at different densities. Curve 1, $\lambda = 48/T^\circ\text{K}$; $\rho = 10.95 \text{ g/cm}^3$. Curve 2, $\rho = 10.9$ (Kingery¹ and Tebo²). Curve 3, $\rho = 8.0$ (Kingery¹ and Tebo²). Curve 4, $\rho = 8.17$ (Hedge³ and BMI). Curve 5,

$$\lambda_{\text{eff}} = \lambda_{\text{UO}_2} \left[1 - r^{\frac{2}{3}} + \frac{r^{\frac{2}{3}}}{1 - r^{\frac{2}{3}} + r^{\frac{2}{3}} (\lambda_{\text{UO}_2} / \lambda_{\text{gas}})} \right]$$

where the porosity $r = 0.087$ ($\rho = 10.0$) and λ_{UO_2} is from curve 1.

Fig. 6—Thermal conductivity of UO_2 measured as a function of temperature at large thermal stresses and after temperature cycling. A, $\lambda = 48/T^\circ\text{K}$, maximal thermal conductivity at $\rho = 10.95 \text{ g/cm}^3$. B, thermal conductivity of sintered UO_2 at $\rho = 10.0$.

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Fig. 7—Thermal conductivity of UO_2 as a function of neutron irradiation at constant temperature. The mean temperature is between 300 and 480°C.

Fig. 8—Thermal conductivity of UO_2 at slightly varying temperature and successively increasing neutron irradiation.

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Fig. 9—Thermal conductivity of UO_2 powder at a density of 6.35 g/cm^3 as a function of temperature for different gases. The formula for λ_{eff} of UO_2 powder at $t < 1400^\circ\text{C}$ is:

$$\frac{1}{\lambda_{\text{eff}}} = \frac{1}{(1-r)^{1/2}} \left\{ \frac{1}{\frac{\sqrt{2} \lambda_{\text{gas}}}{(1-r)^{1/2} [1 - 0.92 (1-r)^{1/2}] + \lambda_{\text{contact}}} + \frac{1}{\lambda_{\text{UO}_2}}} \right\}$$

where the porosity $r = 0.42$ ($\rho = 6.35 \text{ g/cm}^3$, 58 per cent of theoretical) and $\lambda_{\text{contact}} = 0.004$. $\times$, from Shackelford.⁶ $\circ$, from Boeglie and Diessler.⁷ A, $\lambda_{\text{UO}_2} = 48/T^\circ\text{K}$, maximal thermal conductivity at $r = 0$ ($\rho = 10.95$). B, thermal conductivity of sintered UO_2 at $\rho = 10.0$.

Fig. 10 — Thermal conductivity of UO_2 powder at densities of 10.4 and 10.0 g/cm^3 as a function of temperature for different gases. The formula for λ_{eff} of UO_2 powder at $t < 1400^\circ\text{C}$ is:

$$\frac{1}{\lambda_{\text{eff}}} = \frac{1}{(1-r)^{1/2}} \left\{ \frac{1}{\frac{\sqrt{2} \lambda_{\text{gas}}}{(1-r)^{1/2} [1 - 0.92 (1-r)^{1/2}] + \lambda_{\text{contact}}} + \frac{1}{\lambda_{\text{UO}_2}}} \right\}$$

where the porosity $r = 0.050$ ($\rho = 10.4 \text{ g/cm}^3$, 95 per cent of theoretical) (—); $r = 0.087$ ($\rho = 10.0 \text{ g/cm}^3$, 91.3 per cent of theoretical) (---); and $\lambda_{\text{contact}} = 0.004$. A, $\lambda_{\text{UO}_2} = 48/T^\circ\text{K}$, maximal thermal conductivity at $r = 0$ ($\rho = 10.95$). B, thermal conductivity of sintered UO_2 at $\rho = 10.0$.

0.92 depends on the powder grain size, and λ_{contact} is a heat-transfer coefficient in the contact point between the grains. The formula is compared with measurements by Shackelford⁶ and by Boeglie and Diessler⁷ with good agreement for a powder density of 6.35 g/cm³.

In Fig. 10 the calculated thermal conductivity is illustrated for powders with densities of 10.0 and 10.4 g/cm³ and with different gases. From private communication with Lewis⁸ in Canada, we obtained the integrated value $\int \lambda \, dt$ from 275°C to the melting point of UO₂. For un-irradiated UO₂ he gives 47 watts/cm, which is calculated from the curve given by Kingery. For irradiated UO₂ their measurements gave between 30 and 35 watts/cm. The integral can also be calculated from the report by Eichenberg⁹ by using the heat generated in the sample, and for UO₂ in helium gas the value 35 watts/cm is obtained for the integral from about 400 to 1700°C. From our curve for helium, the central temperature should be about 2000°C. With his defective rod and with helium substituted for steam, which has about the same thermal conductivity as argon, he got 33 watts/cm when melting in the center was fully developed. Our diagram gives the same value for argon from 400°C to the melting point.

At the other end of the same rod the integral was 17 watts/cm, and, judging from the central hole, the rod appeared to be melted in the center. From our curve for argon, the central temperature should have been about 2100°C. The melting at the central hole as seen in the picture in the report⁹ is not typical and may have developed from evaporation of the UO₂, which has a vapor pressure at 2100°C of 0.1 mm Hg as given by Ackerman.¹⁰

Our measurements were made with argon, and the value 0.007 watt/cm/°C agrees well with the curve for argon in Fig. 10.

For higher rates of burn-up it is safe to assume that, even if the filling gas is helium, the continuously produced fission-product gases will dominate the heat transfer in the UO₂ body at the end of the in-pile period. In this case the value of the integral should be 28 watts/cm from 400°C to the melting point according to Fig. 10.

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Ceramic Fuel Elements in the $\text{ThO}_2\text{-UO}_2$ and $\text{UO}_2\text{-PuO}_2$ Systems

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ABSTRACT

The techniques for forming solid solutions in either the $\text{ThO}_2\text{-UO}_2$ or $\text{UO}_2\text{-PuO}_2$ system are summarized. Solid solutions in the $\text{ThO}_2\text{-UO}_2$ system can be formed and fabricated by sintering mixtures of ThO_2 and U_3O_8 . The resultant ware was found to have good density and appeared to resist damage from irradiation and corrosion by water. The manufacture of one $\text{ThO}_2\text{-UO}_2$ solid-solution composition for the BORAX-IV fuel elements is discussed. The procedures for forming the $\text{UO}_2\text{-PuO}_2$ solid solutions are given, and the preliminary irradiation studies are discussed.

1 INTRODUCTION

Fuel assemblies for use in boiling water reactors must resist corrosion and erosion caused by the boiling water. It is also essential that the fuel be dimensionally stable and free from harmful phase transformations under long-term irradiation and repeated thermal cycling. The metals thorium, uranium, and plutonium are susceptible to corrosion by water, and they must be carefully clad with a corrosion-resistant material when used in water-cooled reactors. These metals also undergo phase transformations at relatively low temperatures, and these phase transformations may result in distortions in the fuel either during fabrication or in operation of the reactor.

The oxides or common corrosion products of thorium, uranium, and plutonium are resistant to corrosion by water. These oxides are free of harmful phase transformations and have melting points high enough to safeguard against core distortion during operation at high temperatures. Thus it would appear that the oxides of thorium, uranium, and plutonium would be more suitable for use as nuclear fuels than their corresponding metals.

Urania (UO_2) and thoria (ThO_2) have long been used as refractory materials for melting such metals as uranium. Many of the physical properties of these oxides have been evaluated, and currently these oxides are being investigated for use in nuclear reactors. The physical properties of the oxides of plutonium have also been studied, and these oxides have also been considered for use in nuclear reactors. However, the study of plutonium oxides has lagged behind the study of thoria and urania, and information concerning them is not readily available.

U^{235} and Pu^{239} are fissionable, whereas Th^{232} and U^{238} are not but can be converted to fissionable materials through the Th-U^{233} cycle and the $\text{U}^{238}\text{-Pu}^{239}$ cycle. The oxides ThO_2 , UO_2 , and PuO_2 are isomorphic in structure, and the difference in lattice constants of the three oxides is such that the formation of solid solutions would be indicated. This solid solution or mixed-crystal formation would indicate that a breeder fuel in either of the systems $\text{ThO}_2\text{-UO}_2$, $\text{UO}_2\text{-}$

PuO_2 , or ThO_2 - PuO_2 would be feasible. The ThO_2 - UO_2 system has been investigated by Argonne National Laboratory (ANL), Lemont, Ill., and the UO_2 - PuO_2 system has been investigated by Knolls Atomic Power Laboratory (KAPL), Schenectady, N. Y. In order to simplify the presentation of the work in these two systems, each will be discussed separately.

1.1 ThO_2 - UO_2 System

The formation of a complete series of solid solutions between thorium and uranium dioxides was reported by Slowinski and Elliot¹ for the temperature range of 1000 to 1200°C. This complete miscibility was found by Lambertson et al.² to extend up to the liquid phase as shown by the phase diagram³ in Fig. 1. These solid solutions, like pure UO_2 , will oxidize if

Fig. 1— UO_2 - ThO_2 phase equilibrium diagram. x, liquid. o, solid. ●, solid and liquid.

heated in air; however, Gruen⁴ reported that the thorium ion stabilizes the cubic fluorite type structure according to the amount of ThO_2 present. Hund and Niessen⁵ found that the ThO_2 - UO_2 solid solutions retained the cubic fluorite type structure when heated in air to 1200°C for ThO_2 - UO_2 solid solutions containing up to 56.5 mole % UO_2 , whereas above 56.5 mole % a limited fluorite phase existed. Anderson et al.⁶ noted that the fluorite phase was stable up to 1400°C in air for solid solutions containing up to 78 mole % UO_2 . This discrepancy was attributed to the different methods used in preparing the solid solutions; however, both observers indicated that ThO_2 - UO_2 solid solutions once formed would be stable for a breeder type fuel that would in all probability be composed preliminarily of thorium spiked with sufficient enriched uranium to cause criticality.

These solid solutions of ThO_2 and UO_2 were prepared either by coprecipitation of soluble uranium and thorium salts followed by a reduction in either a hydrogen or a carbon monoxide atmosphere^{5,6} or by direct sintering of mixtures of the two oxides² in hydrogen or in a vacuum. These methods tended to ensure the reduction of the uranium oxide to an oxide corresponding very closely to UO_2 and, in the case of compacts, avoided the destructive volume expansion of approximately 30 per cent caused by the oxidation of the cubic UO_2 to the orthorhombic U_3O_8 . The work of Warde⁷ and Hoekstra⁸ indicated that U_3O_8 is stable, when heated in an oxidizing atmosphere, to approximately 1150°C. With prolonged heating the U_3O_8 decomposes to a lower oxide and eventually to UO_2 . Thus it would appear that ThO_2 - UO_2 solid solutions could be prepared by sintering a mixture of ThO_2 and U_3O_8 in air. This procedure would eliminate the need for a protective atmosphere in sintering, and the volume change of U_3O_8 to UO_2 would be comparable to sintering shrinkages usually associated with firing ceramic ware.

Compacts of ThO_2 and U_3O_8 were pressed and sintered in air to 1700 to 1750°C. Compositions containing up to 80 wt. % UO_2 added as U_3O_8 were successfully fabricated.⁹ X-ray diffraction studies of compositions containing up to 60 wt. % UO_2 added as U_3O_8 indicated that ThO_2 - UO_2 solid solutions were formed. For compositions containing more than 60 wt. % UO_2 , there was considerable line broadening of the X-ray patterns with evidence of an additional phase. These observations would parallel the work of Hund,⁵ who observed the formation of a fluorite type phase from compositions containing up to 56.5 mole % UO_2 and the appearance of excess U_3O_8 during the firing of compositions containing more than 56.5 mole % UO_2 . Whereas X-ray diffraction studies indicated a cubic solid solution of ThO_2 - UO_2 , it was doubtful that the U_3O_8 was reduced to UO_2 as Biltz and Muller¹⁰ in their work found that UO_2 can take up oxygen to a composition approximately $\text{UO}_{2.3}$ with no apparent change in volume. Above the composition $\text{UO}_{2.3}$ the volume increases linearly from the composition $\text{UO}_{2.3}$ to U_3O_8 . From this it would appear that the ThO_2 - UO_2 solid solutions formed by air sintering mixtures of U_3O_8 and ThO_2 would have a uranium to oxygen ratio between UO_2 and $\text{UO}_{2.3}$.

The apparent densities (water immersion) of the ThO_2 - UO_2 compositions were relatively low for the initial experiments in fabricating these solid solutions (Fig. 2). From this it would appear that the fired densities vary directly with the forming pressure, decrease as the U_3O_8 content increases. However, in subsequent experiments in which a composition containing 70 wt. % U_3O_8 and 30 wt. % ThO_2 was successfully fabricated, test pieces were found to have apparent densities (water immersion) of 9.2 to 9.3 g/cm³.

The variables involved in producing dense, sintered compacts of ThO_2 and U_3O_8 have not been evaluated. However, it is indicated that forming pressure, binder content, particle-size distribution, pressing characteristics of the raw materials, and rate and conditions of sintering play an important part in the fabrication of dense ThO_2 - UO_2 bodies.

The sintering shrinkages of two compositions were studied as shown in Fig. 3. It is indicated that both the 10 and 20 wt. % U_3O_8 bodies shrink in the same manner. The shrinkages appear to be linear up to about 1300°C, where the rate changes. Above this point the shrinkage is again linear to 1800°C.

Several specimens of ThO_2 - UO_2 solid-solution compositions containing up to 30 wt. % UO_2 added as U_3O_8 which were sintered at 1750°C in air were reheated in air to a temperature of 1400°C for periods as long as 96 hr. These specimens did not change visually nor were any dimensional or weight changes observed. Several specimens of compositions containing up to 25 wt. % UO_2 added as U_3O_8 were also reheated to 1750 to 1850°C without visible change. These tests indicate that the ThO_2 - UO_2 solid solutions in this range would be thermally stable in oxidizing conditions.

Irradiation tests were made on specimens fabricated from two ThO_2 - UO_2 compositions^{10,11} in which the UO_2 was added as highly enriched U_3O_8 . The first body was composed of 97½ wt. % ThO_2 and 2½ wt. % UO_2 , whereas the second body was composed of 90.0 wt. % ThO_2 and 10.0 wt. % UO_2 . Test specimens were formed by dry pressing the mixed oxides into right cylinders ¼ in. in diameter and approximately ½ in. in length. These specimens were fired in a gas-fired kiln to a temperature of 1800°C. The peak temperature was held for 2 hr, the kiln was shut off, and the pellets were allowed to cool in the kiln to room temperature. The average apparent densities (water immersion) of the two bodies ranged from 9.0 to 10.0 g/cm³, and the

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 Table 1—IRRADIATION OF 97½ WT. % ThO_2 - 2½ WT. % UO_2 FUEL SPECIMENS

Sample No.	Reactor	Jacket	Annulus	Burnout, % (total metal atoms)	Surface heat flux, Btu/hr/sq ft	Temperature, °C		Remarks
						Central	Surface	
4335c	CP-5	Bare		0.02	2.9×10^4	435	270	None
4335D	CP-5	Zr ²	Air	0.05	3.4×10^4	465	270	Tested 1100 hr; two-pellet assembly, one cracked
4335E	CP-5	SS	Air	0.05	3.4×10^4	465	270	Tested 1100 hr; two-pellet assembly, one cracked
BF-2	MTR	Bare		0.88	3.1×10^4	450	160	None
BF-5	MTR	Zr ²	Air	0.85	3.0×10^4	450	175	20-mil hole in can
BF-11	MTR	SS	Air	0.72	2.5×10^4	375	150	20-mil hole in can

Fig. 2—Densities of thoria-urania compositions fired in air to 1750°C.

 Fig. 3—Shrinkage vs firing temperature for two urania-thoria compositions.
 ---, 10 per cent U_3O_8 . —, 20 per cent U_3O_8 .

average apparent porosities ranged from 1.0 to 10.0 per cent. A few of the pellets were irradiated bare; however, the majority of the pellets were irradiated encased in cans made of Zircaloy-2, stainless steel, or aluminum-1 wt. % nickel alloy. The annulus between the can wall and the ceramic specimen was filled with either gas (80 per cent He-20 per cent A), lead, or NaK (sodium-potassium eutectic alloy). The irradiation tests were carried out in two reactors available to ANL: the Materials Testing Reactor (MTR), Idaho Falls, Idaho, and the Chicago Pile No. 5 (CP-5), Lemont, Ill.

The results of the irradiation tests of the 97½ wt. % ThO₂-2½ wt. % UO₂ body are summarized in Table 1. The CP-5 tests were made in water autoclaves at temperatures of 500 to 515°F and at pressures of 680 to 810 psi. Burnouts ranged from 0.02 to 0.05 at. % of the total metal atoms. Postirradiation examination revealed that many of the specimens had developed cracks, but the oxide fragments were large, and there was no evidence of distortion of the metal can owing to the fragmentation of the ceramic pellets. Burnout in the MTR tests ranged from 0.20 to 0.95 at. % of the total metal atoms. In these tests two specimens were irradiated bare but were packed in steel wool to prevent mechanical damage. Postirradiation examination revealed that these specimens were free of visible damage and that there was no measurable change in dimensions. One of these specimens (BF-2, Table 1) is shown in Fig. 4. Other speci-

Fig. 4—ThO₂-2.5 per cent UO₂ specimens. (a) Specimen irradiated bare, packed in steel wool; burn-up: 0.88 per cent total metal. Top, before irradiation; bottom, after irradiation. (b) Typical jacketed specimen with 0.020-in. hole.

mens irradiated in either Zircaloy-2 or stainless-steel cans appeared to be free of visible cracks. However, microscopic examination revealed that several of the pellets had developed fine cracks, causing the pellets to break into large fragments when removed from the metal can.

The results of some of the irradiation tests for the 90 wt. % ThO₂-10 wt. % UO₂ body are summarized in Table 2. Burnout in the CP-5 tests ranged from 0.19 to 0.32 at. % of the total metal atoms. The two four-pellet assemblies (Table 2) differed by only 160 hr exposure time at full CP-5 power. However, the general appearance of the two assemblies was not consistent with the exposure time. The first assembly was distorted and contained a lead nodule at one

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 Table 2—IRRADIATION OF 90 WT. % ThO_2 - 10 WT. % UO_2 FUEL SPECIMENS

Sample No.	Reactor	Jacket	Annulus	Burnout, %	Surface	Temperature, °C		Remarks
				(total metal atoms)	heat flux, Btu/hr/sq ft	Central	Surface	
20	CP-5	Al-1% Ni	Lead	0.31	14.6×10^4	955	270	Tested 1630 hr; four-pellet assembly; two pellets cracked; jacket distorted
21	CP-5	Al-1% Ni	Lead	0.32	14.6×10^4	955	270	Tested 1790 hr; four-pellet assembly; pellets cracked
CA-1-1	MTR	Al-1% Ni	Lead	0.34	26.1×10^4	1060	270	Pellets cracked
CA-1-2	MTR	Al-1% Ni	Gas*	0.34	26.1×10^4	1060	270	Pellets cracked
CA-2-1	MTR	Al-1% Ni	Lead	0.64	50.5×10^4	2000	480	Pellets cracked
CA-2-2	MTR	Al-1% Ni	Gas*	0.64	50.5×10^4	2000	480	Jacket cracked and slightly distorted; pellets cracked
CA-3-1	MTR	Al-1% Ni	Lead	1.10	84.0×10^4	3300	760	Jacket had slight fissure; pellets cracked
CA-3-2	MTR	Al-1% Ni	Gas*	1.10	84.0×10^4	3300	760	Pellets cracked
CA-4-1	MTR	Al-1% Ni	Lead	1.25	100.0×10^4	3900	890	Jacket failed; explosive break
CA-4-2	MTR	Al-1% Ni	Gas*	1.25	100.0×10^4	3900	890	Jacket appeared melted; pellets appeared melted in center

*Gas—80 per cent helium - 20 per cent argon.

end of the tube. The two center pellets were cracked, but there was no evidence that this cracking contributed to the distortion of the tube. The end pellets were intact and appeared to be free of cracks. The second assembly showed only minor distortion in the tube, but, when the metal jacket was removed, all four pellets were found to be broken into large fragments.

The MTR specimens were irradiated to burnouts from 0.34 to 1.25 at. % of the total metal atoms. In each test the ceramic pellets were found to develop cracks. The gas-filled assembly irradiated to 0.65 at. % (total metal atoms) was found to have one fissure in the tube wall which may have been caused by the shifting of the oxide fragments. In the lead-filled assembly irradiated to 0.65 at. % (total metal atoms), the pellets were found to be fragmented but appeared to be held in place by the lead. Assemblies in which the central fuel temperature was 2000°C or less generally exhibited only slight dimensional changes, and the condition of these assemblies was considered good. Specimens irradiated to a burnout of 1.25 at. % (total metal atoms) appeared to fail in two ways. In the tests in which the annulus was filled with lead, the failure appeared to be due to gas pressure with a subsequent hoop-tensile stress fracture. In the tests in which the annulus was filled with gas, the failure appeared to be due to the jacket melting. Of interest was the appearance of one of the pellets irradiated to a burnout of 1.25 at. % of the total metal atoms. This specimen exhibited some evidence of melting as shown in Fig. 5.

1.2 Fuel Manufacture for the BORAX-IV Loading

These preliminary irradiation tests indicated that a thorium-uranium solid-solution fuel would be feasible and that the ceramic material could be fabricated by firing in air a mixture of ThO_2 and U_3O_8 . The low thermal conductivity of oxides indicated a high central fuel temperature, and, in order to minimize this high central fuel temperature, the fuel design was established as $\frac{1}{4}$ -

Fig. 5—End view of specimen CA-4-2 with calculated central temperature of 3900°C showing evidence of central melting in the fuel.

in. rods. This diameter was considered the minimum diameter for a ceramic pellet that could be easily dry pressed.

The BORAX-IV reactor was designed to contain 72 fuel assemblies and 10 blanket assemblies. Each assembly consisted of six tube plates with each tube plate containing eight tubes. The fuel assemblies were to be loaded with a thorium-uranium solid solution, and the blanket assemblies were to be loaded with thorium. On the basis of 72 fuel assemblies with each assembly composed of 48 fuel rods, each 24 in. in length, approximately 83,000 in. of fuel would be required, or, on the basis of $\frac{1}{2}$ -in. pellets, 166,000 pellets would be needed. In addition to these fuel pellets, approximately 23,000 thorium pellets would be needed for the blanket assemblies.

To those unfamiliar with the methods used in handling enriched materials, the procedure used in manufacturing the fuel and blanket material for the BORAX-IV reactor may be of interest. The two materials were processed in the same manner; however, only the procedure for the fuel manufacture will be discussed. These methods require strict caution because of the accountability requirements for the highly enriched uranium oxide.

The raw materials, ThO_2 and U_3O_8 , were received as -325 mesh powders. Calcination at 1000°C revealed that the ThO_2 underwent considerable shrinkage, and on weighed samples approximately 0.7 per cent of volatile materials was driven off. The pressing characteristics of the calcined thorium were also improved and so all thorium was calcined at 1000°C before being used. Weighed samples of the U_3O_8 did not appear to change when calcined at 1000°C; therefore this material was used as received.

The pressing mixture consisted of 93.41 wt. % ThO_2 and 6.59 wt. % highly enriched U_3O_8 . The flow sheet for the processing of the oxide materials^{13,14} is shown in Fig. 6. To ease the problem of accountability the U_3O_8 was weighed in a dry box. Approximately 200 g of the oxide was transferred to a tared bottle, and the accurate weight was determined. The weight of ThO_2 necessary was calculated, and this material was weighed in an open hood. The oxides, together with 2½ wt. % of the batch of polyvinyl alcohol, were mixed together for 3 hr in a 1-gal pebble mill containing approximately 1 kg of pebbles. The mixed powder was moistened with approximately 12 wt. % of a water solution containing 0.5 per cent aerosol. The dampened material was forced through a 16 mesh screen to form granules, and these granules were dried at 80°C for 4 hr. Before pressing, 1 wt. % of a mixture of 50 per cent kerosene and 50 per cent oleic acid was added to the dry granulated material as a lubricant. The pellets were produced by pressing at 13,000 to 15,000 psi in a small air-operated press¹⁵ constructed to fit in a dry box (Fig. 7).

CERAMIC FUEL ELEMENTS IN THE ThO_2 - UO_2 AND UO_2 - PuO_2 SYSTEMS

Fig. 6—Flow sheet for manufacture of the ceramic fuel for BORAX-IV.

Fig. 7—View of press in glove box.

This press is essentially double-acting with four cavities. The diameter of the pressed ware was controlled by the die size, and the length was controlled by the amount of material that dropped into the die activity. In operation the length of the pellets was found to vary from $\frac{3}{8}$ to $\frac{3}{4}$ in., and the diameters from 0.267 to 0.268 in.

The pressed ware was laterally transferred by means of a conveyor to an adjoining glove box, where it was inspected visually. The good ware was randomly loaded into alumina crucibles, whereas the defective ware was regranulated through a 16 mesh screen and returned to the press hopper.

The crucibles containing the pressed ware were transferred from the glove box to an electric furnace and heated overnight to 260°C to remove most of the organic binders. The calcined ware was then transferred in the crucibles to a gas-fired furnace where it was fired to 1700 to 1750°C in approximately 16 hr. The peak temperature was held for 2 hr, the furnace was shut off, and the ware was allowed to cool in the furnace to room temperature.

The fired ware had a uniform appearance and rejects due to cracks or chips or otherwise imperfect averaged less than 4 per cent. The fired diameters of the pellets were found to be in the range of 0.229 ± 0.002 in., and the shrinkage due to firing, based on the fired diameters, was found to be 17 per cent. The average apparent density (water immersion) of the thoria pellets was found to be 9.5 g/cm^3 and of the thoria-urania pellets, 9.8 g/cm^3 . The average density for the thoria-urania pellets as calculated from the physical dimensions of the pellets was found to be 8.3 g/cm^3 . This difference can be attributed to errors in measuring the pellets and to surface imperfections and open pores in the pellets.

The average apparent density (water immersion) of 9.8 g/cm^3 for the thoria-urania pellets was estimated to be about 97 per cent of the theoretical density for the thoria-urania mixture. This estimation was made by assuming that all the U_3O_8 was dissociated to UO_2 in the firing process. A plot³ of the theoretical densities of ThO_2 (10.03 g/cm^3) and UO_2 (10.95 g/cm^3) was made as shown in Fig. 8, and the theoretical density of the composition corresponding to the

CERAMIC FUEL ELEMENTS IN THE ThO_2 - UO_2 AND UO_2 - PuO_2 SYSTEMS

Fig. 8—Theoretical density of thoria-urania.

BORAX-IV fuel (93.65 wt. % ThO_2 –6.35 wt. % UO_2) was estimated to be 10.09 g/cm³. From this, the BORAX-IV fuel pellets were calculated to be about 97 per cent of theoretical density.

1.3 Fuel-element Fabrication

The tube plate or jacket material¹⁷ for the BORAX-IV reactor was obtained by extruding an aluminum-nickel alloy (M-388, 1 wt. % nickel in 2S aluminum). The metal was extruded at 425 to 450°C on a 1500-ton horizontal extrusion press using 6-in.-diameter billets. The extrusions were stretch-straightened while still in long lengths and were cut into 36-in. sections. These cut sections were then fabricated into fuel plates as shown by the flow sheet in Fig. 9.

One end of the tube plate was closed as shown in steps 1 to 5 in Fig. 10. The ribs of the tube plate were nulled out to a depth of $\frac{1}{2}$ in., and the interiors of the tubes were coated with a mixture of elemental silicon suspended in an alcohol-glycerine vehicle. The vehicle was removed by heating the end of the tube plate, and the closure was achieved by pressing the coated surfaces together using pressures of the order of 1000–2000 psi and a temperature of 595 to 600°C. The work was allowed to cool to 500°C in the press; then it was removed and allowed to cool in air to room temperature. This high-temperature pressure-brazing technique was found to produce sound joints, and, as shown in the photomicrograph (Fig. 11) of a typical joint, little or no residual aluminum-silicon eutectic remains since the excess was squeezed out during pressing.

The mechanism underlying this process is the hardness of the silicon powder. The hard, sharp grains perforate the oxide film on the aluminum and establish an oxide-free aluminum to silicon interface as shown schematically in Fig. 12. Since the joint surfaces are under pressure

Fig. 9—Flow sheet for fuel and blanket tube-plate fabrication for BORAX-IV.

Fig. 10—Procedure for closing BORAX-IV fuel plates.

1100 Aluminum

Interface

1100 Aluminum

J. H. HANDWERK

Fig. 11 — Hot-pressed closure interface. (Magnification 250 x.)

CERAMIC FUEL ELEMENTS IN THE ThO_2 - UO_2 AND UO_2 - PuO_2 SYSTEMS

Fig. 12—Mechanism of aluminum oxide perforation in silicon bonding (idealized).

and no oxygen can reach the exposed perforated surfaces of the aluminum, reoxidation is prevented. At a sufficiently high temperature the silicon reacts with the aluminum to form the aluminum-silicon eutectic, and, on melting, the eutectic alloy undermines the aluminum oxide on both sides of the joint. The applied pressure forces the liquid alloy and oxide out of the joint area, permitting a sound joint to be formed without the use of a flux.

The tube plates, closed on one end, were leak tested by means of a helium mass spectrograph and then clamped to the loading device. This device consisted of a flat steel plate approximately 6 ft long mounted at an angle of 20 to 30 deg to the horizontal on a Syntron vibrator. A grooved stainless-steel magazine was mounted at the top of the steel bed plate. A clamping and alignment device was located at the lower end of the magazine just above the center of the Syntron vibrator. This device clamped the tube plates to the vibrator and aligned the open tubes with the grooves in the magazine. A sheet-metal gate was inserted between the magazine and the tube plate. This gate prevented the fuel pellets from entering the tube plate while the magazine was being loaded. Eight columns of thoria-urania or thoria pellets 24 to 24 $\frac{3}{16}$ in. long were loaded into the magazine, the gate was removed, and each column was pushed into the tube plate. Vibration was not necessary in loading the majority of the pellets; however, once in a while a pellet would become stuck in the tube plate, preventing the fuel charge from being pushed to the bottom. When this happened, a gentle vibration usually loosened the stuck pellet, and the fuel charge could be pushed completely into the tube plate. An aluminum plug was inserted as the last pellet, and a crimp mark was made just above the aluminum pellet to prevent the charge from floating out during the subsequent lead filling.

Lead bonding was performed by dipping the loaded tube plates into molten lead maintained at 490 to 500°C (Fig. 13). The exterior of the tube plates was painted with a mixture of fine alumina suspended in an alcohol-glycerine carrier, and the inside of the tubes above the aluminum end plug was painted with a suspension of colloidal graphite in alcohol. These coatings served to limit lead adherence to the exterior of the tube plates and to the inside of the tubes above the fuel charge.

The removal of the lead rod cast in the tube above the fuel charge was necessary in order to close the charging end of the tube plate. This was accomplished by inserting a $\frac{1}{8}$ -in.-diameter by 12-in. long stainless-steel cable into each tube before lead dipping and then pulling the cable and the lead from the tube after the lead solidified. Cross sections of a loaded and lead-filled tube plate are shown in Figs. 14a and 14b.

CERAMIC FUEL ELEMENTS IN THE $\text{ThO}_2\text{-UO}_2$ AND $\text{UO}_2\text{-PuO}_2$ SYSTEMS

Fig. 13—Filling the annulus with lead.

CERAMIC FUEL ELEMENTS IN THE $\text{ThO}_2\text{-UO}_2$ AND $\text{UO}_2\text{-PuO}_2$ SYSTEMS

Fig. 14a — Cross section of loaded and lead-filled tube plate etched in 7 per cent NaOH.
(Magnification 1 x.)

Fig. 14b — Partial section of loaded and lead-filled tube plate etched in 7 per cent NaOH.
(Magnification 6 x.)

After removal of the lead from above the aluminum pellet, the final end closure was made as before (Fig. 10, steps 1 through 5). This closure was made under a helium atmosphere that filled the free space above the aluminum pellet and supplied the helium for the final leak testing with the helium mass spectrograph. After this inspection the tube plates (Fig. 10, step 6) were formed into the U channel necessary for spot welding into a subassembly.

A formed fuel plate, along with the aluminum side plates, was assembled into a fixture and secured to the aluminum side plates by spot welding at four locations along the length of the plate. The clamps were removed, and the assembly of the tube plate to the side plates was completed by welding at 1-in. intervals. Additional plates were added in a similar manner until the six-plate fuel subassembly was completed as shown in Fig. 15. The complete fuel assembly as shown in Fig. 16 was produced by welding the end fittings to the top and bottom of the subassembly.

1.4 UO_2 - PuO_2 System

Uranium dioxide and plutonium dioxide were found by Mulford and Ellinger¹⁸ to form a continuous series of solid solutions. In this work X-ray diffraction studies indicated that complete miscibility exists, and the variation of the lattice parameter of the solid solutions was found to be essentially linear; however, a slight negative deviation may exist as shown in Fig. 17.

Some difficulty was experienced in preparing these solid solutions directly from the two oxides. Plutonia appears to be extremely inert, and the reaction rate between UO_2 and PuO_2 at 1000°C is very slow. The complete series of solid solutions, however, was prepared by coprecipitation of soluble uranium and plutonium compounds followed by a calcination in hydrogen at 1000°C . The firing operation was quite important, and caution was necessary in order to avoid the formation of well-crystallized PuO_2 as a separate phase.

The UO_2 - PuO_2 fuel cycle has been studied by KAPL,¹⁹ and multigroup calculations²⁰ have indicated that mixed crystals of uranium-plutonium dioxides would have attractive breeding characteristics for a power reactor. Several UO_2 - PuO_2 solid solutions were prepared by coprecipitation of soluble uranium and plutonium compounds, followed by a calcination at 800°C in hydrogen as shown by the steps outlined in Fig. 18. This process produced a complete solid solution of the uranium and plutonium dioxides as indicated by X-ray diffraction studies.²¹

Preliminary reactor physics calculations indicated that a PuO_2 - UO_2 solid solution²² should have the following requirements: (1) a 1 to 5 PuO_2 to UO_2 mixture fabricated to at least 65 per cent of theoretical density, (2) a maximum depletion of 50 per cent of the original plutonium, and (3) a maximum coolant temperature of 540°C and an average specific power of 1700 watts/g.

A 1 to 5 mole ratio of PuO_2 to UO_2 solid solution was prepared by coprecipitation, followed by a calcination in hydrogen at 800°C . This mixture was dry pressed to 65 per cent of theoretical density into right cylinders 0.187 in. in diameter by 1 in. in length and then assembled into stainless-steel irradiation test assemblies. Each assembly consisted of 0.5 in. of MgO , a 1-in. compact containing 0.42 g of fuel, and then another 0.5 in. of MgO as shown in Fig. 19.

The test specimens were irradiated in a thermal flux of 0.7×10^{14} nvt with an estimated heat output of 470 watts/cm². The first specimen was irradiated in the MTR to an estimated 5 per cent depletion of the plutonium. In this test the coolant temperature was between 650 and 725°C . Postirradiation examination revealed that there was no deformation in the stainless-steel jacket. The specimen was sectioned, and the mixed oxide was found to be sintered to the extent that a central void was formed (Fig. 20); however, there was no evidence of melting in this specimen.

A second specimen was irradiated with a somewhat lower coolant temperature (500°C) to an estimated plutonium depletion of 35 per cent. Postirradiation examination again revealed that there was no distortion in the stainless-steel jacket. This specimen was sectioned, and the mixed oxide was found to be cracked (Fig. 21) and to have sintered to the extent that a central void was formed. Again there was no evidence of melting in the region of the void, and the periphery of the ceramic was found to be a loose very friable powder.

Fig. 15—BORAX-IV fuel subassembly.

Fig. 16—BORAX-IV fuel assembly.

Fig. 17—UO₂-PuO₂ solid solution. Fig. 18—Procedure for forming the UO₂-PuO₂ solid solutions.²² The PuO₂·UO₂ is soluble in HNO₃; the organic is effective at high β , γ level.

CERAMIC FUEL ELEMENTS IN THE $\text{ThO}_2\text{-UO}_2$ AND $\text{UO}_2\text{-PuO}_2$ SYSTEMS

Fig. 19—Radiation test capsule.

Fig. 20—Irradiated fuel element, KAPL-26-1.

Fig. 21—Irradiated fuel element, KAPL-26-2.

Fig. 22—Irradiated fuel element, KAPL-26-3.

In order to eliminate the central void, an irradiation test assembly was made in which the annulus between the pressed oxide and the jacket wall was filled with lead. This specimen was irradiated at a coolant temperature of approximately 500°C . Postirradiation examination revealed that there was no deformation in the stainless-steel jacket, and, after sectioning the element, it was found that no central void had formed as shown by Fig. 22. The lead was found to be on one side of the ceramic pellet; however, this displacement was thought to be due to the uneven temperature on the perimeter of the can which caused the lead to freeze on one side during the shutdown. From these preliminary tests it would appear that an oxide fuel composed of $\text{UO}_2\text{-PuO}_2$ solid solution would be suitable as a breeding reactor fuel.

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Uranium Compounds for New High-temperature Fuels

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ABSTRACT

The trend in nuclear reactors is toward higher temperature operation, and, since uranium and its lower alloys suffer a gross swelling at elevated temperatures due to the accumulation of fission gases, solid fuels in reactors of the future will utilize higher alloy content or, alternatively, consist of uranium compounds.

An exploratory program is now in progress to study various compounds as potential high-temperature fuels. Following a review of the desirable characteristics of such a material, the information available to date is summarized and discussed. The materials being studied include uranium carbides, silicides, nitride, sulfide, beryllide, and others. It is too early to state which, if any, of these materials will compare favorably with UO_2 , which appears to be the best high-temperature fuel at the present time.

The history of steam turbines and gas turbines has shown that the trend of operating temperatures of power-producing plants is inevitably upward. It is safe to assume that reactors of the future will be operated at higher temperatures to achieve greater efficiencies, and this trend is certain to place a serious challenge before nuclear metallurgists. In the recent past, research at Harwell and the Argonne National Laboratory has shown that unalloyed uranium undergoes a gross change in volume when bombarded with neutrons at temperatures above approximately 450°C. This gross distortion is associated with the generation and accumulation of fission gases. The fission process yields atoms of xenon and krypton at the rate of one atom of rare gas for every four atoms of U^{235} fissioned. These gases, which are not soluble in uranium, diffuse to nucleation sites and form small bubbles that expand causing the uranium metal to increase in volume. The magnitude of this volume increase depends upon the temperature and the amount and rate of fission. At a temperature of about 600°C and 1 per cent burn-up of the total atoms present, the volume increase of the uranium metal can be 50 per cent.

This phenomenon would obviously have a very serious effect on the operation of reactors with solid fuels at temperatures above 450°C. There are a number of approaches that can be made to solve or circumvent this problem. One method is to increase the alloy content of uranium such that the material has improved creep strength and hence greater resistance to fission gas swelling. Low alloy additions on the order of 1 to 3 per cent of zirconium, molybdenum, or niobium are not sufficient for this purpose, and one must use as much as 10 to 12 per cent of alloy. Another possibility is to use a thicker fuel-element clad to increase the resistance to growth. An alternative approach, which is the subject of this paper, is the de-

velopment of a new type of fuel which has superior properties under high-temperature irradiation. One such material already exists, namely, UO_2 , and this fuel will be thoroughly discussed by others at this conference. The present paper is concerned with the attempt to seek other compounds of uranium that may replace or supplement the use of UO_2 .

Clearly, there are two possible approaches to a new high-temperature fuel material. In one case the fission gases escape with ease from the fuel, but the element is designed to accommodate or vent them. In the other type of fuel, the fission gases are retained in a dispersed atomic state within the lattice such that they do not accumulate and form bubbles. Experience to date has shown that uranium alloys do not behave in either manner. Apparently the fission gas atoms, being quite large, occupy substitutional sites in the uranium lattice and diffuse substitutionally (diffusion of rare gases in silver, for example, indicates substitutional behavior). Thus the rate of migration of the rare gas atoms in uranium is not as rapid as interstitial diffusion which might facilitate easy escape, nor are the atoms locked into the lattice so as to prevent diffusion and bubble formation. The most promising solution, therefore, appears to be nonmetallic or compound fuels.

Previous research on irradiation stability and fission-product gas retention has suggested that crystals with covalent bonding are superior in these respects. For example, B_4C retains 80 per cent of the fission-product helium in its lattice up to the temperature at which B_4C decomposes. A program is now underway to explore the properties of various uranium compounds, including carbides, sulfides, silicides, beryllides, as well as other types of compounds. A tremendous amount of research is required to fill the gaps in our knowledge, including such properties as the melting point, vapor pressure, chemical stability, oxidation and corrosion resistance, thermal conductivity, resistance to thermal shock, crystal structure, diffusion, irradiation stability, etc. It is much too early to say whether or not we have a promising new high-temperature reactor fuel, but the desirable characteristics of such a material and the information we have gathered to date will be reviewed in this paper.

1 DESIRABLE CHARACTERISTICS

Ideally, the fuel compound will have a number of characteristics, all of which are unlikely to be attained in any one given compound. These characteristics are summarized as follows:

1. A high melting point and only one crystal structure so that the material may be used in bulk form rather than as a dispersion.
2. The constituent of the uranium compound has a low neutron-absorption cross section.
3. Chemical and metallurgical inertness with respect to (a) reactor coolant, (b) the fuel-element cladding, and (c) the matrix material in which the compound might be dispersed.
4. A broad range of homogeneity such that the compound is stable over a range of composition; thus the structure would not be affected by nonstoichiometry caused by poor preparation or uranium depletion by fission.
5. Good stability in high-temperature irradiation; this feature is probably the most important requirement.
6. A high thermal conductivity is important in a bulk uranium compound fuel to facilitate high heat flux and prevent melting at the core of the fuel element.
7. High density of uranium atoms in the compound to keep the fuel volume low.
8. Good mechanical strength and resistance to thermal shock to prevent fracture of the bulk fuel during reactor operation.

The compound UO_2 fulfills many of these requirements, but it lacks structural strength, has a low uranium atom density, and has poor thermal conductivity. Nevertheless, it appears to be the best high-temperature fuel available at this time. The compounds which are being studied as competitors of UO_2 are shown in Table 1. It may be of interest to discuss these various compounds and assess their potential value.

URANIUM COMPOUNDS FOR NEW HIGH-TEMPERATURE FUELS

Table 1— PROPERTIES OF URANIUM COMPOUNDS

Com- pound	Melting point, °C	Crystal structure	X-ray density, g/cm ³	Uranium content, g/cm ³	Thermal conduc- tivity*	Remarks
UB ₂	>1500	Hexagonal, a = 3.12, c = 3.96	12.82	11.75		Would require separated isotope; probably would oxidize readily in air or steam but stable in H ₂ .
UB ₄	>1500	Tetragonal, a = 7.075, c = 3.979	9.38	7.94		Would require separated isotope; probably would oxidize readily in air or steam but stable in H ₂ .
UBe ₁₃	2025	FCC, a = 10.256	4.373	3.06	0.028	Should have good resistance to high- temperature oxidation and corro- sion; provides some moderation.
UC	2375	FCC, a = 4.961	13.63	12.97	0.080	Decomposes in hot water; of interest in gas-cooled and liquid-metal- cooled reactors.
UC ₂	2475	BC; tetragonal, a = 3.524, c = 5.999	11.68	10.61		Reacts with water and air but probably not with H ₂ .
UAl ₂	1590	FCC, a = 7.811	8.14	6.62		Should have good thermal conductivity and good corrosion resistance.
UN	2630	FCC, a = 4.880	14.32	13.52		Probably will be chemically reactive.
US	>2000	BCC, a = 5.484	10.87	9.58		Stable in boiling water but probably has poor oxidation resistance.
U ₃ Si	930	BC; tetragonal, a = 6.029, c = 8.697	15.58	14.99	0.036	Resistance to hot water; oxidizes in air. Poor irradiation stability.
U ₃ Si ₂	~1660	Tetragonal, a = 7.329, c = 3.900	12.20	11.31		
USi	~1600	Orthorhombic, a = 5.66, b = 7.66, c = 3.91	10.40	9.30		Resistance to oxidation in air and wet corrosion increases with increas- ing silicon content for the series of uranium silicates.
U ₂ Si ₃	~1600	BC; tetragonal, a = 3.98, c = 13.74	8.98	7.27		
USi ₂	~1600	Hexagonal, a = 3.86, c = 4.07	9.25	7.48		
USi ₃	1500	Cubic, a = 4.03	8.15	6.02		
UO ₂	2750	Cubic, a = 5.469	10.96	9.66	0.014	Excellent material; good irradiation stability, chemical stability, etc. Poor thermal conductivity.

 * Cal/(sec)(cm²)(°C/cm).

2 URANIUM COMPOUNDS

Uranium forms the borides UB_2 and UB_4 , both of which have melting points above 1500°C . Neither compound has good chemical stability with respect to air or steam, and the use of a boride would require the separated B^{11} isotope. Thus it is thought that uranium borides would be used as fuels only in exceptional circumstances.

The compound UBe_{13} is of interest as a potential high-temperature fuel. Thermodynamic calculations suggest that it has good resistance to high-temperature oxidation and corrosion, and preliminary measurements indicate that its thermal conductivity is superior to that of UO_2 . The presence of beryllium in the compound would provide some moderation of neutrons, and since the unit cell of the structure is large, there should be ample interstitial space for the accommodation or diffusion of fission gas atoms. One of the disadvantages of UBe_{13} is the fact that it provides only 3 g of uranium per cubic centimeter. The melting point of the pure compound is slightly in excess of 2000°C , but inasmuch as the compound does not have a range of homogeneity with respect to composition, there is the danger that premature melting can occur. The phase diagram shows that the beryllium-poor compound will begin to melt at 1100°C , whereas the beryllium-rich compound yields a liquid phase at a temperature slightly below 1300°C . The crystal structure of UBe_{13} is isomorphous with $ZrBe_{13}$, $ThBe_{13}$, and $PuBe_{13}$, thus offering many interesting possibilities for alloying.

Samples of UBe_{13} (natural) have been irradiated to about 0.01 per cent burn-up of the total atoms present at a temperature which is uncertain. No change in microstructure was observed, and practically no gas was evolved upon opening the capsule. Heating to 1900°C gave sublimation, presumably of the compound, and fission gas evolution. Additional samples are now being irradiated for higher burn-ups at temperatures between 400 and 1500°C .

The carbides of uranium, UC and UC_2 , are worthy of detailed experimental investigation. They have high melting points and a higher uranium density than UO_2 . The thermal conductivity of UC is approximately 5 to 6 times greater than UO_2 . These carbides react readily in hot water or in air but might be useful in gas-cooled or in liquid-metal-cooled reactors. Irradiation experiments are in progress.

The compound UAl_2 is being investigated, but it suffers from having only a moderately high melting point and a low uranium density. It is expected, however, that the material possesses good thermal conductivity and good corrosion resistance.

The compound UN has a high melting point and high uranium density, but it is believed that experiments will show that it is rather reactive chemically. Another disadvantage of this compound is the high neutron cross section of nitrogen. No information is available on the irradiation stability.

Uranium sulfide has a melting point in excess of 2000°C with a uranium density approximately that of UO_2 . Uranium sulfide is stable in boiling water but probably has poor oxidation resistance in air at high temperatures. The effects of neutron bombardment are not known.

Uranium forms a whole series of silicides varying in composition from U_3Si to USi_3 . These compounds are of interest because of the low cross section of silicon and the fact that the higher compounds (U_3Si and U_3Si_2) have better uranium densities than UO_2 . The resistance to wet corrosion and oxidation in air increases with increasing silicon content in the series of uranium silicates. Fairly detailed work has been done on the compound U_3Si which has the highest uranium density of any of the compounds shown in Table 1. Its thermal conductivity is superior to UO_2 , but under neutron irradiation it undergoes severe distortion and swelling with a deterioration of corrosion resistance. Moreover, irradiation leads to the decomposition of U_3Si into a two-phase structure consisting of alpha uranium and U_3Si_2 . Further work remains to be done on the other uranium silicides.

In addition to the compounds listed in Table 1, a variety of other types of compounds are being studied. The alkaline earth uranates ($MgO \cdot UO_3$, $CaO \cdot UO_3$, and $BaO \cdot UO_3$) are quite stable and have melting points of 1700 and 1800°C . Irradiation of samples to 0.2 per cent burn-up of the U^{235} atoms at 200°C caused fragmentation and complete release of fission gases from the magnesium and barium uranates. The calcium uranate yielded about 20 per cent of the

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fission gas at room temperature, and little more was released upon heating until 1800°C, at which temperature the compound decomposed.

A sample of UO_2 subjected to similar irradiation gave off much less fission gas upon opening the capsule. This fact combined with the low, x-ray densities of these uranates (between 7.23 and 7.52 g/cm³) suggests that these particular materials have little promise.

Other types of material, such as uranium in a silicate network, might be explored. Silica glass is quite stable under irradiation; the thermal conductivity, elastic constants, and density are practically unchanged by 2×10^{20} neutrons/cm² (fast). The activation energy for the diffusion of argon in a potassium-lime-silicate glass is reported to be 42 kcal; thus low diffusion rates for fission gases in silicate networks can be expected. No results are available as yet for a fuel element of this type.

Very little is known about the ternary compounds of uranium, and some of these might be of interest.

3 SUMMARY

Although it is not likely that a uranium compound can be found which possesses all of the desirable characteristics of a high-temperature fuel material, there is some hope that a satisfactory new material can be found in an exploratory program which is still in progress. The information available for the various compounds being studied is summarized and discussed.

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Dispersion Type Fuel Elements Based on Fissile Ceramics

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1 INTRODUCTION

Dispersion type fuel elements can be defined as elements in which the fissile phase is dispersed in a matrix material that will usually be nonfissile but may be fertile. Weber and Hirsch¹ described dispersion elements as possessing two unique advantages over homogeneous elements: (1) long fuel-element life because of localization of fission-product damage and (2) increased choice of fuel-element structures. Of the fissile compounds listed by these authors as dispersants of interest, those of highest uranium density, with the exception of U_6X compounds and U_3Si , are those which can be classed as ceramics.

In this paper the dispersants discussed are the oxides and carbides of plutonium and uranium, whereas the dispersal mediums dealt with are both ceramic and metallic.

Dispersion type elements will perform use enriched fuel. If a plutonium recycling scheme is adopted, then it may be advantageous to incorporate the plutonium in a dispersion type spike fuel element and obtain a high burn-up of the fissile material.

The case for a dispersion fuel based on highly enriched uranium ceramics is more difficult to make, as will be evident from the considerable amount of attention being devoted to uranium dioxide alone as a fuel. It will be apparent from the papers being presented to this Conference on the topic of uranium dioxide that its chief disadvantages lie in the related properties of low thermal conductivity and low thermal-shock resistance. Materials, both metallic and ceramic, that have superior properties to uranium dioxide in these respects are not difficult to find.

Uranium monocarbide has a room-temperature thermal conductivity of approximately the same value as the metal and a good thermal-shock resistance. Results to date on the irradiation behavior of the bulk material do not give confidence in its stability as a fuel element, considerable amounts of fission gases being released at 600°C. This point cannot be regarded as firmly established because the material irradiated was only of 85 per cent theoretical density, and release of fission gases would also be expected from uranium dioxide of comparable density; high-density oxide retains its fission products. The production of bulk high-density carbide is far more difficult than high-density oxide; therefore the carbide could be more conveniently incorporated in dispersed form in a matrix that will retain fission products.

The fuel dispersions considered will be for use in thermal reactors, so the dispersal mediums will advantageously have a low neutron-absorption cross section. Such diluents will be based primarily on oxygen, carbon, beryllium, magnesium, silicon, aluminum, and zirconium; diluents that might be acceptable if special advantages were displayed could include niobium, titanium, nickel, iron, vanadium, and molybdenum. Higher parasitic neutron absorption in the matrix material will be tolerable for plutonium than for uranium fuels.

2 DISPERSIONS IN METALS

Compared with oxides, metals have high room-temperature thermal conductivities that do not decrease rapidly with increasing temperature and are not prone to failure under conditions of thermal shock. When a metal dispersant is used, the disperse system can be fabricated much as a metal would be, and the fuel core can be bonded to the can, giving a fuel of high integrity.

2.1 Fabrication of Metal-Ceramic Mixtures

The problems that arise in fabrication are the general ones associated with incorporation of a brittle material into a ductile matrix. The ease of fabrication will depend on the volume of brittle phase and its distribution. Powder metallurgical methods of fabrication offer the greatest degree of control over these two variables. It is important that the disperse particles are not too fine with respect to the metallic particles of the matrix; otherwise they may form a continuous network throughout the structure, greatly interfering with the fabrication process and impairing the mechanical properties of the mixture. The disperse particles should preferably be coarser than the metallic particles that are used to form the matrix.

The volume of disperse phase of a suitable particle size that can be accommodated depends largely on the shape and size of article required, the porosity that is permissible, and the engineering tolerances desired in the finished element. Some broad generalizations can be made, based on the experiences in extruding uranium dioxide-iron mixtures and in rolling uranium dioxide-aluminum mixtures in plate form.

The extrusion behavior of the iron-uranium oxide mixtures was studied² using Swedish iron powder of less than 60 μ diameter and stoichiometric uranium dioxide of 76 to 150 μ particle size. Mixtures of these two powders containing up to 50 vol. % oxide were cold compacted at 20 Tsi pressure into mild steel cans and extruded at 1200°C in a conventional steel extrusion press at a constant area reduction of 14 to 1. With oxide contents of up to 30 vol. %, the extrusion pressure varied little compared with mild steel, but above this value the extrusion pressure increased linearly with volume of oxide up to 50 vol. %, the highest oxide concentration used in the experiments. The density of the extruded mixture decreased from 94 per cent theoretical density at 30 vol. % oxide to 90 per cent of the theoretical value at 50 vol. % oxide. This decrease is possibly attributable to the formation of a miniature extrusion defect behind each oxide particle, although no microscopical evidence of this was found.

In extrusion, as the reduction of area (or extrusion ratio) is increased, the extrusion pressure increases. For most metals a relation of the type

$$P = K \log R$$

where P = extrusion pressure, R = reduction of area, and K = extrusion constant is found to hold.

For a 30 vol. % oxide mixture extruded at 1200°C, the variation of P with $\log R$ is not linear, P increasing more rapidly with R than anticipated from the above relation.

The behavior is not unexpected since analogous disperse systems of solids in liquids exhibit a variety of anomalous rheological behaviors. By analogy with such systems, variations in the degree of interference of the dispersed oxide with the flow of the metal matrix can account for the observed discrepancy.

For the investigations into the fabrication of plates of aluminum-uranium dioxide dispersions,³ atomized aluminum powder of less than 60 μ and uranium dioxide powders of less than 1 and of 76 to 150 μ particle size were employed. The mixed powders were compacted at 20 Tsi into plates, placed in an aluminum picture frame, and then hermetically sealed by welding aluminum top and bottom plates to the picture frame. Mixtures containing varying concentrations of oxide of the two particle sizes were assembled into packs in this manner

and hot rolled at 600°C. The rolling reductions were 10 per cent per pass with reheating between each pass, and total reductions of up to 6 to 1 were employed.

When the fine oxide powder was used, major cracking of the 22 vol. % core developed after several passes, indicating mechanical weakness of the core; also gaps developed between the cladding and core at leading and trailing edges, indicating major differences in deformation characteristics between core and cladding. With the coarse oxide no difficulties were encountered in rolling 29 vol. % mixture to a total reduction in thickness of 0.030 in. Cores containing higher concentrations of coarse oxide developed edge cracks; thus 30 vol. % seems to represent about the upper limit for the concentration of brittle phase when fabricating oxide-metal plates by hot rolling.

The fabrication temperature for these metallic-ceramic mixtures must always be such that the matrix metal is sufficiently plastic to accommodate the deformation imposed without causing fragmentation and stringing of dispersed oxide. Fragmentation will have a very undesirable effect upon the mechanical properties of the matrix, and stringing can cause longitudinal permeability.

It is also necessary to keep the working temperature high and maintain the metal matrix plastic so that as little difference as possible exists between the flow properties of the core material and the can; otherwise there will be poor bonding between these portions of the fuel element. In the case of plate elements these differences in properties can also lead to "running away" of the can from the core at the leading edge and, with extrusions, to accentuation of the difficulties normally associated with the extrusion defect.

A technique that has not been discussed very much in connection with the fabrication of metal matrix dispersion fuel elements is the standard powder metallurgical method of cold-compacting and sintering. Thorium is a metal particularly suitable for fabrication from powder since it is extremely ductile and can be cold-compacted at low pressures to give high densities. Hydrostatic cold-compacting has been used very successfully at Harwell by Lloyd.⁴ A compacting pressure of 15 Tsi gives thorium compacts of $\sim 10 \text{ g/cm}^3$ density and sufficiently strong to be machined. Sintering *in vacuo* at 1300°C increases the density to $\sim 11 \text{ g/cm}^3$, and a final swaging operation produces a round rod of accurate dimensions with an over-all metal efficiency of 98 per cent. Fabrication of PuO_2 -thorium dispersions by this method proved relatively simple.⁵ The powders were mixed in a glove box, loaded into the rubber sleeve for pressing, and then posted out of the box in a polythene container. The hydrostatic compacting operation was performed while the powders were still inside the polythene container, and, when complete, the pressed bar was posted back into the box for sintering. The sintering temperature had to be lower than that for pure thorium since reaction occurs between the oxide and thorium with the formation of a liquid plutonium-thorium phase which, while aiding sintering, defeated the object of the exercise.

2.2 Compatibility of Metals and Ceramics and Irradiation Behavior of Metal-Ceramic Mixtures

This latter example of reaction between matrix material and disperse phase leads to the broad problem of compatibility between these two components of the fuel element. Weber and Hirsch quoted the use of a metastable system as an advantage of the disperse system, but the use of such fuel elements may be hazardous because of the possibility of reversion to the stable structure in service. The temperature of operation is usually lower than the fabrication temperature, but the time at operating temperature is much longer than the time of fabrication.

Solid-state reactions between certain materials have been found to be accompanied by large volume expansions, far greater than can be accounted for by the changes of structure alone.⁶ These expansions are believed to be due to diffusional porosity, caused by an excess of vacancies being formed when there is a difference in diffusion rates between the various component atoms of the system. This phenomenon was first encountered in a number of

binary metal systems. Among these were the uranium-aluminum, beryllium-uranium, and beryllium-thorium systems, the phases that exhibited the porosity in these cases being UAl_3 - UAl_4 , UBe_{13} , and $ThBe_{13}$, respectively.⁶

Aluminum will react with uranium dioxide to give the uranium-aluminum compounds, accompanied by an increase in volume. In the solid state this reaction is sluggish and needs an inoculation time³ of more than a day at 600°C. This means that a dispersion of UO_2 in aluminum can be fabricated and safely operated at low temperatures—witness the Geneva reactor. This does not mean that such a fuel element could be safely operated for long periods of time at 400°C without reaction and consequent volume changes.

Uranium monocarbide apparently does not react with aluminum until the latter is molten. Therefore there should be no difficulty in fabricating dispersions of the carbide in aluminum. The upper temperature limit of such a fuel element would be dictated by the ability of the aluminum to contain the fission-product gases released from the carbide by diffusion or recoil. Tests carried out on irradiated DIDO alloy showed that volume increases could be detected⁷ after annealing for 2 hr at 500°C. The upper temperature limit of operation of dispersions in aluminum matrices would thus be below 500°C.

Magnesium could be expected to behave in a similar manner to aluminum.

Beryllium has obvious attractions as a matrix material since it has a high thermal conductivity, reasonably high melting point, and low neutron-absorption cross section. The solid-state reactions⁸ between beryllium and uranium carbide and uranium dioxide start at about 600°C. Since the compound UBe_{13} is one of the reaction products, in both cases there will be a volume increase. When uranium carbide is used, the volume change closely parallels the reaction of uranium with beryllium, but for uranium dioxide the magnitude of the expansion is greatly diminished and is less for nonstoichiometric UO_2 than for stoichiometric material. This evidence points to the fact that one of the phases formed, probably beryllia, acts as a diffusion barrier.⁸ Plutonium dioxide would probably also be reduced by beryllium at similar temperatures, and this could prove more serious than the corresponding case with uranium since a liquid phase would be present at temperatures of about 650°C at some stage of the reaction. Plutonium monocarbide would be expected to behave in a similar manner to its uranium counterpart.

Of the systems considered, only the beryllium- UO_2 fuel would appear to be sensibly stable above 600°C from the compatibility aspect. Above 600°C, however, the creep strength of beryllium begins to fall rapidly;⁹ therefore the ability of beryllium to resist swelling caused by fission-product gases diffusing or recoiling from the oxide particles would also decrease. In addition, distortion of the beryllium because of internal generation of helium and tritium by the $(n,2n)$ and (n,α) reactions could be expected to become apparent at about this temperature.

Zirconium will react with uranium dioxide at an appreciable rate at 800°C when they are both present in powder form. It is usually desirable to work with zirconium hydride powder rather than the metal powder because of the pyrophoricity hazard. Temperatures of about 800°C are needed to decompose the hydride and also for consolidation of zirconium, roll bonding, etc., so that the fabrication of such an element would not be easy. Zirconium will react with uranium carbide, but temperatures in excess of 1300°C are needed before the reaction can be detected. If zirconium hydride powder is used, care will have to be taken because uranium carbide powder prepared by several methods has been shown to adsorb or absorb hydrogen over the temperature range of uranium hydride stability. The upper temperature limit of operation will also be limited by the ability of the zirconium to resist deformation under stresses caused by the release of fission gases by recoil and probably augmented by diffusion from the carbide. High-temperature creep-resistant alloys of zirconium have not yet been developed so that an upper limit of operation of ~500°C seems probable at present.

From these considerations it seems that dispersion fuel elements capable of operation at temperatures above 600°C would have to use metals other than those of low neutron cross section as matrices.

Most of the metals of this second group are creep resistant or form the basis of creep-resistant alloys. Iron, nickel, or molybdenum based alloys would be suitable matrices for the fissile dioxides, but nothing has been published on their compatibility with the fissile carbides. Unless nuclear requirements dictate, there seems to be no advantage in using niobium, vanadium, and titanium.

3 DISPERSIONS IN CERAMICS

For high-temperature dispersion fuel elements, an alternative to the use of the relatively high cross-section metals (iron, nickel, and molybdenum) are the ceramics graphite and the oxides and carbides of beryllium, aluminum, magnesium, silicon, and zirconium.

3.1 Graphite

Graphite possesses a number of properties that are highly desirable in a matrix material for a ceramic dispersion fuel. It has a low neutron cross section, does not melt but rather sublimates at a very high temperature (3200°C), retains its mechanical properties to well above 2000°C, and has a high room-temperature thermal conductivity that does not diminish so rapidly with rising temperature as does the conductivity of oxides.

If the fissile phase is a carbide, then no compatibility problems arise because, even if the monocarbides are used and react with the graphite to give the dicarbides, there is only a very minor volume change. If oxides are used, then chemical reactions are possible.

Carbon will reduce uranium dioxide completely to the monocarbide at 1800°C, with the evolution of carbon monoxide; below about 1200°C, the reaction is very slow, rates of course being influenced by the particle size of the oxide. If nonstoichiometric oxide is used, then the removal of excess oxygen will proceed at temperatures below 1000°C. Above 1000°C, plutonium dioxide is reduced to the sesquioxide by graphite, and above 1200°C formation of the monocarbide starts.¹⁰ These figures indicate the upper temperatures permissible in oxide-graphite fuels if carbon monoxide evolution is to be avoided.

Several factors will determine the maximum temperature attained within a fuel. Variation in can-fuel gap, if a can has to be used to contain the fission products, will be important and will be determined partly by the relative thermal expansions of can and core and partly by dimensional change of the fuel core under irradiation. Diminution of thermal conductivity as a result of irradiation damage must also raise center fuel temperatures.

Graphite has a much lower thermal expansion than any metallic canning material; therefore, if the core is to retain contact with the can, higher center temperatures would be needed than if the coefficients of expansion were matched. Ratchetting upon thermal cycling may also be a problem.

No information is available on the loss of thermal conductivity of graphite owing to neutron or fission-fragment bombardment¹¹ above about 300°C. It is known that fission-fragment damage is more serious than that due to fast neutrons and that the latter can reduce the conductivity by multiples of ten at room temperatures. This effect is known to diminish with increasing irradiation temperature up to 300°C owing to annealing processes and would be expected to continue to diminish still further above 300°C.

On neutron irradiation there is a volume increase in graphite that results from an increase in C spacing that is undercompensated by a decrease of a spacing. Bacon's work¹² has shown that with increasing temperature (up to 300°C for low-neutron doses) the degree of undercompensation diminishes, i.e., the increase in volume diminishes. Extrapolation of these results to higher temperature would give a volume decrease upon irradiation.

Recent irradiation experiments upon dispersions of fissile ceramics in graphite have thrown further light on the problems of the release of fission-product gases and on the dimensional stability of graphite under irradiation at higher temperatures.¹³

Dispersions of 50 wt. % fully enriched UO_2 ($\sim 1 \mu$) and UC_2 ($\sim 20 \mu$) in graphite were irradiated to a burn-up of 0.5 per cent uranium atoms at 600°C. The specimens were in the

form of cylinders, the graphite density being about 1.5 g/cm^3 . The graphite matrix exhibited a fairly strong preferred orientation, with the basal planes tending to lie perpendicular to the cylinder axis; the thermal expansion along the cylinder axis was about five times the diametral expansion.

After irradiation, there were only minor dimensional changes; the diameters had decreased by about 1 per cent, and the lengths had increased, the relative changes being such as to give, on the average, a slight decrease in volume. Too much significance cannot be yet attached to this apparent change that awaits confirmation after longer irradiation times. Appreciable proportions of the total fission-product gases were released for both carbide and oxide dispersions, as might be expected from the particle sizes employed.

Bearing all these facts in mind, it is concluded that the most reliable fuel elements based on a graphite matrix would seem to contain fissile carbides as the disperse phase, the monocarbides—being more stable in moist air—possibly being preferable to the dicarbides.

An impermeable can is essential with such an element if fission products are to be contained, and provision must then be made for accommodation of the fission gases within the cans.

3.2 Oxide Matrices

Beryllia and uranium dioxide are mutually insoluble in the solid state; therefore a fuel element based on this combination of materials would be a true dispersion type element.

The thermal conductivity of beryllia is not quite so high as graphite at room temperature and falls with increasing temperature in a manner common to most oxides. At 800°C , however, its conductivity is still greater than that of uranium metal. Its thermal-shock resistance is high, so there is the possibility that cracking may not occur under irradiation, consequently relieving the can of some of the structural burden.

The effect of irradiation and fission-product damage upon the physical properties of beryllia at high temperature is as yet unknown. Irradiation at room temperature to 10^{18} nvt has been reported to cause a dimensional change of the order of 1 per cent, seriously affecting thermal conductivity and strength,¹⁴ but a second authority¹⁵ quotes a 0.3 per cent expansion in C_0 spacing but nothing detectable in a_0 and no change in thermal conductivity.

With beryllia, as with beryllium, under fast neutron irradiation, the (n,α) and $(n,2n)$ reactions will produce helium and tritium. The manner in which the beryllia reacts to this entrapped gas must be temperature sensitive. There would seem to be no fragmentation troubles at low temperatures, but at some elevated temperature the beryllia will become plastic and dimensional changes due to bubble formation will occur. This latter temperature will not be below 1000°C , and, extrapolating the work of Wygant,¹⁶ beryllia, having a hexagonal structure, might be expected to possess better creep strength in the polycrystalline form than the cubic oxides.

The only data available for fission-product damage in beryllia are given by Billington¹⁴ for 2 and 10 wt. % urania dispersions in beryllia at an unspecified irradiation temperature. Linear dimensions increased by 1 per cent, and the thermal conductivity fell by a factor of 6 after burn-up of only $\sim 3 \times 10^{-4}$ uranium atoms. Absence of any difference between the two concentrations was ascribed to the higher, but still unspecified, temperature of the specimens richer in uranium. This suggests that radiation damage of all types might be expected to diminish in magnitude with increased temperature of operation.

The experimental data on fission-product release from the graphite dispersions and from magnesia dispersions (yet to be described) suggest that at temperatures above 600°C about 20 per cent of the inert-gas fission products will be released from the uranium dioxide particles. Containment of these gases in the dense matrix will lead to stresses on the beryllia additional to those imposed by the helium and tritium. Lack of containment in the beryllia because of diffusion along interconnected pores or cracking would place the onus for fission-product retention on a can. Beryllia has a coefficient of thermal expansion ($\sim 8 \times 10^{-6} \text{ in./in./}^\circ\text{C}$) that is not very much lower than that for a number of metals, but it will still give

rise to higher center temperatures than if the coefficients of expansion of can and fuel were matched.

Plutonium dioxide would be expected to behave in a manner similar to UO_2 , but, if beryllia and plutonium dioxide are used as components of a fuel, a health hazard arises owing to neutron emission resulting from an (α, n) reaction. This must complicate the manufacturing process.

Magnesia has a lower thermal conductivity than beryllia and a lower thermal-shock resistance. American data¹⁵ on the effects of neutron irradiation on single crystals of periclase indicate that fragmentation occurred but U. K. work¹⁷ on similar material at temperatures of $\sim 300^\circ\text{C}$ and 2×10^{20} nvt showed no disintegration, only a change in color. Experiments have been recently carried out by Stubbs and Silver¹⁸ at Harwell on the release of Xe^{135} from dispersion of uranium dioxide in a 75 per cent dense matrix of fused magnesia particles. When the dioxide powder was of submicron particle size and therefore of non-stoichiometric composition, the amount of xenon released remained constant at 2 per cent from 100 to about 600°C but then rose abruptly to about 85 per cent at 800°C . Increase of particle size to 100μ and the change in composition of oxide to stoichiometric UO_2 reduced the emission at 800°C to ~ 20 per cent, the amount of xenon emitted up to 600°C being as for the finer dispersion. The amounts emitted in both cases correspond roughly to the amounts expected to be discharged by recoil alone, which argues for a rapid diffusion of these gases in magnesia at 600°C over the penetration distance ($\sim 7 \mu$) to a free surface. This loss can be minimized by reduction of the free surface of the fuel mixture as a result of increasing the density to > 95 per cent theoretical. Such a density is not readily achieved with magnesia by techniques other than hot-pressing.

A dispersion of urania in magnesia is a metastable structure inasmuch as there is a range of solid solution at the urania-rich end of the system.¹⁹ If the fuel temperature becomes excessive, then solution of the UO_2 may occur, thus losing a major advantage of the true dispersion type element.

Alumina does not take urania into solid solution and vice versa; thus a stable dispersion can be formed. The alumina-plutonium dioxide system would probably be very similar. The thermal conductivity and thermal-shock resistance of alumina fall between those of magnesia and beryllia. Low-temperature neutron irradiation causes no physical changes in polycrystalline material or single crystals, other than in color,¹⁵ but no data are available for fission-product damage. Alumina based refractories can be most readily produced in an impervious form by the addition of glass-forming oxides, e.g., SiO_2 , which ensure that there is a liquid phase present during sintering. The release of Xe^{135} from dispersions¹⁸ of 100μ UO_2 in such an impervious matrix was less than 0.030 per cent at 800°C . Whereas this demonstrates the effectiveness of a dense matrix in retaining fission products, it does not necessarily mean that the use of a glassy bond with a relatively low melting point is the solution to the production of an impervious matrix. The melting point of the bond represents the upper temperature limit of operation of the fuel, and, in addition, uranium oxides will dissolve in some glasses. The fuel structure may thus consist of dispersed particles of so called "matrix material" in a matrix of lower melting point uranium-containing glass.

Zirconia can be considered of little interest as a dispersal medium for UO_2 since there are considerable ranges of solid solution²⁰ and its thermal conductivity is lower than that of UO_2 . The high-temperature form of zirconia may be stabilized by lime additions, but, since the phase change in zirconia itself may be induced by irradiation alone, the long-term stability of the stabilized zirconia under irradiation needs confirmation before its use can be advocated.

Fused silica is unique among oxides in that it (1) offers a matrix material whose thermal conductivity increases with temperature, (2) is stable under irradiation,²¹ and (3) has excellent thermal-shock resistance and high strength. Unfortunately, the thermal conductivity is very low, and the maximum temperature of the fuel element must be kept below 1000°C if devitrification is to be avoided so that fuel elements would be of very small dimensional cross section. Devitrification would result in the formation of the crystalline modifications

of silica that undergo the well-known inversions with their accompanying volume changes on thermal cycling.

3.3 Carbide Matrices

The carbides, in general, have higher room-temperature thermal conductivities, but very little (with the exception of silicon carbide) is known of the variation of their thermal conductivity with temperature.²² Their thermal-shock resistance is better than that of oxides. Practically nothing has been published on the irradiation behavior of the carbides (again with the exception of silicon carbide).

Uranium monocarbide is completely miscible with zirconium, tantalum, and niobium monocarbides, and this behavior could also be expected with other isomorphous carbides.²³ Plutonium monocarbide should behave in a similar manner to uranium monocarbide.

Beryllium carbide, Be_2C , takes a limited amount of uranium monocarbide into solid solution and in any case is unattractive owing to its instability in moist air.

Aluminum carbide, Al_4C_3 , also decomposes in water but with uranium carbide forms a complex carbide,²⁴ as yet unidentified, that is even more unstable than Al_4C_3 .

Nothing is known of the uranium-iron-carbon or uranium-nickel-carbon systems. The tendency of the transition metal carbides to graphitize when exposed to high temperatures for long times is well known and may influence the behavior of such fuels.

The only carbide that seems to be worthy of consideration is silicon carbide. Six crystalline modifications of silicon carbide have been identified to date, but, fortunately, the β form is stable up to about 2200°C. There are four commercially available types of silicon carbide.²² Until recently all silicon carbide materials were bonded with silicon, silicon nitride, or silicates. The refractoriness and mechanical properties at room and elevated temperatures are to a large extent determined by the nature of these bonds. A self-bonded silicon carbide is now available, and two methods of manufacture have been used. The details of only a laboratory process have been published, and this involves hot-compacting under pressures²⁵ of several tons per square inch at 2200 to 2400°C. The commercial process of manufacture has not been disclosed but may involve cold-compacting and sintering of the elemental powders at about 2000°C. It has been claimed that under optimum conditions material of 98 per cent density and 98 per cent purity can be produced. The chief impurities are silicon, carbide, aluminum, and iron. Impermeable silicon carbide with various levels of impurities can therefore be produced.

Irradiation data are again scarce, but a dose of 10^{20} nvt at an unspecified temperature¹⁵ has induced <1 per cent expansion in both the cubic and hexagonal forms of SiC , the damage annealing out at 1200°C.

The chief doubts in the use of silicon carbide must be in the unknown nature of the stable physical form in which uranium or plutonium would be present in an impermeable bonded or self-bonded silicon carbide. The possibility of the existence of low melting-point constituents cannot be dismissed.

4 CONCLUSIONS

Unless metals of neutron-absorption cross section ~ 1 barn can be accepted, there are no metal matrices that will offer a fuel element capable of prolonged operation above 600°C. The use of such relatively high cross-section matrices would probably be more attractive nuclear-wise using plutonium rather than U^{235} as the fissile element. The beryllium-uranium oxide system would appear to offer the maximum operating temperature of dispersions in low cross-section metals.

For operating temperatures in excess of 600°C, using either uranium dioxide or uranium monocarbide as the disperse phase, an impermeable matrix is needed to retain the fission-product gases.

The production of impermeable oxide matrices is not readily achieved in the oxides of interest other than by hot-compacting. Use of a low melting-point glassy bond, while producing impermeable ceramic bodies, may lead to serious restriction of the maximum fuel-element temperature.

Of the oxide matrices discussed, beryllia appears the most attractive, followed by alumina. There is a complete lack of data on the effect of high-temperature neutron irradiation and fission-product damage on the properties of these materials.

Of the carbides only silicon carbide offers any possibilities as a material for a disperse fuel element, but nothing is known of phase equilibriums in the uranium-silicon-carbon system without considering the more complex systems involving the normal additives to silicon carbide, viz., nitrogen, oxygen, aluminum, and iron.

Graphite appears to be an admirable dispersal medium for fissile carbides, but its permeable nature permits release of fission products.

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SESSION V

Corrosion of Uranium Alloys

Corrosion of Uranium, Thorium, and Uranium Alloys in Sodium and Organics^{*}

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ABSTRACT

Sodium and sodium-potassium alloys and the polyphenyl class of organic compounds possess certain advantages over water for use as reactor coolants. There are no reactions between uranium and the pure liquid metals; but thermodynamic data predict that formation of uranium carbide and uranium hydride is possible in reactions with organics and with their pyrolytic and radiolytic products.

Available experimental data are reviewed for uranium and uranium alloys exposed both to sodium and sodium-potassium alloys in static and dynamic systems. Effects of irradiation on corrosion rate do not appear to be significant. The observed corrosion rate of uranium and uranium alloys depends very strongly on the impurity, especially oxygen, content of the liquid metal. In capsule type static corrosion experiments, made with liquid metal with oxygen content near 0.01 wt. % (100 ppm), corrosion rates are of the order of 10 mg/cm²-month at temperatures up to 750°C. UO₂ and UO have been identified as corrosion products. In dynamic systems, corrosion rates of more than 600 mg/cm²-month have been observed at 500°C, with oxygen content ranging near 0.005 wt. % (50 ppm).

Corrosion rates of uranium and uranium alloys in purified biphenyl are of the order of 1 mg/cm²-month at temperatures up to 400°C in static systems. Under dynamic conditions in loop experiments, rates are perhaps five times greater. Formation of UC, through UH₃ as an inferred intermediary, has been observed in monoisopropyl biphenyl under hydrogen gas pressures of the order of 100 psi. Impurities dissolved in the organic, such as air, oxygen, or water, greatly accelerate the corrosion rate.

It is concluded that the corrosion rate of uranium and its alloys in liquid sodium and NaK is low enough to permit the use of a static liquid metal bond between the fuel and a cladding of some other metal. Exposure of relatively large surfaces of fuel to circulating liquid metal coolant appears not feasible, because of the difficulty of adequate control of oxygen in a large volume liquid metal system. There would be no advantage in reactor performance in direct exposure of unclad fuel to an organic coolant; but, in case of accidental exposure by way of a cladding failure, the corrosive attack would be relatively very slow.

1 INTRODUCTION

One of the principal attractions in pursuing development of nonaqueous reactor technology has been the possibility of achieving high temperature without an accompanying high pressure. Sodium and sodium-potassium alloys and certain high-boiling-point organic compounds have accordingly received considerable attention in power reactor development programs in the United States. Sodium and its alloys with potassium, in addition to having relatively wide liquid ranges and high boiling points, possess other advantages such as excellent heat-transfer characteristics, good pumping efficiency, and acceptable nuclear properties. Also, because of their elementary nature, they are free from chemical effects induced by ionizing radiation.

In the last ten years in the United States, many experimental investigations have been made on numerous organic compounds of different chemical types in order to evaluate their resistance to radiation and to high temperature. Although all compounds show some tendency to undergo radiation-induced chemical change, the polyphenyl group of compounds, such as bi-

^{*}This paper may also be identified as Report NAA-SR-MEMO-2169.

phenyl and the terphenyls, appears to possess adequate chemical stability for use as reactor coolants. Their nuclear properties are excellent for reactors operating with neutrons of thermal energies. Their heat-transfer capability falls far short of sodium and is in some ways inferior to water; but it is possible that bulk temperatures in the neighborhood of 325°C (620°F) may be attained with them without excessive pyrolysis, and adequate over-all plant thermal efficiency appears assured.

To the advantages mentioned above for these nonaqueous coolants there can be added the fact that catastrophic chemical reaction between them and uranium is highly improbable. Table 1 (reference 1) summarizes in survey fashion the thermodynamic data for certain chemical reactions of uranium metal and also of sodium and potassium. It may be seen that per mole of uranium metal, the largest free-energy change by far attends the reaction with oxygen. The table further shows what is already well known, that, on thermodynamic criteria alone, uranium will reduce any oxide of sodium or potassium. The free-energy change for reaction with water is relatively large, although not so large as with oxygen. In organic media it is seen that, at least on the basis of free-energy considerations, the production of uranium monocarbide is favored over the formation of uranium hydride.

Observations from corrosion experiments, performed both with sodium and its alloys and with polyphenyls, in direct contact with uranium, have generally borne out the expectation that there would be little reaction between the metal and the pure coolant. In almost every case the observed corrosion has reflected the chemical reactions between uranium and the impurities present in the coolants including, in the case of the polyphenyls, pyrolysis products. Deliberate use in a reactor of unclad fuel in direct contact with coolant is not considered desirable, even if corrosion were not a factor—perhaps primarily because of inevitable contamination of the primary coolant loop by fission-product recoils from the fuel surface. Nevertheless, relative inertness to coolant is a highly useful property in minimizing the consequences of cladding failure.

Table 1—THE EFFECT OF TEMPERATURE ON THE FREE ENERGY OF VARIOUS CORROSION REACTIONS

Reaction	Standard free-energy values, kcal		
	25°C	225°C	400°C
$\text{U(s)} + \frac{3}{2}\text{H}_2(\text{g}) \rightarrow \text{UH}_3(\text{s})$	-17.7	-9.0	-1.6
$\text{U(s)} + \frac{8}{3}\text{H}_2\text{O(l)} \rightarrow \frac{1}{3}\text{U}_3\text{O}_8(\text{s}) + \frac{8}{3}\text{H}_2(\text{g})$	-131.3	-129.0	-127.0
$\text{U(s)} + \text{C(s)} \rightarrow \text{UC(s)}$	-43.6	-44.0	-44.3
$\text{U(s)} + \frac{1}{6}\text{C}_6\text{H}_6(\text{g}) \rightarrow \text{UC(s)} + \frac{1}{2}\text{H}_2(\text{g})$	-48.8	-49.5	-50.1
$\text{U(s)} + 3\text{C}_6\text{H}_6(\text{g}) \rightarrow \text{UH}_3(\text{s}) + \frac{3}{2}\text{C}_{12}\text{H}_{10}(\text{l})$	-23.9	-15.2	-7.8
$\text{U(s)} + \text{O}_2(\text{g}) \rightarrow \text{UO}_2(\text{s})$	-246.6	-238.2	-230.9
$\text{Th(s)} + \text{O}_2(\text{g}) \rightarrow \text{ThO}_2(\text{s})$	-279.2	-269.7	-261.4
$4\text{Na(s or l)} + \text{O}_2(\text{g}) \rightarrow 2\text{Na}_2\text{O(s)}$	-179.8	-166.0	-153.9
$4\text{K(s or l)} + \text{O}_2(\text{g}) \rightarrow 2\text{K}_2\text{O(s)}$	-152.6	-137.8	-124.9
$4\text{Na(s or l)} + \frac{2}{3}\text{Cr}_2\text{O}_3(\text{s}) \rightarrow 2\text{Na}_2\text{O(s)} + \frac{4}{3}\text{Cr(s)}$	-11.1	-5.8	-0.7

2 CORROSION IN SODIUM AND NaK

The impurity contributing principally to corrosion of uranium in sodium is oxygen, present in the metal as Na_2O . To reduce the oxygen content of elementary sodium as received from the chemical suppliers, procedures such as chemical gettering, distillation, and filtration have been utilized. The last, carried out through stainless-steel mesh (or glass) filters at temperatures only slightly above the melting point (97.8°C), supplies sodium with an oxygen content low enough for many uses.

The sodium-potassium alloy compositions most frequently used are approximately 44 wt. % potassium (m.p., 18°C), and the eutectic (approximately 78 wt. % potassium, m.p., -12°C). These are usually purified by distillation by the supplier and further purified by filtration at room temperature.

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Table 2—STATIC CORROSION IN PURIFIED SODIUM AND NaK (References 3-5)

Material	Argonne National Laboratory			Knolls Atomic Power Laboratory		
	Temp., °C	Time, hr	Mg/cm ² -mo	Temp., °C	Time, hr	Mg/cm ² -mo
Uranium	200	144	-0.08*	500	166	-0.1†
	600	144	+3.1*			
	405	160	+7‡§			
	396	160	+1.4¶§			
U-10 wt. % Pu	350	160	-216§			
U-10 wt. % Pu	405	160	-288§			
U-60 wt. % Al				450	124	-30
				500	170	+8
				660	164	-720
U-69 wt. % Al				500	167	-220
Thorium	600	144	+4.5			

*In NaK of 44 wt. % potassium, purified by gettering with uranium.

†In sodium purified by gettering with beryllium or calcium.

‡Small wire specimen.

§In double filtered NaK. Plutonium alloy specimens showed evidence of flaking into the liquid metal.

¶Standard ANL corrosion specimen, 0.97 by 0.61 by 0.106 in.

2.1 Solubility in Sodium

Pure uranium is virtually insoluble in sodium. An upper limit of the order of 0.01 wt. % uranium (100 ppm) is estimated² at 97.8°C. At 300°C, a value of 0.005 wt. % uranium (50 ppm) has been quoted.³ It appears correct to conclude that solubility is of negligible importance in the corrosion of uranium in sodium.

2.2 Corrosion in Static Systems

Early experiments⁴ on small cylinder or sheet specimens of uranium, in rather pure NaK enclosed in a mild steel container, yielded a weight change rate of +0.009 mg/cm²-hr (6.5 mg/cm²-month) at 600°C. This is an initial rate value, from short-time tests (six days). The coating was qualitatively identified as oxide. Other experiments⁵ performed in a type 347 stainless-steel container and using NaK of very high purity gave weight gains at about 400°C ranging from 0.002 to 0.01 mg/cm²-hr (1.4 to 7 mg/cm²-month). Again, these are initial values, for short exposures (seven days). In this case the coating on the uranium appeared from chemical evidence to be UO₂.

Table 2 summarizes available early data on static corrosion. The results show considerable scatter. This probably reflects the variations in oxygen content of the liquid metal, in outgassing procedures carried out on the container, in metallurgical soundness of the specimens, and also in ratios of specimen surface/volume, and of liquid metal volume/specimen surface. All the tests are of relatively short duration, carried out in the absence of radiation. The data in the table are for weight changes only on specimens whose postexposure treatment consisted usually of rinsing in alcohol to remove adherent liquid metal. Metallurgical history of the metals was not known in all cases. Specimens were not stripped to bare metal (nor were they in any of the subsequent liquid metal work reported here). Chemical analysis for oxygen in the liquid metal was usually not made, although the deleterious effects of oxygen on the fuel metal were clearly recognized.⁴ In one series of tests at Argonne National Laboratory, the static corrosion rate of uranium in purified NaK (44 wt. % potassium) was found to be +3 mg/cm²-month at 600°C. In a similar (capsule) test, except that 1.7 wt. % oxygen as O₂ gas had been added to the system, the rate was +29 mg/cm²-month. Both tests were of six-day duration.⁵

In the course of development work for the Sodium Reactor Experiment (SRE) at Atomic International, samples of uranium-thorium alloys and also pure thorium were exposed to sodium and eutectic NaK in type 304 stainless-steel capsules at 750°C for a month.⁶⁻⁷ Results of weight change observations are summarized in Table 3 and are seen to be lower than the range of static corrosion values from earlier work. The sodium was purified by filtration, but the NaK was used as-received. The estimated oxygen content was approximately 0.025 wt. % in the sodium and approximately 0.02 wt. % in the NaK. The capsule atmosphere was purified argon gas. The specimen surface after test showed only slight discoloration. Surveys made after test indicated negligible alpha activity in the liquid metal. The composition of the coating was not determined in the above experiment, but it was very probably a mixture of thorium oxide and uranium oxides.

There is some reason to expect thorium to be more resistant than uranium to oxygen impurity in liquid metal. The adherence of oxides to the base metals is governed by, among other factors, the ratio V_{ox}/V_m (reference 8):

$$E = \frac{V_{ox}}{V_m} = \frac{\text{volume per metal atom in oxide}}{\text{volume per atom in metal}}$$

Maximum adherence would be expected in systems where $E = 1$. For both UO_2 and ThO_2 , the ratio is given by

$$E = \frac{\text{molecular weight oxide}}{\text{atomic weight metal}} \times \frac{\text{density metal}}{\text{density oxide}}$$

For ThO_2 , E is about 1.3; for UO_2 , about 2. On this criterion the oxide on thorium should be more adherent than on uranium and should, in fact, compare favorably with such well known protective oxides as Al_2O_3 ($E = 1.3$ to 1.5).

Table 3—STATIC CORROSION OF URANIUM-THORIUM ALLOYS
IN SODIUM AND NaK AT 750°C*

Material	Fabrication method	Weight change rate, mg/cm ² -mo	
		In sodium	In NaK
Th	Rolled plate	+2	+2
Th-3 wt. % U	Cast	+1	+2
Th-4 wt. % U	Powder metallurgy	-40, +3†	-12

*All exposures, one-month duration. Metal specimens had volume of ~0.5 cm³ and 1 to 2 cm² surface area. Liquid metal volume was about 10 cm³.

NaK was 78 wt. % potassium.

†Duplicate samples.

2.3 Wetting of Fuel Metals by Sodium and NaK

Wettability is a quality of the metal-liquid metal interface that is determined by surface attractive forces. It is related to corrosion, although the latter is usually controlled by chemical processes (solution, reaction). Wetting is of importance in determining the heat-transfer rate from fuel to coolant.

The effect of surface film on heat transfer may be illustrated by consideration of the SRE fuel element which consists of a cluster of seven thin-walled stainless-steel fuel tubes.⁹ Each tube contains twelve beta heat-treated uranium slugs, $\frac{3}{4}$ in. in diameter by 6 in. long (1.9 by 15.3 cm). The slugs are stacked along the length of the tube to form a 6-ft-long active fuel zone (183 cm); and about 7.3 cu in. (120 cm³) of NaK is added to provide a 10 by 10⁻³ in. (2.5 by 10⁻² cm) thick bond between uranium and steel. The fuel element is shown in Fig. 1. It is estimated that if the NaK contained 0.01 wt. % oxygen, and if all the oxygen reacted with the uranium

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surface, an oxide layer 2 by 10^{-3} in. (5 by 10^{-3} cm) thick would form, which at peak SRE heat flux of 340,000 Btu/hr-ft² (107 watts/cm²) would cause an increase in the temperature¹⁰ drop from slug center to surface of 12°C.

The above estimate assumes that the oxide layer is interposed between metal and liquid metal. Experimental results¹⁰ indicate, however, that direct contact between metal and liquid metal is achieved rather readily. Tests were made to determine the "wetting temperature." At this temperature a drop of liquid metal begins to spread freely over the surface of the metal; that is, the contact angle is less than 90 deg.

By using metal specimens that had been outgassed at 350°C in a vacuum of 10^{-5} mm Hg, in an atmosphere of carefully purified argon, the results summarized in Table 4 were obtained.

These results indicate that there is no significant difference between sodium and NaK. Other tests showed that there was essentially no difference in wetting temperatures among different metals. Thorium, thorium-uranium alloys, uranium, and even stainless steels all wet near 200°C. Previous wetting reduces subsequent wetting temperatures. Surface roughness increases the wetting temperature, as does heavy oxidation.

If the oxide coating is very thin, as would be the case on an electropolished surface briefly exposed to air, wetting is attained simply by dipping. The wetting temperatures in practice were frequently below those observed in the controlled experiments. Figure 2 shows an SRE fuel slug, partly coated by immersion, very shortly after the slug was electropolished in NaK at 175°C. Adherence was excellent.

Fig. 1—SRE fuel element.

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Table 4—WETTING TEMPERATURE AS FUNCTION OF WETTING FLUID

Material*	Fluid	Range of wetting temperature, °C
Cast Th	Sodium	240–250
Cast Th	NaK†	235–245
Th–4 wt. % U	Sodium	190–225
Th–4 wt. % U	NaK	198–228
Th–5 wt. % U	Sodium	200–223
Th–5 wt. % U	NaK	202–215

*All specimens were metallographically polished.

†NaK was 78 wt. % potassium.

2.4 Corrosion in Dynamic Systems

Dynamic corrosion tests¹¹ have been made at Oak Ridge National Laboratory in a rocking type apparatus, shown in Fig. 3. The uranium used was alpha-rolled material, electropolished prior to test. Specimens were retained in the hot zone during test. The sodium was once-filtered just above the melting point. Oxygen content was probably between 0.02 and 0.025 wt. % (200 to 250 ppm). Capsules were made of type 347 stainless steel, stringently purified by hydrogen firing and evacuating.

Tests were run at 815°C (1500°F), 649°C (1200°F), and 537°C (1000°F). The 815°C tests resulted in capsule failure, presumably because of formation of the eutectics U_6Fe plus UFe_2 (m.p., 725°C), or U_6Ni plus Ni (m.p., 737°C). There were no capsule failures at lower temperatures. Results of the latter tests, all of which were of 100 hr duration, are summarized in Table 5.

All specimens were covered by a surface layer of thickness varying from 2 by 10^{-3} to 6 by 10^{-3} in. (0.8 by 10^{-3} to 2.4 by 10^{-3} cm). Both UO_2 and UO were identified in all layers by x-ray diffraction. The uranium content of the sodium was determined after test. Also, micro-drillings were taken from the hot and cold zones of the 347 stainless-steel containers and analyzed for uranium content. The weight loss from the 538°C run (SS-190) is reflected in the high uranium pickup by the stainless-steel container. The container wall generally showed no evidence of attack. However, there is some evidence that constituents of the stainless steel

Fig. 2—NaK adherence to uranium.

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deposited on the uranium specimens, from the following tests. Successive layers, 10 by 10^{-3} in. thick, were cut from the surface and chemically analyzed. In specimen SS-189 (see Table 5), the iron found in the first and second layers, respectively, was 0.045 and 0.011 wt. %. In SS-190, the values were 0.049 and 0.014 wt. %.

Figure 4 is a representative photomicrograph of the uranium before test. The dark areas are uranium carbide stringers. All the specimens after electropolishing and prior to test were found to contain carbide stringers but no uniform oxide surface layer. Figure 5 shows the uranium surface condition after test. Oxide layer thickness from 2 to 6 by 10^{-3} in. is apparent. The carbide stringers show attack to a depth of 20 by 10^{-3} in.

The oxide formation in these tests must be attributed principally to the reaction with oxygen initially present in the sodium. The mechanism of transfer to the stainless-steel surface is not known. The role of the carbide stringers is also not known, but it appears probable that there would be less attack in stringer-free metal.

The corrosion rate in loop type experiments where unclad uranium is exposed to a relatively large volume of flowing sodium has been investigated at Argonne National Laboratory.^{12,13} The loop capacity was 30 gal (114 liters). Maximum temperature at the sample was 500°C (932°F), but the loop was not isothermal, so that there was opportunity for thermal mass transfer. The test loop is shown schematically in Fig. 6. It was made of type 347 stainless steel, in 2 in. and 6 in. sizes.

Filtered sodium was charged to the loop. Sodium flowed from the electromagnetic pump, the coldest point in the loop, past the electric immersion heaters and over the specimens. For specimen temperature of 500°C, the highest sodium temperature in the loop was about 600°C and the lowest was about 400°C. Samples for oxygen determination were withdrawn from an outlet that permitted removal of a well-mixed sample. Determination of oxygen was made by a distillation technique. In tests with unirradiated uranium corrosion was monitored by weight loss. Tests were also made with irradiated specimens, and corrosion was qualitatively followed by monitoring the build-up of radioactivity at several points on the loop.

The unirradiated normal uranium was cast and rolled to final size, $\frac{1}{8}$ -in. (0.32 cm) diameter, and $1\frac{1}{4}$ in. (3.2 cm) long. The irradiated specimens were identical to these, except that they had been irradiated to burn-ups of the order of 0.006 to 0.02 per cent of total uranium atoms. Results are summarized in Table 6 and shown graphically in Fig. 7.

An average corrosion rate of $-616 \text{ mg/cm}^2\text{-month}$ was observed for the unirradiated specimens. All specimens appeared rough and pitted following exposure. From the trends shown in Fig. 7 it may be concluded that the products of uranium corrosion by sodium are transported, perhaps as a suspension in the flowing sodium, and settle out in low velocity sections of a circulating system (flanges, surge tank, etc.). The radioactivity growth rate—and inferentially the uranium corrosion rate—shows an increase with increasing temperature and

Table 5—"ROCKING" CORROSION TESTS ON SYSTEM U-Na-347 SS*

Test code number	Temperature hot zone/cold zone	Weight U in sodium after test,† mg	Specimen weight change rate, $\text{mg/cm}^2\text{-hr}$	U plated on container, mg/cm^2	Total U plated, mg
SS-188	{ 676°C (1250°F) 565°C (1050°F)	16.1	+ 0.047		
SS-189	{ 648°C (1200°F) 526°C (980°F)	24	+ 0.065	700 2940	1.05 4.4
SS-190	{ 538°C (1000°F) 400°C (752°F)	26.2	- 0.029	10,000 470	15.0 0.7
SS-191	{ 538°C (1000°F) 396°C (745°F)	24.2	- 0.013		

*All tests 100-hr duration.

†Chemical form of uranium not determined (could have been UO_2 in suspension).

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Fig. 3—Uranium specimen in stainless-steel test capsule (a simplified schematic of a seesaw furnace test).

Fig. 4—Uranium before test. Unetched. (Magnification 500X.)

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Fig. 5—Surface of uranium after test (SS-190). Unetched. (Magnification 250X.)

Fig. 6—Schematic diagram of sodium corrosion loop.

Table 6—LOOP CORROSION TESTS ON UNIRRADIATED AND IRRADIATED URANIUM

Specimen dimensions	Irradiation history	Test history	Oxygen content	Observations
$\frac{1}{8}$ in. dia. by $1\frac{1}{4}$ in. long	None	781 hr total, in 8-hr increments; 400–500°C; flow 8 ft/sec	0.061 to 0.001 wt. % (610 to 10 ppm); mostly between 0.008 and 0.001 wt. %	Average corrosion rate: –616 mg/cm ² -mo; specimens lost a total of 6.7 g, or 18.9% of initial weight
$\frac{1}{8}$ in. dia. by $1\frac{1}{4}$ in. long	0.006 to 0.02% burn-up	1705 hr, continuous; 504 hr at 360°C; then 384 hr at 450°C; then 817 hr at 500°C; flow varied from 1.4 to 2.9 ft/sec	0.008 to 0.001 wt. % (80 to 10 ppm); usually near 0.004 wt. %	Gamma radiation level near surge tank rose from 20 mr/hr at 500 hr, to 220 mr/hr at 1705 hr, increasing with temperature and with flow rate

also with increasing sodium flow rate. The corrosion product that accumulated on the inside of the loop piping was identified as UO_2 . (No uranium was found in the sodium.) It appears therefore that the oxide sloughs off as it forms on the uranium specimens, so that the curves of Fig. 7 reflect a combined corrosion-erosion phenomenon.

Several other points are noteworthy. The total weight loss of 6.7 g uranium in the 781-hr unirradiated test corresponds roughly to a reduction of loop oxygen content at a rate of just less than 0.001 wt. %/month (10 ppm/month). Also, the ratio of sodium volume to uranium surface in this test was about 12 liters/cm², which greatly exceeds the ratio in small capsule type static corrosion experiments.

Additional experiments have been conducted at Argonne National Laboratory in which a prototype fuel pin for the second Experimental Breeder Reactor (EBR-II) was exposed to flowing sodium through a small hole drilled in the pin cladding.¹⁴ The results of a 3500-hr run at about 540°C, made with an irradiated uranium slug, and with sodium flowing past the defected cladding at 35 to 40 ft/sec in a closed loop, indicated that corrosion was undetectably low.

The slug used was normal uranium, 0.164 in. in diameter by 12.2 in. long (0.416 cm by 36.1 cm). The cladding was type 304 stainless-steel tubing, 0.172 in. I.D. by 0.188 in. O.D. by 18 in. long (0.437 cm by 0.477 cm by 45.7 cm). The radial annulus, 0.004 in. (0.01 cm) thick, was filled with sodium in the course of operating the test. The tubing was closed at top and bottom by welded plugs, except that the top plug contained a drilled hole 0.04 in. (0.1 cm) in diameter. The assembled fuel pin was mounted, in a loop constructed of stainless steel, so that the hole was at the downstream end. The loop contained about 10 liters of sodium.

Oxygen concentration in the loop was reduced by cold-trapping to 0.002 wt. % (20 ppm) before operation of the test section began, and subsequently maintained at that value. Temperature at the test section was maintained usually at 540°C, except that at weekly intervals the temperature was briefly lowered to 250°C, to promote the "breathing" of sodium into and out of the annular space. A total of 14 temperature cycles were made during the test. No radioactivity was detected at any time either in sodium samples withdrawn at weekly intervals or in surveys of the loop exterior.

The lower corrosion rate inferred from this defected-cladding experiment, compared with that observed in the previous loop corrosion test, may be explained by differences in the uranium environment. These include the fact that no part of the uranium was directly exposed to flowing sodium; and the oxygen content of the sodium was at all times very low (0.002 wt. %).

2.5 Effects of Radiation on Corrosion

Radiation has no apparent effect on the corrosion rate of uranium by sodium or by NaK at temperatures up to about 600°C. Evidence for this conclusion is available from four different experimental sources.

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Fig. 7 — Activity build-up, dynamic loop test with preirradiated uranium specimens.

(a) *Foil Experiments.* Early experiments (Knolls Atomic Power Laboratory) with highly enriched uranium foils irradiated to burn-up of 0.42 to 10.8 at. %, in sodium at 450°C, resulted in disintegration of the foils.¹⁵ That this was a fission effect in the enriched uranium, and not a radiation-corrosion effect, was demonstrated by the following check experiments. Foils identical in dimensions to the enriched ones but made of natural and of highly depleted uranium were exposed in sodium contained in the same capsule material (iron). Duration of run, temperature, and irradiation conditions were the same as in the enriched foil runs. The normal and depleted foils were found after test to show only relatively minor surface effects. No disintegration occurred. Oxygen content was probably no more than 0.01 wt. % in all experiments.

(b) *Cyclotron Irradiation.* A specimen of alpha-rolled uranium was irradiated (Atomics International), while immersed in sodium at bulk temperatures near 475°C, with protons whose energy at the sodium-uranium interface was 5 Mev.¹⁶ This is below the energy at which protons can cause fission in uranium. The uranium and sodium were contained in a type 347 stainless-steel capsule, provided with a thin window to admit protons from the 60-in. cyclotron at the University of California at Berkeley.

After 64 hr at temperature, under an irradiation of 121 μ a-hr, the capsule was opened for examination. No weight change was detected in the uranium specimen. No alpha activity was detected in the sodium. It is concluded that no corrosion occurred, even though post-run metallographic examination of the uranium showed that the irradiated surface had been heated at least to the alpha-beta transition temperature, about 660°C, at some time during the run.

(c) *Slug Irradiation.* A uranium slug 0.364 in. in diameter by 1 in. long (0.92 cm by 2.5 cm), immersed in NaK in a type 347 stainless-steel capsule, was irradiated (Argonne National Laboratory) for a period of 30 days in the central thimble of the CP-3 reactor.¹⁶ The temperature was approximately 375°C. A weight loss of 0.7 mg was observed, corresponding to a corrosion rate of the order of -0.1 mg/cm²-month. This rate is less than that observed in the absence of radiation (see Table 4). (In light of the difficulty of making accurate weighings of irradiated uranium in a hot cell, perhaps the safer conclusion is that the corrosion rate is not greater than in unirradiated tests.)

(d) *EBR-I Post-meltdown Observations.* Observations¹⁷ have been made on the core of EBR-I, which was removed from the reactor following an experimental power excursion that resulted in partial melting of the core. Temperature at the fuel-NaK bond interface was in the range 500 to 600°C in experimental operation just prior to the excursion. The fuel was in the form of cast slugs of uranium-2 wt. % zirconium alloy, 0.364 in. in diameter by 1.9 in. long (0.92 by 4.8 cm), bonded by a layer of NaK to the thin-walled stainless-steel cladding. Post-removal examination indicates no evidence of corrosive attack on the fuel alloy in elements where no cladding failure occurred.¹⁸ Extensive formation of eutectics, between uranium and the constituents of the stainless-steel cladding, indicate that the temperature attained during the excursion exceeded 750°C.

3 CORROSION IN ORGANICS

The poor heat-transfer characteristics of the polyphenyls—for example, thermal conductivity of about 0.07 Btu/hr-ft-°F (2.9×10^{-4} cal/sec-cm-°C)—as well as radiation decomposition rule out the use of these organics as more or less static liquid bonds in direct contact with the fuel metal. Fuel elements for organic moderated reactors are metal-clad. The Organic Moderated Reactor Experiment (OMRE) operates with type 304 stainless-steel-clad plates,⁹ and the use of aluminum cladding is under consideration in other OMR's.¹⁹

Contact between fuel metal and the organic coolant can occur, therefore, only as a result of cladding failure. There have been rather few experimental investigations that have been aimed at determining corrosion rates. None is known that duplicates exactly the conditions surrounding an actual cladding failure in a reactor.

3.1 Radiolysis and Pyrolysis of Polyphenyls

An organic coolant in an operating power reactor presents a somewhat complex chemical environment. From studies of the radiation chemistry of polyphenyls at elevated temperatures it has been established that the liquid reacts to form gaseous products (principally hydrogen), solid polymeric materials, which remain dissolved in the liquid up to certain concentration levels, and some elemental carbon. Listed in Table 7 are a few properties of some organic

Table 7—SOME PROPERTIES OF ORGANIC MODERATOR COOLANTS

	Biphenyl	Santowax-R*	Santowax-OM†	Monoisopropyl‡ biphenyl	Water
Melting point, °C	70	60 to 145	38	-40	0
Boiling point, °C	255	371	343	290	100
Vapor pressure, psia at 620°F (327°C)	54	6	11	35	1794
Vapor pressure, psia at 800°F (427°C)	220	38	57	190	(Supercritical)
Hydrogen density (10^{22} atoms H/cm ³) at 620°F (327°C)	3.04	3.18	3.18	3.74	2.16

*Commercial mixture of isomeric terphenyls.

†Commercial mixture of *o*- and *m*-terphenyls (approximately 2:1) plus some *p*-terphenyls.

‡Commercial mixture of 62 per cent *m*- and 38 per cent *o*-terphenyls.

coolants that have either received consideration or are actually being used in reactor experiments. Recent reactor experiments in the United States have been principally concerned with biphenyl, isopropyl biphenyl, and the eutectic between ortho- and meta-terphenyl.

The changes in composition of an organic, induced during exposure in an operating reactor, are illustrated²⁰ in Fig. 8. The curves show the changes in percentages of some of the principle radiolytic and pyrolytic products dissolved in Santowax-OM, as a function of exposure in the Materials Testing Reactor (MTR) at Idaho Falls. Also shown is the increase in concentration of polymeric material (defined as having a boiling point above that of the starting material). In this experiment, the Santowax-OM was pumped through a loop built of mild steel piping past a heater section located near the core of the MTR. The heater section consisted of a stainless-steel-clad enriched-uranium fuel element. The system was initially pressurized with nitrogen at 200 psi and maintained near that pressure. The temperature range was 550 to 600°F (288 to 315°C). Neutron flux at the hot zone was near $10^{13}/\text{cm}^2\text{-sec}$.

All the products listed as well as the parent material show at least thermodynamic possibility of reacting with uranium. Hydrogen, however, is probably the most important constituent in such reactions.

3.2 Corrosion in Static Systems

Impurities dissolved in polyphenyls, principally air and water, account for the corrosion observed on uranium at relatively low temperatures. Figure 9 shows macrophotographs of metal specimens after exposure in several different fluids for periods up to two months, over the temperature range from about 70 to 350°F (about 20 to 177°C) (reference 21), taken from studies at Atomics International. The flaky deposit, which was only loosely adherent, was identified by x-ray diffraction as UO_2 . Also shown in Fig. 9 is a photomicrograph of the surface structure, taken after a one-week exposure in Santowax-R at 350°F (177°C). The weight gain rate for this specimen was $0.006 \text{ mg}/\text{cm}^2\text{-hr}$ (equivalent to $4.5 \text{ mg}/\text{cm}^2\text{-month}$); but there was evidence that the rate accelerated with time. Use of nitrogen or CO_2 instead of air reduced the rate by a factor²² of 10.

Fig. 8—Principal solutes in Santowax-OM exposed in MTR.

In the above tests, specimens were cut from as-cast depleted uranium rods into disks $\frac{3}{4}$ in. in diameter by $\frac{1}{8}$ in. (1.9 by 0.32 cm; surface area is 7.6 cm²). The disks were electrolytically etched, cleaned and dried, and immediately immersed in the liquid organic contained in a heated vessel that was open to air. The liquid was agitated by a stirrer, which provided circulation over the entire surface of the specimens mounted in a rack. The organic layer over the specimens was about 10 cm thick.

(a) *Corrosion in Chlorinated Biphenyl.* Static corrosion of uranium in "Arochlor 1248," a commercially available mixture of chlorinated biphenyls, was investigated over the temperature range 60 to 310°C while exposed to air and inert atmospheres.²³ Results are given in Table 8. Corrosion rates listed are for stripped specimens.

The product was identified by qualitative chemical tests as a mixture of UO₂ and a soluble chloride, probably UO₂Cl₂. Uranium specimens were exposed in 200 cm³ of organic in glass vessels, open to the air (except that tank helium was passed over the liquid surface in the last two runs.)

There is no interest in using chlorinated biphenyl as a reactor coolant, for reasons other than corrosion of fuel metal. The data in Table 8 do point up the desirability of eliminating chloride impurity from polyphenyls for coolant use.

(b) *Corrosion in Biphenyl.* An extensive series of experiments was performed at Argonne National Laboratory on corrosion of uranium and several of its alloys in biphenyl, under static conditions over a temperature range²⁴ from 500 to 750°F (260 to 400°C). Tests were performed in 100-cm³-capacity stainless-steel (type 304 or 347) autoclaves. Specimens were held in stainless-steel racks that permitted free access of liquid to all but a very small part of the specimen area, as shown in Fig. 10. Specimens were cut from stock to a size approximately $1\frac{1}{2}$ by $\frac{3}{4}$ in. (3.9 by 1.9 cm), with thickness from 0.059 to 0.071 in. (0.15 to 0.18 cm). Wherever possible the original stock was used for specimens at all temperatures. After the specimens were scrubbed, carefully dried, and degreased, they were loaded into the autoclaves.

In all tests, the biphenyl was deaired by heating it to boiling (or near boiling) in the autoclave, which was then closed as soon as possible. Some tests were performed under a blanket of nitrogen gas initially at 515 psia (35 atm). Autoclaves used in the latter tests were provided with a pressure gauge and vent line to permit maintenance of pressure by bleeding off gas. The biphenyl was commercial grade, and the same charge was used throughout the test wherever possible.

At intervals through the runs (some of which lasted over 6900 hr), the autoclaves were opened to permit removal of specimens and then quickly closed. Specimens were degreased, dried, weighed, and then returned to the autoclaves using the same deairing procedure as on initial loading. The observed corrosion rates for fuels and for several structural materials are summarized in Table 9 for runs made without added cover gas.

The data listed in Table 9 are average rates, calculated from measured weight changes over the entire test interval. Where duplicate specimens were run, results check within 10 to 35 per cent. The erratic temperature variation may reflect different metallurgical history (as well as composition), which was not known for all stock, or the effects of removing specimens for weighings during the runs. Rates determined from the intermediate weighings showed some scatter, even on the same specimen.

On all specimens where significant corrosion occurred, rather loose powdery deposits were found. These were not generally identified; under the test conditions some carbon from pyrolysis of the biphenyl is to be expected. The corrosion product on both the uranium and uranium-molybdenum alloy that partly disintegrated in the 680°F run was found by x-ray diffraction to contain UC. This was verified by chemical analysis. Cause of the failure of these two specimens was not established.

A few corrosion tests were made in biphenyl under an initial pressure of 515 psia (35 atm) of nitrogen gas. After 2029 hr at 500°F, the average weight change rate for the aluminum-8.2 wt. % uranium alloy was +0.006 mg/cm²-month. However, duplicate specimens of uranium-2 wt. % zirconium alloy disintegrated after 337 hr. X-ray diffraction and chemical analyses established the corrosion product in the latter alloy as UN₂.

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 Monoisopropyl biphenyl
 Room temperature ($\sim 20^{\circ}\text{C}$)
 Not stirred
 Exposure: two months

 Biphenyl, 200°F (93°C)
 Stirred
 Exposure: one month

Biphenyl, 200°F (93°C)
 Stirred
 Exposure: two months

Portion of surface (500X)
 Santowax-R, 350°F (177°C)
 Stirred
 Exposure: one week

Mount
 U oxide, ~ 0.0008 in. (0.002 cm)
 U metal

 Santowax-R, 350°F (177°C)
 Stirred
 Exposure: one month

Santowax-R, 350°F (177°C)
 Stirred
 Exposure: two months

Fig. 9—Uranium immersed in organics, in vessel open to air.

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Table 8—CORROSION OF URANIUM BY "AROCHLOR"

Temp., °C	Atmosphere	Exposure, hr	Corrosion rate, mg/cm ² -mo
60	Air	742	5.3
100	Air	598	33.4
200	Air	286	277
200	Helium	191	131
310	Helium	48	655

(c) *Corrosion in Orthoterphenyl.* The terphenyls have higher boiling points than biphenyl (see Table 7). They are also more resistant to pyrolysis, and (particularly the para isomer) more stable under irradiation. The greater chemical inertness implied by the last two properties should permit exposure to uranium at higher temperatures than in biphenyl, without increase in corrosion rate.

Preliminary survey tests over the temperature range 700 to 900°F (371 to 482°C) were made with uranium and thorium immersed in *o*-terphenyl contained in stainless-steel capsules sealed with an argon gas atmosphere.²⁶ Each capsule contained one specimen each of uranium, thorium, and also aluminum. Capsules were opened after two, four, six, and eight weeks at temperature. Observations are summarized in Table 10.

(d) *Corrosion in Monoisopropyl Biphenyl.* The greater liquid range and hydrogen density of MIPB, compared to biphenyl, are advantages in reactor application, although the presence of the alkyl side-chain makes this compound less stable than biphenyl toward both pyrolysis and radiolysis.

Fig. 10—Autoclave components.

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At Hanford Atomic Products Operation, screening experiments were made with unclad and defected-clad uranium specimens, exposed to MIPB in stainless-steel containers at temperatures²⁷ up to 400°C. In these experiments uranium specimens $\frac{3}{4}$ by $\frac{1}{2}$ by $\frac{1}{8}$ in. (1.9 by 1.3 by 0.32 cm; surface area is 7 cm²) cut from beta heat-treated bar were immersed in about 50 cm³ of MIPB, in a container of about 100 cm³ volume. Both normal and preirradiated uranium specimens were used; they exhibited no differences in behavior in these tests.

Table 9—STATIC CORROSION IN BIPHENYL^a

Material	Weight change rate, ^b mg/cm ² -mo		
	500°F (260°C) ^c	680°F (360°C) ^d	750°F (400°C) ^e
Uranium	-4.06	f	-2.73
U-2 wt. % Mo	-3.12	g	-2.29 ^h
U-2 wt. % Zr	-4.82 ^h	-5.14 ^{h,i}	
U-5 wt. % Zr	-3.58	-1.87 ⁱ	
U-5 wt. % Zr-1.5 wt. % Nb	-0.369	-1.55 ⁱ	
Zr-2.5 wt. % Sn-9 wt. % U	+0.016	-1.84 ⁱ	
Al-8.2 wt. % U	-0.003	-0.004 ^j	
Type 2S Al	-0.001	-0.007	
Type 347 stainless steel	-0.003	-0.003	
Zircaloy-2	+0.017	+0.224	+0.252

^aNo added cover gas.

^bAverage rates for entire test period.

^cFirst four materials in this column were exposed for 4508 hr; last six, 4463 hr.

^dTemperature during all these runs was also maintained at 750°F over an appreciable fraction of the total exposure.

^eTotal exposure 3825 hr; 3562 hr at 750°F, 263 hr at 680°F.

^fCracking noted after 1163 hr; partial disintegration after 2310 hr.

^gBlistering and cracking noted after 2310 hr; partial disintegration after 3094 hr.

^hAverage of two determinations.

ⁱTotal exposure 6919 hr; more than half of this at 750°F.

^jTotal exposure 4718 hr; 3094 hr at 680°F, 1624 hr at 750°F.

Table 10—STATIC CORROSION IN *o*-TERPHENYL

Material*	2 weeks	4 weeks	6 weeks	8 weeks
700°F (371°C)				
Uranium	-0.5†	-0.1	0.0	0.0
Thorium	-4.6	-1.5	-0.8	-0.6
800°F (427°C)				
Uranium	-0.4	-0.7	-4.5	‡
Thorium	-3.3	§	-15.5	‡
900°F (482°C)				
Uranium	+1.0	¶		
Thorium	+75.0	¶		

*The aluminum specimens were essentially unchanged in all tests.

†Weight change rate, mg/cm²-month, for specimen removed after indicated exposure.

‡Specimen disintegrated.

§Partial disintegration.

¶Tests discontinued because of pyrolysis of organic.

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(e) *Results with Unclad Uranium.* The results of the experiments with unclad uranium indicate that hydrogen pressure determines the extent of the reaction. Attack on the uranium was limited to relatively light surface corrosion, provided the pressure did not exceed a threshold value, which increased with temperature. The data are summarized in Table 11. The threshold for reaction at 300° appears to be below 1 atm. At 350°, it is between 55 and 65 psia; at 375°, near 165 psia; and at 400°, near 225 psia. In all cases, the only corrosion product found was UC. This was identified by x-ray diffraction and verified by chemical analysis.

Hydrogen, methane, ethane, and ethylene are among the principle pyrolysis products of MIPB, that remain in solution. The role of pressure in the corrosion reaction has been taken²⁷ to indicate that uranium hydride, UH_3 , is an intermediary in the corrosion process. No hydride was found in these tests; but the formation of UH_3 by reaction of uranium metal with a hydrogenated aromatic (tetralin) has been reported elsewhere.²⁸ Also, UH_3 has been stated to react with C_2H_4 (ethylene) to form a carbide,²⁹ possibly UC.

It may be seen from Table 9 that the uranium specimens in biphenyl showed a weight loss of less than 15 mg/cm² after 160 days at 400°C. The pressure in the capsules of the Table 9 experiments was close to, if not greater than 225 psia. Comparison with the results in Table 11 leads to the conclusion that biphenyl is less corrosive than MIPB.

(f) *Experiments with Defected-Clad Uranium.* To assess the consequences of defective cladding on a fuel element, tests were made with uranium slugs clad with type 2S aluminum. Slugs were machined from beta heat-treated rod to dimensions 0.5 in. diameter by 2 in. long (1.3 by 5 cm). The cladding was closed at both ends, except that a $\frac{1}{16}$ -in.-diameter (0.16 cm) hole was drilled through to the uranium at one end. Each slug was immersed in MIPB in a stainless-steel pressure vessel. Table 12 contains a summary of the experimental results.

Table 11—REACTION OF UNCLAD URANIUM WITH MIPB

Temp., °C	Maximum pressure		Exposure, days	Observations
	Psia	Atm		
300	14.7	(1)	106	Surface attack
350	55	(3.7)	28	Surface attack
	65	(4.4)	39	One-fourth destroyed
375	125	(8.5)	6	Surface attack
	175	(11.9)	9	One-half destroyed
	185	(12.6)	13	Surface attack
	175	(9.9)	14	One-fourth destroyed
	295	(20.0)	14	Destroyed
	185	(12.6)	20	One-half destroyed
400	115	(7.8)	1	Surface attack
	145	(9.9)	2	Surface attack
	205	(13.9)	3	Surface attack
	215	(14.6)	7	Surface attack
	215	(14.6)	11	Surface attack
	215	(14.6)	14	Surface attack
	215	(14.6)	21	One-half destroyed
	195	(13.3)	25	Surface attack
	225	(15.3)	37	Surface attack
	225	(15.3)	44	Surface attack
	225	(15.3)	59	Surface attack
	285	(19.4)	5	One-fourth destroyed
	440	(30)	5	One-half destroyed
	515	(35)	5	Three-fourths destroyed
	735	(50)	7	Destroyed
	900	(60)	7	Destroyed
	1000	(70)	19	Destroyed

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Table 12—REACTION OF DEFECTED-CLAD URANIUM WITH MIPB

Temp., °C	Pressure		Time, days	Observations
	Psia	Atm		
350	55	(3.7)	12	No attack
	95	(6.5)	19	No attack
	115	(7.8)	34	Starting to swell to hole
400	135	(9.2)	2	No attack
	<215	<(14.6)	11	No attack
	<215	<(14.6)	21	No attack
	<215	<(14.6)	37	No attack
	<215	<(14.6)	56	No attack
	245	(16.7)	4	No attack
	425	(28.9)	7	No attack
	575	(39.1)	12	Swelling at hole
	595	(40.5)	17	Badly swollen
	617	(42.0)	19	Badly swollen
	695	(47.2)	7	Swelling at hole

It appears that the reaction rate through a relatively small opening in fuel-element cladding would be slow enough, in practical reactor operation, so as not to require immediate shutdown for replacement.

(g) *Corrosion in Dynamic Systems.* Specimens of uranium-7 wt. % zirconium alloy, along with other materials, were exposed in a large loop to 800°F (427°C) biphenyl, at flow rates up to 27 ft/sec (8.2 m/sec) for a total of 60 days³⁰ (see Fig. 11 and Table 13). The loop, which was constructed of carbon steel, is shown schematically in Fig. 12.

The loop was charged with about 1000 lb (465 kg) of commercially pure biphenyl. Water content of the biphenyl was between 0.005 and 0.015 wt. % during the first 30-day run. Oxygen impurity was not measured. The loop was initially pressurized to 315 psia with nitrogen gas. As operation progressed, pressure was maintained at this value by venting, so that the nitrogen was diluted somewhat by gas formed by pyrolysis.

The zirconium-7 wt. % uranium specimens were pickled, washed, dried, and weighed prior to insertion in the loop. Specimen dimensions are shown in Fig. 12, which shows schematically the arrangement of 18 specimens.

During the operation of the loop for a second 30-day period, at essentially the same conditions as for the first, there was a short interval in which the temperature exceeded 1012°F (535°C). The uranium-zirconium alloy specimens were dimensionally distorted and heavily coated by a layer of brown, loosely-adherent material. The coating probably consisted of a mixture of zirconium hydride and oxides of uranium and zirconium. In general, all the zirconium metal and alloy specimens were found to be in comparably poor condition.

(h) *Effects of Radiation on Corrosion.* No experimental data are available on systems under irradiation; and only a few tests have been made with preirradiated fuel.²⁶ These indicate no detectable difference from unirradiated material.

4 CONCLUSIONS

4.1 Metal Fuels in Sodium and NaK

Reproducible data from well-controlled corrosion experiments are meager. Corrosion products UO_2 and UO have been identified, arising from chemical reaction with impure oxygen. Available data indicate a corrosion rate from 1 to 10 mg/cm^2 -month in liquid metal, of oxygen content <0.01 wt. %. Older data give the higher values. Tests at temperatures up to 750°C are included in the above rate range. A low rate appears to be indicated by available reactor operating experience (EBR-I; SRE).

Fig. 11—Specimens for biphenyl dynamic corrosion loop.

The corrosion rate in dynamic systems depends on local conditions: fluid velocity, the degree of contact between the metal and liquid metal, temperature and temperature differences in the loop; and—most important—the oxygen content. Corrosion rates near $-600 \text{ mg/cm}^2\text{-month}$ have been obtained for uranium at 500°C in loop experiments.

Data are too slight to determine the most corrosion-resistant among uranium, high uranium alloys, and thorium. Thorium appears to be more resistant than uranium at 750°C in a static system. Low uranium alloys, such as aluminum-uranium, follow the corrosion pattern of the major constituent.

As cast, heat treated, and rolled metal exhibit no difference in corrosion rate in liquid metal.

There is no effect of radiation on the corrosion rate at temperatures to 600°C .

Use of sodium or NaK as a liquid bond inside a metal clad or a fuel element appears satisfactory from a corrosion standpoint, at least to 750°C .

Table 13—DYNAMIC CORROSION IN BIPHENYL AT 800°F (427°C)

Material	Weight change rate ($\text{mg/cm}^2\text{-month}$)*				
	27 ft/sec				
	Position 1	Position 2	9 ft/sec	4 ft/sec	Static
Zr-7 wt. % U	+3.10	+2.28	+2.28	+2.52	+1.41
Carbon steel (A 212)	+0.08	+0.05	+0.38	+0.22	+0.18
Zircaloy-2	+2.59	+2.70	+2.88	+1.88	+2.62

*30-day run.

Fig. 12 — Biphenyl dynamic corrosion loop.

4.2 Metal Fuels in Organics

Relatively few investigations have been made on these systems.

Uranium is corroded by dissolved air and water when immersed in organics (biphenyl or derivatives) at temperatures as low as 200°F (93°C). UO_2 has been identified as a corrosion product. Chlorinated biphenyl corrodes uranium even in the absence of oxygen or water.

In static biphenyl the corrosion rate of uranium is about 3 mg/cm²-month at 400°C. UC has been identified as a corrosion product in these systems. When nitrogen is used as a cover gas, UN_2 may be formed.

Among the high uranium alloys, uranium-2 wt. % molybdenum is slightly more resistant to static 750°F (400°C) biphenyl than pure uranium; uranium-zirconium alloys are slightly less resistant. Under these same conditions, the corrosion rate of aluminum-8.2 wt. % urani-

um is $0.004 \text{ mg/cm}^2\text{-month}$ (less than that observed for 2S aluminum). Exploratory static tests at 700°F (371°C) indicate that uranium is more resistant than thorium to corrosion in ortho-terphenyl.

Flow velocity increases the corrosion rate of a zirconium-8 wt. % uranium alloy in bi-phenyl at 800°F (427°C): from $1.4 \text{ mg/cm}^2\text{-month}$ (static) to $3 \text{ mg/cm}^2\text{-month}$ (27 ft/sec).

From a corrosion standpoint no fuel alloy can be recommended on the basis of available data, for use without cladding in an organic-cooled reactor. Corrosion rates are low enough to ensure that no operating problem would result if there were a cladding failure, with almost any metal fuel alloy.

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SESSION VI

**Irradiation Effects on Uranium,
Its Alloys, and Its Compounds**

Irradiation Effects in Uranium*

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ABSTRACT

A review of pertinent physical metallurgical properties of irradiated uranium is presented. Included under mechanical properties are hardness, bend, and tensile data. In the case of tensile properties the variables considered are burn-up, irradiation temperature, U^{235} content, composition (to 3 wt. % alloy), postirradiation annealing, and tensile testing temperature. Drastic reductions in ductility occur at burn-ups as low as 0.02 at. %. Recovery of damage is limited on postirradiation annealing.

Changes in such physical properties as density, thermal conductivity, electrical resistivity, and modulus of elasticity are reported. Thermal conductivity decreases 10 to 15 per cent at nominal burn-ups.

The effect of irradiation on the microstructure of uranium is reported. Macroscopic, optical and electron microscopic, and fractographic results are presented. Precipitation, microcracking, and micro-brittleness were detected. Solid-state studies, including recrystallization and solid and noble-gas diffusion, are reported. No direct evidence of a change in diffusion due to irradiation has been obtained.

Structural changes have been observed by means of X-ray diffraction; line broadening, line asymmetry, and some line shift have been observed.

Dimensional instability of uranium is discussed; typical results and possible mechanisms advanced to explain these results are reported.

The impact of these changes in physical metallurgical properties on the behavior of uranium fuel elements is discussed.

1 INTRODUCTION

The quantitative data covering the significant properties of irradiated natural uranium and alloys containing greater than 95 per cent uranium are relatively limited. This is unfortunate because the designer of fuel elements should have access to information such as tensile elongation, yield strength, thermal conductivity, and creep rates in the unirradiated and irradiated states at the proposed temperatures of fuel-element operation. Obviously, any other irradiated-uranium data which permit the designer to better understand the behavior of irradiated fuels will also be of value. Structural changes observed by X-ray diffraction, as well as knowledge of dimensional instability and of microstructural changes detected with the optical and electron microscopes, fall within the category of supporting information.

This paper is a résumé of pertinent physical metallurgical information determined in laboratories in the U. S. on irradiated uranium. Essentially all such physical metallurgical information from the U. S. has been declassified.

2 MECHANICAL PROPERTIES

Significant data are available covering changes in hardness, bend, and tensile properties. In the latter case the tensile properties have been determined as functions of burn-up, irradiation

*This paper may also be identified as Report HW-51444.

tion temperature, U^{235} content, and composition; additional variables were postirradiation annealing and tensile testing temperature. Studies range from the extensive to the limited and cursory.

2.1 Hardness

Hardness values are not very useful in interpreting the extent of damage in irradiated uranium. It is safe to say that there will be an increase in hardness with fission-product build-up, but a quantitative prediction of the change in other mechanical properties cannot be made on the basis of present data. Typical hardness values are given in Table 1. No attempt has been made to convert to one hardness scale owing to the dubious validity of such conversions.

2.2 Bend Test

Based on the very limited bend-test data available at present, no definite conclusions can be drawn as to the behavior of massive uranium irradiated to high burn-ups and subjected to flexing. It is safe to predict that the material will fail brittly, based on comparable tensile data.

Alpha-rolled and beta heat-treated wires were exposed in the Brookhaven reactor to 5.5×10^{18} and 2.0×10^{19} nvt and then were bend tested.⁴ After irradiation the force to produce a given plastic deformation was increased for both types of wire. Both alpha- and beta-treated wires failed by brittle fracture after the 5.5×10^{18} nvt exposure. After an exposure of only 2×10^{19} nvt, the deflection obtained for the beta heat-treated and alpha-rolled wires decreased by 82 and 72 per cent, respectively. Wires irradiated at 190°C (375°F) were "harder," i.e., the force to produce a given plastic deformation was higher than for those wires irradiated at 25°C (77°F). For these exposures all or nearly all of the observed effects anneal out at 700°C (1292°F).

Bend-test data were obtained in 1944–1945 on alpha-rolled and gamma-extruded uranium; a slight decrease in load and a 26 to 51 per cent decrease in deflection to fracture after relatively low exposures were observed.⁵ Exposures are difficult to establish, but they are probably in the 2×10^{18} nvt range.

2.3 Tensile Tests

Hueschen, Kemper, and Kelly have investigated the effects of burn-up, irradiation temperature, U^{235} content, postirradiation annealing, and testing temperature on the properties of natural uranium.⁶

Table 1—TYPICAL HARDNESS VALUES OF URANIUM BEFORE AND AFTER IRRADIATION

Specimen history	Integrated neutron flux	Burn-up,* at. %	Hardness		Ref.	Remarks
			Pre-irradiation	Post-irradiation		
Beta heat-treated tapered pin	2×10^{18}	0.008	82 R _G	88–98 R _G	1	Temp. range, 50–900°C (120–1650°F)
Beta heat-treated wafers	7.2×10^{19}	0.028	71–78 R _G	84–89 R _G	2	Center softer than edge
~1.5 in. in diameter	1.7×10^{20}	0.065	71–78 R _G	89–94 R _G	2	At center
	1.7×10^{20}	0.065	71–78 R _G	98–103 R _G	2	Near edge
Metallography	3.3×10^{19}	0.013	214 ± 12 DPH	275 ± 10 DPH	3	
Specimen	3.3×10^{20}	0.13	214 ± 12 DPH	315 ± 20 DPH	3	

*An arbitrary conversion has been made from values of integrated neutron flux (nvt) to atomic per cent burn-up by multiplying nvt by a factor 4.1×10^{-21} . This ignores fast-neutron fission and flux depression but is essentially correct on the basis of radiocesium analyses.

2.4 Tensile Changes Due to Burn-up

Definite differences in uranium tensile properties have been observed as the total atomic per cent burn-up increases. Table 2 contains tensile data on uranium irradiated to extremely low levels of burn-up (4×10^{-5} and 4×10^{-6} at. %).⁷ These specimens were flats cut from beta heat-treated ingot sheet; the maximum temperature during irradiation was approximately 50°C (120°F). After discharge most of the specimens were refrigerated 1 year at slightly below 0°C (32°F). Examination of the data reveals definite recovery in one specimen held 14 months at room temperature. The secondary hardening observed after a 400°C (750°F) anneal cannot be explained. The observed room-temperature properties and the elevated-temperature recovery of tensile properties are attributed to the generation of dislocations or Frenkel defects during irradiation and their subsequent removal by annealing rather than to a mechanism consisting of fission-product build-up and development of microcracks.

The drastic effect of a nominal atomic per cent burn-up of the tensile properties of natural uranium is strikingly apparent in Fig. 1.⁸ The elongation in the 0.250-in. tensile specimens decreases from 20 per cent to less than 1 per cent, the yield strength is almost doubled, and the ultimate strength decreases 20 per cent. All this damage occurs before 0.02 at. % burn-up, far below economic burn-up in power fuel elements. Such damage is believed to be due to fission products and microcracks formed during irradiation.

2.5 Irradiation Temperature

The effect of irradiation temperature on the properties of natural uranium is shown in Table 3, which is abstracted from reference 6 with some additions of later data.

Some reduction in ultimate and yield strength occurs when the specimens are irradiated at elevated temperatures, but no improvement in ductility is observed even when the uranium is

Table 2—EFFECT OF LOW-TEMPERATURE EXPOSURE
ON THE TENSILE PROPERTIES OF URANIUM

Sample	Exposure, nvt	Sample history	Ultimate strength, 10 ³ psi	Yield strength (0.2%), 10 ³ psi	Elongation in 1 in., %	Modulus, 10 ⁶ psi
Av. of six controls			70.55	26.8 ± 3.0	7.7 ± 1	21.9 to 24.6
2-2	1 × 10 ¹⁶	As irradiated	72.7	39.2	7.0	24.8
2-3	1 × 10 ¹⁶	As irradiated	63.4	34.8	4.4*	30.5
2-6	1 × 10 ¹⁶	As irradiated	72.2	32.2	6.6*	28.7
3-2	1 × 10 ¹⁷	As irradiated	64.7	39.1	4.1	20.9
3-3	1 × 10 ¹⁷	As irradiated	71.2	41.3	4.9	33.6
3-5	1 × 10 ¹⁷	As irradiated	74.0	42.2	6.6	26.6
Annealed Samples						
2-4	1 × 10 ¹⁶	10 hr, 200°C (390°F)	62.0	25.2	5.6	20.9
2-1	1 × 10 ¹⁶	10 hr, 300°C (570°F)	82.5	25.0	10.8	25.6
2-5	1 × 10 ¹⁶	10 hr, 400°C (750°F)	79.6	28.1	10.1	15.3
3-6	1 × 10 ¹⁷	14 months, room temp.	72.7	31.4	6.4*	23.8
3-1	1 × 10 ¹⁷	10 hr, 300°C (570°F)	86.6	34.6	10.0	23.8
3-4	1 × 10 ¹⁷	10 hr, 400°C (750°F)	80.2	43.7	8.4	16.4

*Broke outside gauge length.

Fig. 1—Room-temperature properties of irradiated uranium: effect of exposure.

irradiated at 800°C (1470°F).⁹ This latter temperature was obtained by surrounding the 0.250-in. tensile specimen with machined sleeves of uranium. One distinct difference observed was the freedom from bumping in the surface of the tensile specimen irradiated at 800°C (1470°F). Such bumping invariably occurs in lower temperature irradiations.

2.6 U²³⁵ Content

A valid question in the interpretation of radiation-induced damage in uranium is the relative importance of displaced atoms and fission events in the introduction of damage. One possible means of investigating these effects is to fix the level of fast and thermal integrated flux and, by varying the U²³⁵ content, change the number of fission events. Depleted uranium (0.028 at. % U²³⁵) was utilized to obtain an approximate comparison with natural uranium (0.71 at. % U²³⁵). Specimens of the depleted uranium were irradiated to 0.3×10^{20} and 3×10^{20} nvt. These levels correspond to burn-ups of 0.0005 and 0.005 per cent, far lower than natural uranium, which would have achieved burn-ups of 0.01 and 0.11 per cent. Natural uranium would have been irradiated to 1.3×10^{18} and 1.2×10^{19} nvt to reach the lower burn-ups. The burn-up levels are calculated without regard for fast-neutron fission, which introduces an error; however, the error should not be excessive. Surfaces of specimens of the depleted uranium were warped and roughened after the higher exposure, whereas they were smooth at the lower level. Tensile properties of the specimens tested at the 0.0005 per cent burn-up level were: ultimate tensile strength, 110,800 psi; 0.2 per cent yield strength, 82,000 psi; and elongation in 1 in., 2.4 per cent.¹⁰ Damage is still severe, as can be seen in Table 3 by comparing with natural uranium the specimens that reached 0.018 per cent burn-up.

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Table 3—EFFECT OF EXPOSURE AND EXPOSURE TEMPERATURE ON ROOM-TEMPERATURE PROPERTIES OF URANIUM

Material	Exposure, total at. % burn-up	Irradiation temp.		Ultimate tensile strength, 10 ³ psi	Yield strength (0.2%), 10 ³ psi	Elongation in 1 in., %
		°C	°F			
Material A*						
controls	0			104	31	17 ± 1
Material A	0.072	150	300	76	71.5	0.36
Material B*						
controls	0			97.1	37.8	19 ± 1
Material B (NaK canned)	0.062	150	300	93.5	59	0.6
Material B (NaK canned)	0.072 (est.)	300–400	570–750	78	45	0.4
Material B	0.018	150	300	84.4	60.3	0.8
Material B	0.018	150	300	72.2	54.4	0.7
Material B	0.031	150	300	75.5	69.4	0.5
Material B	0.031	150	300	92.2	76.8	0.8
Material B	0.031	150	300	89.1	79.4	0.8
Material B	0.075	150	300	87.5	82.6	0.5
Material B	0.075	150	300	88.5	75	0.5
Material B	0.10	150	300	77.4	73.4	0.55
Material B (sleeves on specimen)	0.02	800	1470	61.0		<1.0

*Both materials A and B are natural uranium varying slightly in trace-element concentrations.

2.7 Alloy Effect

Very few tensile tests have been carried out on irradiated uranium alloys. Three alloys that have been investigated are uranium–0.35 at. % chromium, uranium–0.5 at. % titanium, and uranium–23 at. % silicon. These alloys were irradiated in NaK-filled capsules at the Materials Testing Reactor (MTR). Results are shown in Table 4.¹¹ The uranium–0.5 at. % titanium specimen was so severely bumped and warped that it could not be tested. Results on the uranium–0.35 at. % chromium are slightly better than natural uranium, possibly due to grain refinement. Even so, the improvement is minor. In the case of the epsilonized uranium–23 at. % silicon, the weight per cent addition of silicon is minor, but the atomic per cent is large enough to change the crystal structure. The tensile properties were very poor; the specimens fractured conchoidally in a fashion usually seen in ceramics. Based on these very limited results, no apparent postirradiation mechanical-property advantage appears to occur as a result of alloying.

2.8 Postirradiation Annealing

Fairly extensive results are available on the effects of postirradiation annealing on the tensile properties of irradiated natural uranium.^{6,8} A complete survey of data available to date is given in Table 5 and Fig. 2. Previous discussion⁶ indicated that there is little or no recovery in ductility on annealing, even when it is carried out in the gamma range (>770°C); however, later data,⁸ in which the heating and cooling rates above 600°C (1110°F) were only 10°C/hr, revealed a definite recovery in elongation from less than 1 per cent in the as-irradiated 0.075 at. % burn-up specimen to 12.4 per cent, and from 0.55 per cent in the case of 0.1 at. % burn-up specimens to 4.6 per cent. A beta-phase anneal also causes some recovery, as does a 600°C (1110°F) anneal in lower burn-up specimens (0.018 and 0.031 at. %).

Table 4—POSTIRRADIATION TENSILE PROPERTIES
OF URANIUM AND URANIUM ALLOYS

Alloy	Ultimate tensile strength, 10 ³ psi	Yield strength (0.2%), 10 ³ psi	Elongation in 1 in., %	Surface condition
U-23 at. % Si (2.9 wt. %)	31.1		0.17	Smooth; straight
Natural U	50.6		0.18	Rough; badly warped
U-23 at. % Si (2.9 wt. %)	16.4		0.20	Smooth; badly warped
U-0.35 at. % Cr (<0.1 wt. %)	106	106	0.64	Slightly rough; straight
Natural U	61.2	59.5	0.42	Rough; warped
U-0.5 at. % Ti (0.1 wt. %)	42.2		0.14	Rough; badly warped

Table 5—EFFECT OF IRRADIATION AND POSTIRRADIATION ANNEALING
ON ROOM-TEMPERATURE TENSILE PROPERTIES OF URANIUM

Exposure, at. % burn-up	Annealing temp.		Annealing time, hr	Ultimate strength, 10 ³ psi	Yield strength (0.2%), 10 ³ psi	Elongation in 1 in., %
	°C	°F				
Control				97.1	37.8	19 ± 1
0.018	As irradiated			78.0 av.	57.0 av.	0.75 av.
0.018	400	750	10	75.0	39.2	2.5
0.018	400	750	25	76.0	39.2	2.6
0.018	400	750	100	74.9	48.1	1.6
0.018	600	1110	10	84.5	35.2	5.7
0.031	As irradiated			83.0 av.	73.0 av.	0.7 av.
0.031	400	750	100	79.3	56.6	1.1
0.031	600	1110	10	82.3	42.2	2.7
0.075	As irradiated			88.0 av.	79.0 av.	0.5 av.
0.075	400	750	10	80.7	62.8	0.7
0.075	400	750	25	77.7	57.2	0.7
0.075	400	750	100	82.3	63.5	0.8
0.075	600	1110	10	87.5	53.0	1.2
0.075	600	1110	25	81.0	70.5	0.9
0.075	600	1110	100	87.2	50.6	1.2
0.075	700	1290	10	52.5 av.	40.8 av.	0.95 av.
0.075	700	1290	3*	40.0	24.3	1.14
0.075	700	1290	10†	49.1	18.7	2.1
0.075	800	1470	10†	36.1	17.3	12.4
0.10	As irradiated			77.4 av.	73.4 av.	0.55 av.
0.10	800	1470	10†	32.2	29.1	4.6

*Heated at 10°C/hr, held 3 hr, and furnace cooled (~150°C/hr).

†Heated and cooled from 600°C at 10°C/hr.

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Fig. 2— Properties of irradiated uranium after vacuum annealing.

Obviously a fuel element will be subjected to more rapid heating and cooling rates than those mentioned above; therefore it is probable that the thermal stresses developed at more rapid heating and cooling rates will lead to splitting or fracturing of uranium subjected to higher burn-ups. This was graphically borne out in previous gamma-phase anneals where the specimens were furnace cooled. These broke at low loads, and the fracture consisted in part of very large partially oxidized facets, indicating a prior break. This occurred more than once and is believed to be due to the existence of a network of microcracks generated during irradiation which propagate along certain crystallographic planes during the phase transformations. Definite strains due to the volume differential between the phases will result. Very slow cooling permits relaxation of stresses, whereas rapid cooling is believed to cause crack propagation. The re-formation of grains and the redistribution of fission products during high-temperature annealing apparently improve the macroductility but not the microductility. This is apparent on examination of the fractures, as will be shown in a later section.

2.9 Effect of Tensile Testing Temperature

A tensile test at best is only a fair criterion for the behavior of a metal in some fabricated shape. Such a test is even less applicable when the material is operating at some temperature

markedly different from room temperature. To minimize this effect, tests have been conducted at elevated temperatures. Results are given in Fig. 3.⁶ It is readily apparent that uranium is very weak above 600°C (1110°F), and little has been gained in recovery of ductility.

2.10 Significance of Tensile Data

An evaluation of the tensile data indicates that the fuel-element designer cannot depend on uranium to retain satisfactory properties before and during irradiation. There is a high probability that the uranium will break up at even moderate burn-ups, and therefore it is necessary to depend on the jacket or cladding to retain the material. Of course, it does not follow that the uranium behaves in such a brittle fashion when under the dynamic conditions of neutron bombardment and elevated temperatures. Only creep data or other dynamic tests conducted under reactor operation will tell this. Unfortunately very little such information is available.

3 PHYSICAL PROPERTIES

Information on such physical properties as thermal conductivity, electrical resistivity, density, and moduli are still quite limited. Typical results are reported in the following sections.

Fig. 3—Elevated-temperature properties of irradiated uranium.

3.1 Thermal Conductivity

Data on the postirradiation thermal conductivity of normal irradiated uranium are very limited. This property is an important one because decreases in thermal conductivity on irradiation might increase uranium core temperatures to an unsafe level.

One team of investigators reported that the thermal conductivity of uranium measured during irradiation was reduced 15 per cent at 1×10^{19} nvt, after which some recovery of conductivity occurred to an exposure of 1.4×10^{20} nvt.¹² Similar results based on postirradiation measurements were reported by Siegel and Billington.¹³

Subsequent investigations indicated that there was a decrease in thermal conductivity of about 15 per cent at 7.5×10^{19} nvt, after which no further decrease was observed out to an exposure of 1.7×10^{20} nvt.¹⁴

The limited data indicate a decrease in thermal conductivity of about 10 to 15 per cent. Since the predicted accuracy of the methods used to obtain these data is probably ± 20 per cent at best, the validity of the results in an absolute sense is dubious. Qualitatively, however, the results are quite valuable in that they indicate that there is no gross change in thermal conductivity of uranium after irradiation.

A uranium-1.6 wt. % zirconium alloy irradiated to 0.21 and 0.75 at. % burn-up was tested to determine irradiation-induced changes in thermal conductivity. A heat-wave technique was utilized. The value of an unirradiated specimen was 0.063 cal/sec/cm/ $^{\circ}$ C of 200 $^{\circ}$ C, whereas the values at 0.21 and 0.75 at. % burn-up were 0.058 and 0.057, respectively, representing reductions of 8 and 9.5 per cent in thermal conductivity.¹⁵ There were two possible sources of error: (1) the unirradiated specimen was not from the same heat as the irradiated, and (2) it was assumed that the density was unaffected by irradiation, which is undoubtedly not true. A decrease in density will result in a lower calculated thermal conductivity. Even so, this does not represent a large decrease in thermal conductivity.

3.2 Electrical Resistivity

Electrical resistivity measurements as such are valuable in interpreting the fundamental mechanism of radiation damage or in predicting thermal conductivities by applying the Wiedemann-Franz ratio rather than because of their intrinsic value in reactor applications. A few typical values are given below.

A 4 per cent increase in electrical resistivity at 20 $^{\circ}$ C (70 $^{\circ}$ F) was noted for a section cut from a beta heat-treated uranium fuel element after an exposure to ~ 0.01 at. % burn-up.¹⁶ The temperature coefficient of resistance was found to be slightly lower for the irradiated material.

Samples of uranium wire exposed in the CP-3 reactor for approximately 4.5×10^{17} nvt at 25 $^{\circ}$ C (77 $^{\circ}$ F) increased 1 per cent in electrical resistivity.¹⁷ This exposure resulted in the production of 4.2×10^{-4} at. % fission-product impurities. The only fabrication history known is that the sample was annealed at 400 $^{\circ}$ C (752 $^{\circ}$ F) for 1 hr prior to irradiation.

3.3 Density

Density determinations made at Argonne National Laboratory are given in Table 6.^{18,19} These are typical for uranium or its alloys irradiated at nominal temperatures when burn-ups are not excessively high. At higher irradiation temperatures the decrease in density is very marked, particularly in gamma irradiations even at burn-ups of less than 0.1 at. %. In the latter case with limited restraint, decreases in density exceeding 15 per cent have been observed.

3.4 Modulus of Elasticity

An apparent increase in modulus of elasticity has been observed after irradiating to 0.072 per cent burn-up at 150 $^{\circ}$ C (300 $^{\circ}$ F). The increase was 10 to 15 per cent based on tensile-test data.⁶

Table 6— DENSITY CHANGES IN IRRADIATED URANIUM

Total at. % burn-up	Irradiation temp.		Density decrease, %	Remarks
	°C	°F		
0.05	Unknown		0.4	300°C rolled
0.10	Unknown		0.9	300°C rolled
0.15	Unknown		1.5	300°C rolled
0.05	Unknown		0.2	Beta heat-treated
0.10	Unknown		0.4	
0.15	Unknown		0.7	
1.26	190	375	3.3	Unknown, believed alpha rolled
1.46	220	430	2.8	
1.63	240	465	2.7	
1.75	250	480	2.6	

4 MICROSTRUCTURAL EFFECTS

One of the most valuable tools for investigating irradiation damage in fissionable materials is metallography. These studies are essential in determining the fracture modes, grain-boundary states, and grain damage. A combination of optical and electron microscopy together with X-ray diffraction should yield many data necessary in preparing a realistic hypothesis of the radiation-damage mechanism.

4.1 Optical Microscopy

The macrostudy of uranium, excluding bulk geometry measurements, customarily requires etching to reveal the grain structure on the specimen surface. Considerable effort has been expended in an attempt to develop a satisfactory method for macroetching irradiated uranium. Cathodic vacuum etching is believed to be the most satisfactory because a surface cathodically vacuum etched after polishing suffices for both macroexamination and microexamination and does not deteriorate as rapidly as a chemically etched surface. The relation of cracks, voids, and grain disposition with respect to the bulk geometry can be studied by low-power examination, an example of which is given in Fig. 4. The two photographs illustrate the dependence of contrast among the various grains on the type of illumination used. Many grains appear to be as large as 1 mm in diameter, an erroneous value due to the lack of selectivity and resolution afforded by macrotechniques. The apparent grain macrostructure, however, frequently reveals zone and orientation effects not discernible by microexamination methods.

A direct comparison of the microstructure before and after irradiation, in which the same grains are examined, permits a better interpretation of the types and degrees of damage occurring in uranium. Bierlein^{8,20} has developed the techniques necessary for such studies, and he has successfully conducted preirradiation and postirradiation studies on the same uranium surfaces which were etched, replicated, irradiated in NaK-filled capsules to burn-ups of 0.03, 0.07, and 0.10 per cent, and then re-replicated. Typical results are shown in Fig. 5. Some broadening of twins is apparent, but no gross changes are observed by optical microscopy.

4.2 Electron Microscopy

The electron microscope has marked advantages in the examination of irradiation damage owing to the high magnifications possible and the unlimited depth of field. Studies of areas of the replicas of the same surface of uranium before and after irradiation have been made using the electron microscope. Definite evidence of grain-boundary segregation, protrusions on

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Fig. 4—Optical macrographs of uranium irradiated to 7×10^{19} nvt. Note the effect of illumination on the appearance of the macrostructure. (Magnification 2.5x.)

Fig. 5—Microstructure of uranium before and after irradiation (0.07 per cent burn-up). Cellulose acetate replicas. (Magnification 750 $\times$.)

twin boundaries, and microcracking has been found. Due to difficulties in locating the same field, a direct comparison of the same fields before irradiation has not been made. Such studies are still under way. Figure 6 is a collection of electron micrographs displaying these defects.

4.3 Microfractographs

A careful study of the fractures of irradiated metals will yield valuable information concerning the mode of failure, whether transgranular or intergranular, degree of ductility or brittleness, and extent of grain-boundary segregation in so far as it might influence fracture. Techniques developed by Bierlein⁸ permit remote replication of fractures. A particularly interesting study is shown in Fig. 7A, the microfractograph of the tensile fracture of uranium irradiated to 0.1 at. % burn-up, which was annealed by heating at 10°C/hr to 800°C (1470°F), holding 10 hr, and then cooling at the same rate. This specimen had a ductility of 4.6 per cent compared to as-irradiated values of 0.55 per cent. This is attributed to macroductility because an examination of the fracture definitely indicates the absence of microductility. Comparing Figs. 7A and 7B, the structure of unirradiated uranium fractured by impact on a notched bar at -192°C (-310°F) reveals a marked similarity. The "river" structure is typical of brittle metals. The surprising thing is the development of such a structure in a specimen loaded uniaxially at room temperature. Figure 7C is typical for a tensile specimen of unirradiated uranium fractured at room temperature, and Fig. 7D illustrates the ductile fracture occurring in the fracture of a V-notch Charpy specimen broken at room temperature.

The value of such studies of microstructure is readily apparent when one considers the possibility of visual observation of defects that have been hypothesized as causing failure. This is true in the case of the microcracks that were believed to exist since they could explain the loss in ductility of uranium on irradiation and the lack of recovery during annealing or elevated-temperature testing.

5 REACTIONS IN THE SOLID STATE

Certain reactions occurring in fuel elements can profoundly influence the methods of fabrication and cladding. For example, the rate of diffusion of fuel into the jacket or recrystallization of the core material may serve as limiting factors in the life of the element. When the fuel diffuses through the jacket and then reacts with the coolant, the element has exceeded its life expectancy. Of concern, therefore, is the effect of radiation when superposed on the usual diffusion and recrystallization variables of temperature and time.

5.1 Diffusion

There are very limited data available on the effect of irradiation on diffusion rates. Uranium-stainless steel has been investigated at fluxes of 4×10^{11} to 3×10^{12} nv and temperatures of 500 to 700°C (930 to 1290°F) over a period of 16 days.²¹ The lowest temperature at which diffusion was observed was 380°C (720°F) after 16 days. A definite difference was observed in activation energy, but the apparent effect of fluxes to 3×10^{12} nv was essentially nil on the diffusion of uranium and stainless steel.

A greater change has been observed in the case of U-Zr and U-Ti. Measurements in pin type, prebonded couples²²⁻²⁴ are included in Table 7.

Studies are under way at Hanford Atomic Products Operation to evaluate the effect of irradiation on the diffusion rates of U-Al, U-AlSi, and U-Zr couples. Irradiations have been completed, but no quantitative data are available.^{1,3}

One other type of diffusion is important. This is the diffusion of fission products, particularly the noble gases krypton and xenon, through the uranium. Postirradiation studies by Reynolds²⁶ on uranium wires indicate a steplike release of the gases. An initial period in which no gas is released is followed by a burst of gas. The amount of gas released is a function of temperature. There is some indication that a limited quantity of such gaseous fission products is released during irradiation. The diffusion coefficient for xenon in irradiated uranium is quoted as 1.5×10^{-13} cm²/sec at 600°C (1112°F) or about 100 times faster than nongaseous fission products.²⁷

Fig. 6—Electron micrographs of uranium irradiated to a burn-up of 0.03 per cent at a temperature of less than 300°C. Positive replicas. Upper left: segregation at a grain boundary (magnification 7000 $\times$). Upper right: doughnut-shaped protrusions along twin boundaries (magnification 5000 $\times$). Lower left: long narrow crack (magnification 8000 $\times$). Lower right: short discontinuous cracks that are deflected at the vertical grain boundary (magnification 8000 $\times$).

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Fig. 7—Microfractographs of uranium. A, uranium irradiated to 0.1 at. % burn-up; tensile fracture at room temperature (magnification 6000 $\times$). B, unirradiated uranium; impact fracture at -190°C (magnification 4500 $\times$). C, unirradiated uranium; tensile fracture at room temperature (magnification 3000 $\times$). D, unirradiated uranium; impact fracture at room temperature (magnification 4500 $\times$).

Table 7 — DIFFUSION IN U-Zr AND U-Ti COUPLES

Couple	Nominal temp.		Time in reactor	Burn-up, %	Penetration of the couple by the uranium, in.
	°C	°F			
U-Zr	415	780	96 days	2.5	0.002
U-Ti	415	780	96 days	2.5	0.003
U-Zr*	415	780	4 years		0.001

* Reference 25.

5.2 Recrystallization

No quantitative experiments are known in which the effect of irradiation on recrystallization rate has been studied. A change observed in uranium grain structure has been attributed to heating into the beta region;¹ however, such an effect is probably due to temperature resulting from the flux rather than the flux per se.

This extremely interesting and potentially rewarding field of research should be studied further since such changes can have a profound effect on the stability, corrosion resistance, and physical and mechanical properties of alloys and since these alloys are possible choices as fuel-element materials at elevated temperatures.

5.3 Deformation Mechanisms

Several studies have been made of the various deformation mechanisms in unirradiated uranium. Slip, twinning, and kink band formation are known to be the means of deformation, with the relative order of deformation by the various mechanisms and the slip or twin planes a function of the test temperature. Unfortunately, there is little or no information correlating the deformation mechanisms in irradiated uranium with those in unirradiated uranium. Since build-up of fission products results in an alloy differing markedly from the pure uranium, it is difficult to select an appropriate basis of comparison between the unirradiated and irradiated metal.

When considering macroscopic plasticity, an analysis of existent tensile data on irradiated uranium indicates that there is a gross decrease in such plastic flow. Whether this is due to a shift in tensile transition temperature, alloying due to fissioning, generation of microcracks, gross irradiation damage, or a combination of all these factors is unknown. It is probably safest to say the change is due to fission-product concentration.

There is no evidence of slip occurring in irradiated uranium. This lack of evidence is understandable since the slip must generally occur on polished surfaces to be identified metallographically. Polished and precharacterized specimens of uranium, which were inserted in Zircaloy-2 capsules containing NaK as a heat-transfer medium and then charged into the MTR, did not exhibit slip on reexamination.

Extensive twinning has been observed in uranium irradiated to 6.8×10^{19} nvt. This twinning was accompanied by slight grain growth.^{28,29} Metallographic examination generally discloses twinning accompanied by a microstructure which can best be described as smudged. It cannot be stated definitely that this twin results solely from irradiation. Annealing tends to define the microstructures somewhat. This is another field requiring extensive research. With sufficient information, an intelligent interpretation of the role of twinning in deformation during irradiation will be possible.

An interpretation of the modes of fracture of irradiated uranium will be an essential factor coupled with the information on the diffusion of fission products. An intergranular fracture coupled with evidence of intergranular diffusion would indicate quite conclusively the influence of fission products on the mode of fracture.

The best way to summarize the state of knowledge on deformation mechanisms in irradiated uranium is to say that there are essentially no quantitative data. A great deal of work must be done in this field.

6 STRUCTURAL PROPERTIES

Potentially, X-ray diffraction is an invaluable tool in recording and assisting in the interpretation of irradiation damage and recovery mechanisms in uranium. Owing to the radioactivity of the test specimens, there is a special problem in equipment design. A double-crystal X-ray spectrometer is required to separate beta and gamma emission from the specimen from the diffracted X-ray beam. Such a unit is plagued with problems in beam intensity and sensitivity, and therefore the instrument is not so precise as a standard X-ray diffraction unit.

With all the limitations of a double-crystal unit, it has still been possible to detect line broadening, line shift, and asymmetry in irradiated uranium compared to unirradiated uranium. The evidence of damage is available, but it is not possible to interpret the information quantitatively because of the lack of theoretical knowledge in the field of anisotropic materials.

Some evidence of recovery has been observed in uranium exposed to a limited number of spike cycles. Specimens examined after irradiation for 2 weeks in a poison-column facility were found to have a diffraction pattern characterized by asymmetry and slight line shift.³⁰ Subsequent examination after holding at room temperature gave the same diffraction pattern observed with unirradiated uranium. Current experiments to reproduce these results have not proved successful. Additional work must be done before it can be definitely concluded that lattice recovery occurs at or near room temperature in irradiated uranium.

A uranium single crystal irradiated to low total exposures (7.3×10^{19} nvt) and then subjected to X-ray diffraction revealed diffuse Laue spots corresponding to the (0 2 0) and (0 2 1) planes; there were also a few high index planes present on the Laue photogram. Such results indicate substantial fragmentation; there was little or no rotation of the lattice typical in a growth deformation.³¹

Studies of uranium foils irradiated to 1.9×10^{17} nvt at 175°C (345°F) indicated that line broadening occurred, which could be ascribed to microstresses; annealing at 250 and 500°C (480 and 930°F) was insufficient to cause recovery, but after 16 hr at 600°C (1110°F) the observed diffraction line shape was essentially the same as that in the unirradiated state.³²

7 IRRADIATION-DAMAGE HYPOTHESES

The most significant effects of integrated neutron flux on natural uranium are the pronounced loss in ductility, the disintegration of the metal at nominal burn-ups, the increases in volume, and the growth of preferred oriented specimens. The latter two items will be dealt with in Sec. 9.

The changes in tensile properties are much too great to be attributed to vacancy-interstitial or thermal spike effects. The decrease in room-temperature ductility from about 20 to less than 0.5 per cent after irradiation and the limited effects of 400 and 700°C (750 and 1290°F) anneals indicate that either a critical dispersion of fission products⁶ or extensive internal cracking⁸ or both are responsible for the loss in properties.

It is quite probable that the noble gases xenon and krypton have a pronounced effect on the mechanical properties, and they are believed to be primarily responsible for the disintegration of alpha uranium after relatively short burn-ups. Varley³³ and Seitz³⁴ believe that these gases may result in cracking or fracture of the uranium by a build-up either interstitially³³ or at voids or cracks.³⁴ Unalloyed enriched uranium disintegrates after relatively low burn-ups and resembles coke, suggesting that the formation and expansion of gas bubbles may play a part in the disintegration.

A suggested mechanism for minimizing irradiation damage due to gaseous fission products has been advanced.³⁵ The introduction of a second phase as small discrete particles should result in the diffusion of the gases to these sites and their being anchored as monatomic or multiatomic layers. Limited work with uranium two-phase alloys does indicate that the alloys can be exposed to longer burn-ups before disintegrating.

8 FISSION-PRODUCT EFFECTS

Aside from the obvious changes in physical and mechanical properties attributable to fission-product build-up, there are also problems of reactor contamination due to the diffusion and release of the more mobile atoms such as the noble gases krypton and xenon. Relatively low concentrations of such gases pose a definite radioactive contamination problem if they escape into the pile coolant. Generally, the release of such products indicates a fuel-element failure, but it is conceivable that diffusion rates will be sufficiently high in power reactors to result in a continuous release of gases into the coolant.

The fission event can be summarized as the capture of fast or slow neutrons by the uranium, followed by a splitting of the nucleus into two new nuclei. The percentage distribution of the elements formed by such fissioning is a function of several factors.

The fission event is accompanied by the release of approximately 200 Mev of energy, most of which is retained by the two fission products. These ionized particles smash through the uranium lattice, dislodging uranium atoms, generating vacancies and interstitials, probably causing localized melting of the lattice due to the energy release, and finally lodging as foreign atoms in the lattice. Obviously, changes of this magnitude cannot be duplicated in alloys of comparable composition compounded by melting and casting or powder-metallurgy techniques.

The damage caused by fissioning and the fission products may be annealed to some extent, but elevated temperatures cause other effects. At sufficiently high temperatures, the gaseous fission products, krypton and xenon, diffuse and agglomerate causing macrovoid generation, gross decreases in uranium density, and, possibly, pronounced swelling. Porosity has been observed in a cored rod of uranium. An aluminum-clad uranium rod containing a $\frac{3}{8}$ -in. hole and insulated at the uranium-aluminum interface with an anodized layer to increase the uranium temperature during irradiation was exposed at the MTR. No dimensional changes were observed in the case of the canned rod after irradiation, but on examination of the sectioned rod it was found that the hole had disappeared owing to flow of uranium and that a gross change in density had occurred.³⁶ It is quite possible that this phenomenon was caused by movement of vacancies and interstitials and the agglomeration of the diffusion gaseous fission atoms, resulting in extensive internal porosity. This is in agreement with a hypothesis which predicts that irradiated uranium will suffer a large increase in volume due to internal gas pressure if the creep of the metal is sufficient to avoid fracture. Based on this hypothesis, a solid massive fuel element of uranium is not believed practicable at high temperatures owing to formation of gas bubbles in the matrix.

Postirradiation tests on the diffusion of krypton and xenon in uranium indicate that thermal cycling or holding at elevated temperatures causes pronounced swelling accompanied by escape of the gas from the uranium rods.³⁷

9 DIMENSIONAL INSTABILITY

Unalloyed uranium is used extensively as a reactor fuel. Unfortunately, uranium is anisotropic and exhibits pronounced dimensional instability when preferentially oriented. Fuel-element stability is one of the most important factors in a heterogeneous reactor since dimensional changes may result in restriction or plugging of the annulus, causing overheating and failure of the element, or the changes in dimension may rupture the jacket, resulting in contamination of the coolant at least.

The phenomenon of dimensional instability of uranium has been studied by the Americans, British, and Russians. Substantial agreement exists as to some factors favoring growth, whereas there is some disagreement in other facets of the problem. Some factors on which there is substantial agreement are:

1. A [010] direction orientation results in maximum growth.
2. A [100] direction orientation results in maximum shrinkage.
3. A [001] direction orientation results in little or no change in dimension.
4. Duplex orientations may promote or prevent growth or shrinkage, depending on type and degree of orientation.

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5. Single crystals deform under irradiation but not under thermal cycling.
6. A random orientation is stable when irradiated or thermally cycled.
7. High- (400°C) or low- (-100°C) temperature operation during irradiation minimizes dimensional instability.
8. There appears to be no limit on the degree of dimensional change under irradiation.
9. Growth appears to be a direct function of integrated flux.

Some factors on which there is inadequate information or lack of agreement are:

1. Increased metal purity may increase the rate of irradiation growth.
2. Growth rate appears greatest for oriented polycrystalline uranium and decreases as metal approaches or becomes a single crystal (definite disagreement on this).
3. Dimensional instability produced by irradiation and thermal cycling is qualitatively similar (definite disagreement).

9.1 Thermal Cycling and Irradiation-induced Growth

Based on present data, there appears to be no correlation between dimensional instability produced by thermal cycling and that occurring when irradiated. No growth occurs in single crystals when thermally cycled, whereas they grow under irradiation.³⁸

Growth is dependent upon the texture, but there is no correlation of growth as a function of texture when the growth occurs by irradiation and by thermal cycling. A comparison of growth rates in uranium having different textures is given in Table 8.³⁹

There is still disagreement on the effect of grain size on growth. The only valid application of thermal cycling as an explanation of growth under irradiation appears to be that such a phenomenon might supplement growth due to a grain-boundary effect. This has been advanced to explain the different rates of growth under irradiation.³⁸ An oriented polycrystal grew more than a single pseudocrystal, which grew more than a true single crystal, in the ratio 6:3:2. British⁴⁰ results contradict these data; single crystals and polycrystalline material similarly oriented were reported to grow at the same rate. Differences in metal purity may account for some of these discrepancies.

A comparison of growth due to thermal cycling and irradiation as a function of orientation is given in Table 9.³⁸

Figure 8 illustrates the degree of growth of uranium as a function of orientation.³⁰ In this instance polycrystalline material was oriented by controlling the rolling temperature. Orientations were determined by comparison with a randomly oriented specimen.

9.2 Alloying Effects on Dimensional Stability

A study has been made of the effect of limited additions of chromium to uranium on the dimensional stability during irradiation.⁴¹ Results are reported in Table 10. Examination of the data reveals no beneficial or deleterious effect due to the chromium additions.

9.3 Mechanisms of Growth

Excellent surveys of the early growth mechanisms proposed to explain dimensional instability have been made.^{39,42} These sources are suggested as references.

Table 8—GROWTH RATES OF URANIUM
HAVING DIFFERENT TEXTURES

Texture	Predominant component	Approximate elongation, (%)	
		In 0.01% burn-up	In 100 thermal cycles
(100) + (110)	(100)	-0.8	+1.49
(010) + (110)	(010)	+1.0	+4.9
(110) + (010)	(110)	±0.0	+3.3
(010) + (110)	(010)	+0.9	+4.4

Table 9 — GROWTH OF URANIUM BY THERMAL CYCLING AND IRRADIATION

Texture and orientation data	Thermal cycling data*		Irradiation data			Comments
	No. of cycles	$G^{\dagger} \times 10^{-6}$	Reactor	$nvt \times 10^{-19}$	Elongation	
Textured Polycrystalline Wire						
(0 1 0) fiber texture predominant	174	442	Hanford	11.8	59.8 [‡]	Restrained in containers because of excessive growth
	174	442	Hanford	21.4	103.5 [‡]	
	174	442	MTR	21.6 [§]	56.9 [‡]	
	174	442	MTR	21.6 [§]	54.4 [‡]	
	174	442	MTR	39.3 [§]	110.1 [‡]	Held in additional mild steel split tube during irradiation
	174	442	MTR	39.3 [§]	139.0 [‡]	
	174	442	MTR	39.3 [§]	142.3 [‡]	
β -treated Polycrystalline Wire						
Nearly random	1091	45	Hanford	11.8	2.6	
	1091	45	Hanford	21.4	2.4	
	1091	45	MTR	21.6 [§]	4.2	
	1091	45	MTR	39.3 [§]	4.9	
Transformation Single Crystal						
(0 0 1) pole within 10° of wire axis	362	0	Hanford	11.8	1.1	Cross section became elliptical; major axis roughly 15% longer than original diameter
Unknown	769	0	Hanford	21.4	104.7 [‡]	Sample flattened in cross section
(0 1 0) pole within 10° of wire axis	1075	0	MTR	21.6 [§]	30.0	Became elliptical in cross section
			MTR	39.3 [§]	59.8 [‡]	Became elliptical in cross section
Recrystallization Single Crystal						
(0 1 0) pole within 15° of wire axis	?	0 [¶]	MTR	21.6 [§]	19.4	Became elliptical in cross section; minor axis near 1 0 0, direction of shortening; major axis near 0 0 1, little or no change

* Thermal cycling range: 100 to 500°C.

[†] $G = 1/N \ln L/L_0$, where N is the number of cycles, L is the instantaneous length, and L_0 is the original length.[‡] Approximate minimum values, specimens twisted.[§] Values may be too high by a factor of 2.[¶] Argonne reports no change for their true single crystals after thermal cycling.

Any mechanism proposed must explain the effects of the following factors: (1) growth in polycrystalline and single-crystal uranium, (2) integrated flux, (3) metal purity, (4) the pronounced influence of specimen temperature during irradiation, and (5) the preferred orientation.

The three mechanisms best explaining the observed effects are the diffusion mechanism originally proposed by Siegel⁴³ and later revised,⁴⁴ the modified twinning mechanism,⁴⁴ and the dislocation climb mechanism proposed by Cottrell.⁴⁵

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The twinning mechanism is as follows: Surrounding every thermally spiked volume is a region of uniform compressive stress which causes local plastic yielding by twinning preferentially in the $[010]$ direction. This $[010]$ extension stresses the surrounding matrix, which is relieved by equal amounts of slip of the $\{110\}$ planes in the appropriate $\langle 1\bar{1}0 \rangle$ directions to cause extension in the $[010]$ direction. Tension in the $[010]$ direction does not produce a resolved shear stress on the (010) plane, and therefore slip does not occur on this plane. Macrodeformation is by $\{110\} \langle 1\bar{1}0 \rangle$ shears, which agrees with experimental results of extension in the $[010]$ direction, contraction in the $[100]$ direction, and no change in the $[001]$ direction. Some reversal should occur on cooling, but it is not completely reversible. The size of the fission spike appears to be too small and its duration too short for a twinning mechanism to operate; the available data do not validate or invalidate this mechanism. However, preirradiation and postirradiation metallographic studies reveal no increase in twins within the same grains.

Fig. 8—Effects of preferred orientation on the dimensional stability of uranium during irradiation. Exposure, 10^{20} to 3×10^{20} nvt; temperature, 100 to 150°C.

The diffusion mechanism of growth appears to explain most phenomena. The simplest way of obtaining the observed change in shape is by rearrangement of atoms in the (001) planes, which are composed of close-packed rows parallel to the $[100]$ direction. Assuming that the effect of irradiation is to knock atoms out of the close-packed rows, the lattice can be maintained in the correct alpha structure (1) by forming extra interstitial close-packed pairs of (100) rows, giving an extension of the crystal in the $[010]$ direction, and (2) by the vacant sites in the original close-packed (100) rows diffusing along the (100) rows to the grain boundary, giving a contraction of the grain in the $[100]$ direction.

If the vacancies diffuse to dislocation lines of the $(010)[100]$ slip system, thus removing the (100) planes, while the interstitials form extra planes between the (010) corrugated planes, this combination of changes produces a change of shape in agreement with that observed under irradiation. Both diffusion mechanisms giving the observed mode of growth are similar to the Wigner growth of graphite on irradiation in that the favored interstitial sites are assumed to be between the slip planes.

The correct variation of growth rate with the temperature can also be obtained from a diffusion mechanism. This mechanism is most efficient when the lowest proportion of vacancies and interstitials recombines and they are mutually annihilated. The growth rate is therefore highest when the vacancy concentration under irradiation is lowest. The rapid decrease of

Table 10—SIGNIFICANT IRRADIATION DATA ON URANIUM-CHROMIUM ALLOYS

Cr, at. %	Exposure, nvt $\times 10^{-19}$	Approx. burn-up, %	Av. change in length, %	Av. change in diameter, %	Remarks
0.0	7.7	0.032	+3.4	-1.8	Surface smooth; warped in longitudinal plane bisecting contact points in inserts
0.0	7.7	0.032	3.1	-1.3	Surface smooth; warped
0.0*	7.9	0.032	+0.3	+0.2	Surface bumpy; no warping
0.15	7.9	0.032	10.8	-4.3	Surface smooth; warped
0.15	7.9	0.032	2.2	-1.7	Surface smooth; warped
0.23	7.9	0.032	2.2	-0.86	Surface smooth; warped in longitudinal plane bisecting contact points in inserts
0.23	7.9	0.032	13.9	-6.1	Surface smooth; badly warped
0.58	7.9	0.032	15.9	-4.7	Longitudinal ridges and valleys full length of specimen; badly warped
0.62	7.9	0.032	16.8	-6.9	Surface smooth; badly warped
0.85	7.9	0.032	16.4	-5.8	Surface striated; badly warped
0.83	7.7	0.031	3.2	-0.65	Surface smooth; warped in plane bisecting contact points in in- serts
0.90	7.7	0.031	2.0	-0.43	Surface smooth; warped

*Inadvertently beta heat-treated during dilatometry.

growth rate with temperature from 400 to 500°C (750 to 930°F) may therefore be due to the rapid increase in the equilibrium concentration of thermal vacancies over this temperature range, so that interstitials are absorbed by vacant sites before they can form "extra planes" which are large enough to be stable. Annealing occurs in uranium at 500°C (930°F), and it is therefore reasonable to suppose that the supply of very mobile vacancies is large enough to prevent the build-up of extra interstitial planes under irradiation at this temperature. On the other hand, the increase in growth rate below 200°C (390°F) is due to an increase in concentration of vacancies with increase in temperature being caused by an increase in the mobility of the vacancies so that they do not fall to the equilibrium concentration that would be present in the absence of irradiation. Moreover, at low temperatures, vacancies due to their low mobility would contribute less to the growth process. Since below 200°C (390°F) vacancies arise from the fission process, then an increase in flux will increase the vacancy concentration and so decrease the efficiency of the growth process; whereas above 200°C (390°F) the vacancies arise from the thermal vibrations and are at the equilibrium concentration. Therefore a change in flux does not in this range change the growth for a given burn-up. The mechanism has one major weakness in that it assumes a knowledge on the part of the atoms of what they should do.

Cottrell⁴⁵ proposes an alternate growth mechanism based on dislocation climb. A thermal spike should cross at least one dislocation line based on a normal dislocation population. The mechanism is one in which atoms are deposited on one dislocation while being removed from another. Since very few dislocations have slip vectors along the *c* axis, the lack of growth in

this direction can be accounted for. Lack of growth above 450°C (840°F) is attributed to rapid relaxation before the uranium grows. This mechanism will not explain the lack of growth at very low temperatures.

10 INFLUENCE OF CHANGES IN PROPERTIES ON FUEL-ELEMENT DESIGN

Certain qualitative conclusions may be drawn from the preceding physical metallurgical data dealing with irradiated uranium. These are of concern to the fuel-element designer who is considering natural uranium or uranium containing nominal alloy additions as a potential fuel material. There is a very high probability that the uranium will be notch brittle. This is borne out by tensile data and an analysis of the microfractographs. Internal or external cracks existing prior to or developed during irradiation can lead to fuel-element failure by splitting. Such effects should be most pronounced during reactor shutdown or start-up due to thermal stress developed by a high rate of temperature change coupled with the severe thermal gradient in the uranium. It is also quite probable that variations in reactor specific power resulting in a thermal cycling of the uranium will adversely influence fuel-element life. This can be predicted on the basis of postirradiation annealing results at other than very slow rates of heating or cooling. The effect is particularly noticeable in cycling through the beta-gamma transition.

An obvious requirement in a fuel element is dimensional stability. A beta heat-treatment will produce stability provided that it is sufficiently carefully controlled. Inadequate control that fails to remove the preferred orientation will yield specimens which grow and warp.

The geometry of the fuel element is also an important consideration. We do not know enough about the effect of irradiation on thermal conductivity, which must be known for optimizing fuel-element design. Obviously, any geometry which results in large changes in surface-to-core temperature or which develops severe internal stresses may fail owing to the notch brittleness of the uranium.

Another problem facing the designer is the desirability of a bond vs. no bond between fuel and cladding. On the basis of the limited diffusion data available, no definite conclusions can be drawn regarding the effect of irradiation on diffusion rate; however, one thing is apparent: the ductility of the diffusion zone is not enhanced by irradiation. Therefore there is a definite possibility that the bond will fracture during irradiation. Another factor militating against a bond is the probability that the jacket on a bonded element will almost certainly split, no matter how ductile the jacket material is, if the uranium splits. This is obvious when one considers the infinitesimal gauge length of a bonded jacket where even a small split in the fuel results in a several hundred per cent elongation of the jacket. Under these circumstances it is probable that even a strong jacket will split when bonded although it may not do so when unbonded.

A few of the consequences of the changes in properties occurring in uranium because of irradiation have been outlined together with the information available on such changes. It is felt that the relative paucity of such data limits the fuel-element designer and offers a challenge to the investigators engaged in determining the effects of irradiation on fissionable materials.

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Effects of Irradiation on Bulk Uranium Dioxide

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ABSTRACT

The irradiation experiments required to validate the use of bulk UO_2 as fuel in the Pressurized Water Reactor (PWR) are described. The performance of fuel elements consisting of bulk UO_2 fuel pellets encased in Zircaloy-2 tubing has been measured at burn-up levels up to about 25,000 Mwd/ton, both with non-defective fuel elements and with those containing deliberately introduced defects. These defects permitted access of steam to the interior of the fuel elements. Finally, the behavior of assemblies of such elements in rigidly connected structures has been tested.

The volatile noncondensable fission-product gases xenon and krypton have been found to migrate in UO_2 by a diffusional mechanism. Their release to an external surface is sensitive to diffusion path and interconnected porosity and hence to fuel material density. No appreciable structure changes, as revealed by X-ray diffraction, have been detected in uranium oxides of the fluorite structure at low burn-up levels; the diffraction peaks of higher uranium oxides of orthorhombic structure were almost completely obliterated after the same low burn-up. Likewise, no evidence has been noted of appreciable changes in density, metallographic structure, resistance to thermal fracture, or thermal conductivity in UO_2 at the highest burn-ups investigated.

Thermal performance characteristics of Zircaloy-2-clad UO_2 fuel elements were found, on the basis of observation of temperature-induced structural changes, to be sensitive to initial assembly clearance between oxide and cladding and to the nature of the gas atmosphere within the tubing, whether helium or steam. The thermal performance could not be correlated with measured thermal properties of the oxide. Such fuel elements were found to be highly resistant to damage by power cycling or by "waterlogging", when fabricated of high-density oxide. Suitably fabricated UO_2 pellets of high density were found to be highly resistant against erosion or release of solid oxide particles to the coolant. Fission products released through defects in the cladding to a high-temperature water system were best correlated by use of an "escape coefficient" defined as the fractional amount of each nuclide present within the fuel escaping per unit time. Most of those isotopes which do escape from a defective rod through a recoil or diffusional mechanism are those which do not lead to excessive system contamination, whereas the escape coefficients of nuclides which adsorb strongly to container walls, and hence lead to high system contamination, are very low.

Assemblies of fuel elements tested under conditions of marked asymmetry of neutron flux and hence of fuel-element temperature, and also under conditions simulating extreme fuel failures, revealed no tendency to warpage of structures or progression of failure to fuel elements adjacent to those which were defective initially.

1 INTRODUCTION

When, in mid-1954, the decision was made to explore the applicability of UO_2 as the blanket fuel material for the Shippingport plant reactor (PWR), little or no published information was extant on the performance and usefulness of bulk UO_2 as a fuel material, particularly at the

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high power densities, high burn-ups, and high uranium loadings required in a power reactor. It was known that UO_2 could be fabricated into useful shapes by various ceramic techniques; this topic is discussed in another paper at this conference.¹ The status of this development in mid-1955 was reviewed at the Geneva Conference by Johnson and Curtis.² Likewise, primarily as a result of irradiation information accumulated on dispersions of UO_2 in nonfissionable metal matrices as discussed in still another paper,³ it was inferred that UO_2 would exhibit desirable operational characteristics. The results of out-of-pile experiments that were considered necessary to validate the use of UO_2 in bulk form as a fuel material in the PWR are discussed by Belle and Lustman.⁴ The irradiation information accumulated in the course of testing bulk UO_2 fuel elements for the PWR application will be reviewed in this paper.

The utilization of bulk UO_2 as the fuel material in a pressurized water system posed a number of questions concerning limitations on fuel-element performance which had to be answered by in-pile experiments. Since many of these questions were specific to the particular fuel-element geometry and environment chosen, relatively few in-pile tests were performed to determine irradiation characteristics of UO_2 itself as distinguished from its performance in a fuel element. Much of the information given here on the performance of UO_2 was derived from measurements made during the course of fuel-element tests. The types of problems that were visualized as possible important limitations to the utilization of UO_2 are illustrated by the following:

1. Thermal capabilities of a specific fuel-element geometry.
2. Heat-transfer bond between ceramic and clad.
3. Likelihood of "progressive failure" (progressive failure is defined as the failure of adjacent elements resulting from the in-pile failure of a fuel element).
4. Release of fission gases from the fuel.
5. Contamination of the loop system resulting from release of fission products through cladding defects.
6. Ability to continue operation with fuel-element cladding defects.
7. Density or volume changes upon irradiation, leading to excessive cladding strain at prolonged fuel burn-ups.
8. Failure of sound fuel elements by "ratcheting" (ratcheting is defined as a conceivable mode of failure resulting from fracture of the ceramic fuel, redistribution upon power cycling, and consequent application of excessive strain to the cladding by virtue of differential temperatures and thermal expansivities between fuel and cladding).
9. Extensive failure of fuel elements containing small cladding defects by waterlogging (waterlogging is defined as extensive failure of defective fuel elements caused by entry of water at high pressure in crevices and cracks in fuel and annular openings between fuel and cladding during reactor shutdown and development of excessive pressures within cladding due to flashing of water to steam during subsequent reactor start-ups if the steam cannot escape from the fuel element either because of the restricted size of the defect or because of its blocking).
10. Effect of fabrication or geometrical variations on fuel-element performance.
11. Behavior of fuel-element assemblies, particularly under conditions such that unequal heat generation is developed between adjacent elements in rigidly connected structures.
12. Unforeseen deleterious effects arising from long-continued irradiation exposure.

To answer these questions for PWR Core 1, a total of about 360 fuel-element samples have been, or are in the process of being, irradiated and examined at the Bettis Plant. The results for samples thus irradiated and the conditions of assembly and test are listed in Sec. 3.

That information which was derived from these and other experiments pertaining to the behavior of UO_2 under irradiation is discussed in Sec. 4. In Sec. 5 the considerations affecting the performance of bulk UO_2 sheathed in metal tubes and exposed in high-temperature water environments are discussed, and in Sec. 6 the performance of assemblies of such fuel elements is described.

It is concluded from these experiments that the validity of application of bulk UO_2 sheathed in metal tubes as a fuel material in high-temperature pressurized water reactors has been

established, at least to the relatively moderate burn-ups anticipated in the Core 1 PWR (10,000 to 15,000 Mwd/ton), and that the performance capabilities of such fuel elements appear capable of extrapolation to even more extreme conditions.

2 FABRICATION OF SPECIMENS

As discussed previously, most of the oxide specimens irradiated were fabricated in the form of right cylinders by cold pressing and hydrogen sintering Mallinckrodt Chemical Works (MCW) oxide and then inserting the resulting pellets in Zircaloy-2 tubing with welded end caps. The nominal pellet and tubing dimensions used in most of the irradiation exposures are shown in Fig. 1. In general, the fabrication process developed by Glatter and coworkers⁵ for the manufacture of the PWR Core 1 fuel was followed, often to the extent of using production equipment for sample preparation. In certain cases deviations from production practices were required; thus those fuel pellets which were exposed at low neutron fluxes, and therefore required enrichment, were prepared from enriched uranyl nitrate solution in the laboratory. However, the subsequent pyrolysis and reduction to UO_2 simulated as closely as was feasible in the laboratory the reduction methods employed by Mallinckrodt⁶ so as to minimize the necessity for extrapolating results from one method of preparation to another. In certain cases pellets of proper enrichment were made by mixing 93 per cent enriched UO_2 with natural UO_2 ; for the sintering times and temperatures used, diffusion data of Auskern and Belle⁴ indicated that a uniform concentration of U^{235} would be obtained in the resultant pellet. Particular pains were taken to size the test pellets by grinding and the tubing by selection so as to obtain controlled axial and diametral clearances between fuel and cladding.

Certain tests, described in Sec. 3, were performed utilizing UO_2 fabricated by extrusion and by slip casting; the fabrication processes used in these techniques were developed and described by Glatter.⁷ An addition of 0.2 wt. % titanium dioxide was made to these samples to aid in their sintering. In all other cases the purity of the oxide met the specifications required for PWR manufacture:

Specification		Typical analysis of laboratory powders
Total uranium, 87.9 wt. % min.		88.1 wt. %
Hexavalent uranium, 1.9 wt. % max.		1.14 wt. %
Impurities	Ppm (max.)	Ppm
C	115	
F	30	
Cr	10	8
Cu	4	48
Fe	30	22
Mo	1	
Ni	15	28
Pb	1	2
Sn	4	11
B	0.15	
Cd	0.5	
Si	0.45	<10

Such compacts, when sintered, show no metallographic trace of impurities or second phases and, aside from void structure, are truly single-phase structures of high purity. A typical preirradiation microstructure of pellets fabricated by the reference techniques is shown in Fig. 2.

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Fig. 1—PWR Core 1 blanket fuel rod.

Initially in the evaluation program, samples were prepared by hot pressing at 1400 to 1500°C in graphite dies. This procedure was soon abandoned as a fabrication technique because of nonuniformity of density distribution through the compacts with the technique employed; thus a few of the early results were obtained with material of questionable purity and characteristics. Also, certain of the early cold-pressed and sintered samples were sintered in a vacuum graphite resistor furnace; in these cases sufficient carbon contamination was included in the compacts to result in their "desintering" upon hot-water corrosion testing. A few samples are being irradiated with high oxygen-to-uranium ratios obtained by sintering in steam at 1400°C. In those cases where it was desired to study the effect of density variation, particularly at high densities, use was made of ball-milled powder to promote densification. Where deviation was made from the reference specimen shape or fabrication procedure, particular note of such deviation is made in Sec. 3.

3 EXPERIMENTAL TECHNIQUES AND RESULTS

3.1 Description of Samples

The PWR Core 1 blanket fuel rod consists of 0.357-in.-diameter cold-pressed and sintered 93 to 95 per cent of theoretical density natural UO_2 pellets encased in 0.359-in.-I.D. by 0.411-in.-O.D. Zircaloy-2 tubing as shown in Fig. 1. A heat-transfer bond between the pellets and the clad is provided by helium gas at a pressure of 1 atm. This atmosphere is provided by welding the end caps to the tubes in welding boxes containing purified helium. Most of the specimens used in testing this configuration were either 5- or 10 $\frac{1}{4}$ -in.-long rods ranging in diameter from 0.300 to 0.500 in., with the majority of the samples consisting of the 0.411-in. reference diameter rods. The first irradiation test performed at Bettis on bulk UO_2 specimens consisted of 0.300-in.-diameter UO_2 spheres clad in Zircaloy-2. Many different types of UO_2 were investigated, as can be noted in Tables 1 to 4. A description of the various methods utilized for irradiating the samples follows.

One type of test was intended to reveal gross effects of burn-up and specimen-fabrication variables on various samples. The rods were sealed in Zircaloy-2 capsules containing an alloy of sodium and potassium (NaK), liquid at room temperature, as a heat-transfer agent. A cross section of a typical capsule is shown in Fig. 3. Most of such irradiations were performed

Fig. 2—Microstructure of 94 per cent dense cold-pressed and sintered natural UO_2 . (Magnification 250 $\times$.)

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Fig. 3—Typical NaK-filled Zircaloy-2 irradiation capsule.

in the Materials Testing Reactor (MTR). Most of the experiments involving Zircaloy-2-clad rods exposed in NaK capsules are listed in Table 1. The irradiation conditions in capsule tests are quite different from those existing in the PWR, particularly, of course, with respect to environmental conditions. By judicious selection of the NaK annulus at various nominal heat fluxes, it is possible to approximate reference cladding temperatures.

One of the concerns with the PWR blanket fuel element was the possibility of growth occurring by a thermal ratcheting mechanism. (This is discussed in some detail in Sec. 5.4.) Therefore a series of encapsulated rods was attached to a mechanism for moving the rods in and out of the high-flux zone in the MTR, and the samples were cycled during the irradiation. The results of the cycling tests in capsules are shown in Table 2. Of course, it should be noted that all tests performed in testing reactors are cycled to a certain extent as a result of normal reactor operation.

The third type of test involved the irradiation of both nondefective rods and rods with a 0.005-in.-diameter defect in high-pressure, high-temperature loops. This particular defect was chosen as representative of those considered most likely to escape detection during the various inspection steps. Information on the rate of fission-product release from the defective rods is obtained during loop operation, as well as information from the postirradiation examination of the rods. Irradiation conditions in these tests closely approach the operating conditions in the PWR, and many of the quantitative data described later have been gained from such tests. A considerable portion of the loop testing of individual rods was done in the X-1 loop in the NRX reactor at Chalk River, Ontario, Canada, as part of a joint Atomic Energy of Canada, Ltd. (AECL)-USAEC cooperative program. Another loop utilized for testing individual rods was the WAPD 29 loop in the MTR. In addition, to test the aforementioned thermal ratcheting behavior of rods irradiated in high-temperature, high-pressure water loops, the L-42 loop at the MTR was built to permit such rods to be cycled during the irradiation, and two PWR rods were tested in this facility. The results of these series of tests are shown in Table 3.

In addition to establishing the performance of individual rods, it became necessary to test prototype subassemblies in high-pressure, high-temperature water loops. Two such tests were run in the HT-1 loop at the MTR, two tests were run in the Central Thimble loop in the NRX reactor, and a test is currently in progress in the WAPD 30 loop at the MTR. The results of these series of tests are shown in Table 4.

3.2 Loop Test Facilities

Experimental loop facilities are similar to the conventional high-temperature, high-pressure loops used for materials corrosion testing, with necessary modifications for in-reactor operation. Typically, they consist of a closed circuit containing in-pile and out-of-pile test sections, heater, cooler, and canned rotor pumps. Pressure is controlled by an electrically heated pressurizer, which acts also as a surge tank. A bypass purification system contains coolers, filters, ion exchangers, conductivity cells, and sample connections. Delayed-neutron and gamma activity monitors indicate and record activity levels. Instrumentation is provided to control and record temperature, pressure, flow, and pressure drop. Interlocks to the reactor control circuits provide alarms or automatic scrams in the event of operating difficulties such as excessive radiation level or loss of flow.

A schematic diagram of the X-1 loop in the NRX reactor (AECL, Chalk River, Ontario), which was built and operated as part of a cooperative USAEC-AECL program, is shown in Fig. 4. Other loops are similar, differing in details dependent upon the nature of the test and physical configuration of the reactor. Loop volumes vary between 13 and 100 gal.

Operating conditions are adjusted to the requirements of the test and normally fall in the ranges of 500 to 600°F for water temperature, 1800 to 2000 psi for pressure, and 8 to 10 ft/sec for linear velocity past the specimen. The purification system rate constant is normally about 10^{-4} system volumes per second.

(Text continues on page 631.)

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Table 1—DESCRIPTION AND SUMMARY OF AVAILABLE DATA ON UNCYCLED ZIRCALOY-2-CLAD UO_2 FUEL ELEMENTS

Spec. No.	Heat flux,* Btu/hr/sq ft × 10 ⁻³	Burn-up,* Mwd/ton	Calc. central temp., °C	UO ₂ diam.	Specimen dimensions, in.			Dimensional changes		Molten zone diam.	Fission- gas release, % Kr ⁸⁵
					Clearance Diam.	Clearance Axial	Tubing O.D.	Over-all length	Diam.		
Experiment WAPD 14-1											
1	390 (e)	2,200	900	0.300	0.001	0	0.343	2.505	0	0	Not melted
2	590 (e)	3,300	1,830	0.300	0.001	0	0.342	2.505	0	0	Not melted
3	640 (e)	350	2,030	0.300	0.001	0	0.341	2.505	0	0	Not melted
4	570 (e)	3,100	1,420	0.300	0.001	0	0.343	2.510	0	0	Not melted
5	320 (e)	1,800	700	0.300	0.001	0	0.342	2.506	0	0	Not melted
6	50 (e)	300	100	0.300	0.001	0	0.342	2.497	0	0	Not melted
Remarks: This was the first experiment on this type of element. The rods contained hydrostatically pressed and sintered 95% dense natural UO ₂ . There was no external change in the rods.											
Experiment WAPD 14-2											
A-6 spheres		2,100							0		
B-6 spheres		2,100							0		
C-4 spheres		2,100							0		
D-6 spheres		2,100							0		
Remarks: 0.300-in.-diameter UO ₂ spheres clad in 0.075-in. Zircaloy-2 were included in this experiment. Natural UO ₂ was utilized for all the samples. Type A samples were 70% cold pressed, type B samples were 80% cold pressed, type C samples were 90% cold pressed, and type D samples were 95% dense hydrostatically pressed and sintered. The UO ₂ in the 70% dense samples apparently sintered during the irradiation, whereas the only changes noted in the other spheres were thermal cracks.											
Experiment WAPD 14-3											
1	220 (e)	870		0.383	0.001	0	0.460	3.893	0	+0.005	Not melted
2	230 (e)	1,300		0.383	0.001	0	0.460	3.863	0	+0.003	Not melted
5	240 (e)	950		0.382	0.001	0	0.460	4.014	+0.036	0	Not melted
6	100 (e)	450		0.386	0.001	0	0.460	3.818	+0.007	+0.006	Not melted
1E	1,730 (e)	6,800	>2,750	0.382	0.001	0	0.458	3.913	+0.002	+0.008	Melted
2E	2,750 (e)	10,500	>2,750	0.382	0.001	0	0.458	3.915	+0.074	0	Melted
3E	3,000 (e)	8,800	>2,750	0.382	0.001	0	0.461	3.915	+0.023	+0.006	Melted
4E	760 (e)	4,600	>2,750	0.382	0.001	0	0.460	3.916	0	0	Melted
7C	350 (e)	1,400		0.506	0.002	0	0.576	4.992	0	0	Not melted
8C	350 (e)	1,400		0.506	0.002	0	0.578	5.002	-0.028	0	Not melted
9C	350 (e)	1,400		0.507	0.002	0	0.578	4.994	-0.008	0	Not melted
10C	500 (e)	1,900		0.506	0.001	0	0.506	5.018	-0.080	+0.011	Not melted
Remarks: This test was designed to determine the effect of heat flux, specimen diameter, and material on UO ₂ specimens fabricated by cold pressing to 75 to 80% of theoretical density. Specimens 1, 2, 5, and 6 contained 80% dense natural UO ₂ , specimens 1E to 4E contained 80% dense UO ₂ enriched to 5.5 wt. % U ²³⁵ in total uranium, and specimens 7C to 10C contained 75% dense natural UO ₂ . Specimens 1, 2, 5, and 6 split during the irradiation, but analysis of the UO ₂ used in these specimens revealed the presence of 0.5 wt. % water due to insufficient drying of the specimens. Specimens 1E, 2E, 3E, and 4E were found to have bulged due to the melting of the UO ₂ , and specimen 2E burned through the cladding. However, these specimens were irradiated in a position having twice the requested thermal-neutron flux. No gross changes were evident in samples 7C, 8C, 9C, and 10C.											
Experiments 14-9, -10, and -11											
7	20 (f)	600		0.437	0.003	0	0.500	4.592	0	0	Not melted
8	90 (f)	2,370		0.437	0.002	0	0.500	4.643	0	0	Not melted
12C	60 (f)	1,800		0.439	0.002	0	0.500	4.602	0	0	Not melted
13C	80 (f)	2,240		0.439	0.002	0	0.500	4.595	0	0	Not melted
42S	35 (f)	890	360	0.343	0.003	0	0.402	4.582	0	0	Not melted
43C	100 (f)	2,200	800	0.343	0.003	0	0.402	4.667	0	0	Not melted
50S	100 (f)	2,780	1,030	0.343	0.003	0	0.402	4.590	0	0	Not melted
51S	70 (f)	1,650	570	0.343	0.003	0	0.402	4.649	0	0	Not melted
53S	20 (f)	590	300	0.439	0.002	0	0.501	4.636	0	0	Not melted
54S	65 (f)	1,320	700	0.439	0.002	0	0.501	4.596	0	0	Not melted
56S	65 (f)	1,410	700	0.439	0.002	0	0.501	4.601	0	0	Not melted
57S	40 (f)	1,050	500	0.439	0.002	0	0.501	4.630	0	0	Not melted
Remarks: This series of experiments was meant to study the long-term burn-up effects both on cold-pressed and on cold-pressed and sintered natural UO ₂ samples. Unfortunately, the samples were irradiated in a lower thermal-neutron flux than was requested, and therefore the burn-ups are relatively low. Specimens 7 and 8 contained 80% dense cold-pressed UO ₂ ; 12C and 13C contained 70% dense cold-pressed UO ₂ ; 42S, 43S, 56S, and 57S contained 92% dense cold-pressed and sintered UO ₂ ; and specimens 50S, 51S, 53S, and 54S contained 89% dense cold-pressed and sintered UO ₂ . There was essentially no change in the specimens as a result of the irradiation. The fission-gas release values indicate that the higher density samples retain a considerably greater portion of the fission gas than the low-density samples.											

Table 1—(Continued)

Spec. No.	Heat flux* Btu/hr/sq ft × 10 ⁻³	Burn-up,* Mwd/ton	Calc. central temp., °C	UO ₂ diam.	Specimen dimensions, in.				Dimensional changes		Molten zone diam.	Fission- gas release, % Kr ⁸⁵
					Clearance Diam.	Axial	Tubing O.D.	Over-all length	Diam.	Length		
Experiments 14-12 and -13												
12H	170 (e)	1,800	1,270	0.3445	0.0015	0	0.402	5.240	0	0	Not melted	
13H	300 (e)	3,800	2,200	0.3445	0.0015	0	0.401	5.239	0	0	Not melted	
16H	340 (e)	4,200	2,420	0.3445	0.0015	0	0.402	5.238	0	0	Not melted	0.8
17H	250 (e)	2,700	1,850	0.3445	0.0015	0	0.401	5.238	0	0	Not melted	
14H	220 (f)	4,400	1,600	0.3445	0.0015	0	0.402	5.249	0	0	Not melted	
15H	370 (f)	10,900	2,650	0.3445	0.0015	0	0.402	5.237	0	0	Not melted	5.0
18H	420 (f)	13,500	>2,750	0.3445	0.0015	0	0.400	5.240	0	0	Not melted	8.1
19H	300 (f)	6,900	2,200	0.3445	0.0015	0	0.402	5.238	0	0	Not melted	

Remarks: These two experiments were designed to study the effect of irradiation at high heat fluxes and to high burn-ups on hot-pressed natural UO₂. Samples 12H to 15H contained 95% dense hot-pressed UO₂ made from steam-oxidized material, and samples 16H to 19H contained 91% dense hot-pressed UO₂ made from MCW UO₂. The steam-oxidized UO₂ is made by oxidizing uranium in an autoclave at 650°F and saturation pressure. MCW UO₂ is made by reducing UO₃ with cracked ammonia. The results of these experiments indicate that hot-pressed UO₂ is quite stable when irradiated to high burn-ups and high heat fluxes.

Experiment 14-14

82S	330 (e)	14,000	2,400	0.3445	0.002	0.080	0.414	5.205	0	0	Not melted	
83S	540 (e)	22,000	>2,750	0.3445	0.002	0.080	0.414	5.222	+0.012	0	0.200	
84S	600 (e)	25,000	>2,750	0.3445	0.002	0.080	0.414	5.224	+0.015	0	0.230	
85S	300 (e)	12,000	2,200	0.3445	0.002	0.080	0.414	5.206	0	0	Not melted	

Remarks: This experiment was designed to determine the effect of irradiation to extremely high burn-ups on PWR reference rods. The samples contained 93% dense cold-pressed and sintered natural UO₂ and were assembled to reference specifications. The Zircaloy-2 tubing for these rods, however, was machined from bar stock rather than extruded as is the case for the PWR reference rods, and this machined tubing was of somewhat dubious quality. The rods were irradiated in the MTR lattice for 1½ years and achieved an estimated burn-up of 25,000 Mwd/ton. Unfortunately, the cladding split on all the rods, permitting the NaK to attack the UO₂ and also preventing any fission-gas studies. In an attempt to determine if the cladding split because of a deterioration in the mechanical properties as a result of the high irradiation exposure, the hardness of the cladding of a high- and a low-flux specimen was measured. Although no control hardness values are available, the hardness of the cladding on both of the samples was within the range of as-fabricated tubing.

Experiments 14-15 and -16

96S	250 (f)	525	1,850	0.357	0.0015	0	0.414	4.558	0	0	Not melted	
100S	1,000 (f)	2,020	>2,750	0.357	0.0015	0	0.414	4.566	+0.050	+0.054	Gross melting	
101S	1,430 (f)	2,450	>2,750	0.357	0.0015	0	0.414	4.533	+0.114	+0.066	Gross melting	
104S	760 (f)	1,500	>2,750	0.357	0.0015	0	0.414	4.570	0	0	Not melted	
105S	180 (f)	460	1,400	0.357	0.0015	0	0.414	4.560	0	0	Not melted	
109S	940 (f)	1,840	>2,750	0.257	0.0015	0	0.414	4.564	+0.065		Gross melting	
113S	1,400 (f)	2,390	>2,750	0.357	0.0015	0	0.414	4.567	+0.057		Gross melting	42.5
114S	790 (f)	1,620	>2,750	0.357	0.0015	0	0.414	4.558	0	0	Not melted	

Remarks: These experiments were designed to determine the effect of irradiation on PWR reference rods irradiated at extremely high heat fluxes. The rods contained 93% dense cold-pressed and sintered natural UO₂. The Zircaloy-2 tubing was made by the reference extrusion process. It is estimated that a heat flux in excess of 950,000 Btu/hr/sq ft occurred in the four higher exposure rods. The thermal conditions in rods 100S and 101S caused the Zircaloy-2 cladding to melt. The cladding on rods 109S and 113S did not melt, but considerable bulging was noted. The 42.5% fission-gas release from specimen 113S was produced by the gross melting that occurred in the UO₂ in this specimen.

Experiment 14-18

9B2	300 (f)	6,430	1,400	0.357	0.002	0	0.413	4.544	0	0	Not melted	0.25
9B3	900 (f)	12,400	>2,750	0.357	0.002	0	0.413	4.560	+0.009	+0.009	0.250	13.6
10B1	890 (f)	12,100	>2,750	0.357	0.002	0	0.413	4.506	+0.008	+0.015	0.275	15.3
10B2	300 (f)	6,100	2,200	0.357	0.002	0	0.413	4.518	0	0	Not melted	

Remarks: This experiment was designed to determine the effect of irradiation to very high burn-ups of 93% dense cold-pressed and sintered UO₂ enriched 6.24 wt. % U²³⁵ in total uranium. The Zircaloy-2 tubing was manufactured by the reference extrusion process. The UO₂ in the two higher exposure rods was molten over a considerable portion of the diameter, yet very small dimensional changes occurred in the samples. The fission-gas release values indicate that molten UO₂ retains considerably less of the fission gas than UO₂ irradiated below the melting point.

EFFECTS OF IRRADIATION ON BULK URANIUM DIOXIDE

Table 1—(Continued)

Spec. No.	Heat flux,* Btu/hr/sq ft × 10 ⁻³	Burn-up,* Mwd/ton	Calc. central temp., °C	UO ₂ diam.	Specimen dimensions, in.			Dimensional changes		Molten zone diam.	Fission- gas release, % Kr ⁸⁵
					Clearance Diam.	Tubing Axial O.D.	Over-all length	Diam.	Length		
Experiment 14-19											
24B1	340 (f)	6,700	2,400	0.351	0.008	0	0.413		0		Not melted
24B2	670 (f)	14,400	>2,750	0.351	0.008	0	0.413		+0.002		0.290
24B3	840 (f)	15,500	>2,750	0.351	0.008	0	0.413		+0.018		0.325
25B1	340 (f)	7,930	2,400	0.351	0.008	0	0.413		0		Not melted
Remarks: This experiment was designed to determine the effect of large diametral clearances (0.008 in.) on the behavior of reference PWR rods irradiated at high heat fluxes. Although a considerable portion of the UO ₂ melted in the two higher exposure samples, the heat fluxes are not known to a sufficient degree of accuracy to ascertain the effect of the 0.008-in. diametral clearance as opposed to the reference 0.002- to 0.004-in. diametral clearance. Again, the effect of melting in the UO ₂ can be noted in regard to the amount of fission gas released.											
Experiment 14-21											
2	330 (f)	3,400	2,400	0.356	0.004	0.080	0.414	4.529	0	0	Not melted
5	760 (f)	6,400	>2,750	0.356	0.004	0.080	0.414	4.616	0	0	0.225
6	760 (f)	6,400	>2,750	0.356	0.004	0.080	0.414	4.512	+0.002	+0.020	0.270
8	310 (f)	3,500	2,300	0.356	0.004	0.080	0.414	4.449	0	0	Not melted
Remarks: This experiment was designed to determine the effect of irradiation on 95% dense extruded natural UO ₂ rods containing 0.2 wt. % TiO ₂ as an additive. The results indicate that this type of material apparently behaves in an identical manner to 93% dense cold-pressed and sintered UO ₂ .											
Experiment 14-24											
14	300 (f)	1,500	2,200	0.356	0.003	0.040	0.413	4.489	0	0	Not melted
19	710 (f)	2,650	>2,750	0.356	0.003	0.042	0.413	4.484	0	0	Grain growth
20	770 (f)	2,700	>2,750	0.356	0.003	0.044	0.413	4.488	0	+0.009	0.175
21	310 (f)	1,700	2,300	0.356	0.003	0.053	0.413	4.484	0	0	Not melted
Remarks: This experiment was designed to determine the effect of irradiation on 95% dense slip-cast UO ₂ containing 0.2 wt. % TiO ₂ as an additive. Again, the results indicate that this type of material apparently behaves in an identical manner to 93% dense cold-pressed and sintered UO ₂ .											
Experiment 14-25											
A	115 (f)	192	900	0.356	0.003	0.046	0.416	4.512			Defective capsule
B	180 (f)	300	1,400	0.356	0.003	0.049	0.416	4.510	0	+0.009	Not melted
H	180 (f)	300	1,400	0.362	0.003	0.043	0.418	4.504	0	+0.012	Not melted
I	115 (f)	200	900	0.362	0.003	0.045	0.418	4.507	0	+0.009	Not melted
L	350 (f)	1,920	2,550	0.362	0.003	0.042	0.418	4.505	+0.003	+0.003	Not melted
J	1,000 (f)	3,300	>2,750	0.362	0.003	0.043	0.418	4.508	+0.004	+0.032	0.225
F	1,030 (f)	3,260	>2,750	0.356	0.003	0.046	0.416	4.511	+0.009	+0.025	0.270
D	430 (f)	2,100	>2,750	0.356	0.003	0.042	0.416	4.507	0	+0.006	Not melted
Remarks: This experiment was designed to test the effect of irradiation on cold-pressed and sintered 95% dense natural UO ₂ containing 0.2 wt. % TiO ₂ as an additive. Specimens A, B, F, and D contained standard centerless ground UO ₂ , and specimens H, I, J, and L contained unground UO ₂ pellets. As in the experiments containing extruded and slip-cast UO ₂ with TiO ₂ as an additive, there was no apparent difference in the behavior of this material as compared to 93% dense cold-pressed and sintered UO ₂ without additives.											
Experiments 14-29 and -30											
1C	100 (e)	220	800	0.3625	0.002	0	0.418	2.176	0	0	
1R	100 (e)	220	800	0.355	0.002	0	0.418	2.063	0	0	
2C	230 (e)	500	1,730	0.3625	0.002	0	0.418	2.161	0	0	
2R	230 (e)	500	1,730	0.355	0.002	0	0.418	2.059	0	0	
3C	230 (e)	500	1,730	0.3625	0.002	0	0.418	2.161	0	0	
3R	230 (e)	500	1,730	0.355	0.002	0	0.418	2.063	0	0	
4C	130 (e)	280	1,030	0.3625	0.002	0	0.418	2.190	0	0	
4R	130 (e)	280	1,030	0.355	0.002	0	0.418	2.058	0	0	
5C	100 (e)	In-pile	800	0.3625	0.002	0	0.418	2.173			
5R	100 (e)	In-pile	800	0.355	0.002	0	0.418	2.058			
6C	165 (e)	In-pile	1,260	0.3625	0.002	0	0.418	2.176			
6R	165 (e)	In-pile	1,260	0.355	0.002	0	0.418	2.060			
7C	130 (e)	In-pile	1,030	0.3625	0.022	0	0.418	2.170			
7R	130 (e)	In-pile	1,030	0.355	0.002	0	0.418	2.060			
8C	65 (e)	In-pile	560	0.3625	0.002	0	0.418	2.180			
8R	65 (e)	In-pile	560	0.355	0.002	0	0.418	2.063			
Remarks: These two experiments were designed to ascertain the effect of high oxygen ratios on the fission-gas release rate of UO ₂ . Specimens 1C to 8C contained 95% dense natural uranium oxide that was sintered in steam rather than in hydrogen. The oxygen-to-uranium ratio of this material is 2.08 to 2.13. Specimens 1R to 8R contained 94% dense natural uranium oxide which was sintered in hydrogen and which therefore had an oxygen-to-uranium ratio of 2.00. The samples were arranged by pairs so that the fission-gas release rate of the two materials could be compared. As of this writing, the first group of specimens has been removed from the pile, but fission-gas release data are not yet available. Specimens 5C to 8C and 5R to 8R are still in-pile.											

Table 1—(Continued)

Experiment WAPD-114A							
Spec. No.	Heat flux,* Btu/hr/sq ft $\times 10^{-3}$	Spec. No.	Heat flux,* Btu/hr/sq ft $\times 10^{-3}$	Spec. No.	Heat flux,* Btu/hr/sq ft $\times 10^{-3}$	Spec. No.	Heat flux,* Btu/hr/sq ft $\times 10^{-3}$
231	110 (e)	2	175 (e)	55	400 (e)	244	270 (e)
221	100 (e)	13	190 (e)	47	380 (e)	254	310 (e)
171	125 (e)	23	195 (e)	35	205 (e)	164	110 (e)
161	110 (e)	33	205 (e)	25	195 (e)	174	125 (e)
251	315 (e)	41	390 (e)	15	400 (e)	224	100 (e)
241	270 (e)	51	400 (e)	3	175 (e)	234	110 (e)
311	330 (e)	61	420 (e)	323	190 (e)	12	145 (e)
301	280 (e)	72	440 (e)	83	185 (e)	22	195 (e)
303	280 (e)	101	440 (e)	37	185 (e)	32	185 (e)
313	330 (e)	331	420 (e)	27	165 (e)	82	185 (e)
243	270 (e)	63	420 (e)	17	145 (e)	322	155 (e)
253	315 (e)	52	420 (e)	4	135 (e)	14	185 (e)
163	110 (e)	43	400 (e)	232	110 (e)	24	190 (e)
173	125 (e)	73	450 (e)	222	100 (e)	34	210 (e)
223	100 (e)	75	450 (e)	172	125 (e)	42	380 (e)
233	110 (e)	45	400 (e)	162	110 (e)	62	420 (e)
1	135 (e)	54	420 (e)	252	310 (e)	102	440 (e)
11	145 (e)	65	430 (e)	242	270 (e)	332	420 (e)
21	170 (e)	333	420 (e)	312	330 (e)	64	430 (e)
31	185 (e)	103	440 (e)	302	280 (e)	53	415 (e)
81	185 (e)	77	440 (e)	304	280 (e)	44	400 (e)
321	190 (e)	67	420 (e)	314	330 (e)	74	450 (e)

Remarks: This experiment is designed to ascertain the rate of fission-gas release from a variety of uranium oxide materials. Included in the experiment are 60 and 70% dense cold-pressed U_3O_8 ; 60 and 70% cold-pressed UO_2 ; 86, 89, 92, and 96% cold-pressed and sintered UO_2 ; and 91 and 96% cold-pressed and steam-sintered $UO_{2.1}$. Two enrichments are included for each type of material, and the samples are arranged so that a fourfold difference is produced in the burn-up rate. The samples are arranged in such a manner that the results will be amenable to statistical analysis. This experiment is still in-pile.

* Heat flux, burn-up, and calculated center temperatures are based on estimates of nominal reactor fluxes when indicated by (e) and fission-monitor results when indicated by (f). The estimates are good only to $\pm 50\%$, and the fission-monitor data are thought to be somewhat more accurate. The inconsistencies noted between the calculated center temperatures and the observed melting are presumably produced by these inaccuracies.

Table 2—DATA ON IRRADIATION-CYCLED ZIRCALOY-2-CLAD UO_2 FUEL ELEMENTS

Spec. No.	Heat flux,* Btu/hr/sq ft $\times 10^{-3}$	Burn-up,* Mwd/ton	UO ₂ diam.	Specimen dimensions, in.				No. of cycles	Dimensional changes	
				Clearance		Tubing O.D.	Over-all length		Diam.	Length
				Diam.	Axial					
Experiments WAPD-19-1 and -2										
8H	335	740	0.345	0.0005	0	0.402	5.134	4,700	0	0
9H	450	980	0.345	0.0005	0	0.402	5.126	4,700	0	0
10H	310	740	0.345	0.0005	0	0.402	5.292	4,700	0	0
16H	390	810	0.345	0.0005	0	0.402	5.153	4,700	0	+0.007
19S	460	980	0.344	0.0014	0	0.402	5.153	4,700	0	0
20S	380	810	0.344	0.0019	0	0.402	5.191	4,700	0	+0.008

Remarks: This experiment was designed to ascertain the effect of material variables on possible dimensional changes induced by irradiation cycling. Specimen 10H contained 81% dense hot-pressed natural UO_2 ; specimens 8H and 9H contained 88% dense hot-pressed natural UO_2 ; and specimens 16H, 19S, and 20S contained 91% dense cold-pressed natural UO_2 . No significant changes were noted in the dimensions of the samples as a result of the irradiation cycling.

Experiment WAPD-19-4									
J-4	160	490	0.355	0.004	0.150	0.414	9.738	7,500	0 +0.007
N-25-4	245	720	0.357	0.001	0	0.414	9.749	7,500	0 +0.009
14	160	490	0.357	0.0018	0	0.414	9.743	7,500	0 +0.013
N-2-8-B	245	720	0.357	0.0018	0.150	0.414	9.739	7,500	0 +0.006
N-2-11-4	160	490	0.357	0.0014	0.150	0.414	9.735	7,500	0 0
B-7	245	720	0.355	0.0035	0.150	0.414	9.742	7,500	0 +0.006
K-2	160	490	0.355	0.003	0	0.414	9.746	7,500	0 +0.009
K-4	245	720	0.355	0.0035	0	0.414	9.743	7,500	0 +0.009

Remarks: This experiment was designed to determine the effect of varying diametral and axial clearances on any possible growth induced by irradiation-cycling the rods. All the rods contained 92% dense cold-pressed and sintered natural UO_2 . Except for very slight increases in length, the results indicate that no changes were produced in the rods as a result of the irradiation.

Experiment WAPD-19-7									
N-5-9-C	450	18,000	0.357	0.002	0.150	0.414	10.298	7,000	0 0
N-5-7-C	450	18,000	0.357	0.002	0.058	0.414	10.302	7,000	0 0
N-5-9-B	450	9,000	0.355	0.004	0.150	0.414	10.303	7,000	0 0
N-5-10-B	450	9,000	0.355	0.004	0.055	0.414	10.297	7,000	0 0

Remarks: This test was designed to determine the effect of irradiation cycling to very high burn-ups on the possible dimensional instability of cycled rods. The rods contained 95% dense cold-pressed and sintered UO_2 enriched 6.2 wt. % U^{235} in total uranium. No dimensional changes were produced as a result of the irradiation.

* Based on estimates of thermal-neutron flux in various reactor locations; considered accurate to only $\pm 50\%$.

EFFECTS OF IRRADIATION ON BULK URANIUM DIOXIDE

Table 3—DESCRIPTION AND SUMMARY OF AVAILABLE DATA ON ZIRCALOY-2-CLAD UO_2 RODS IRRADIATED IN HIGH-PRESSURE, HIGH-TEMPERATURE LOOPS

Spec. No.	Heat flux,* Btu/hr/sq ft $\times 10^{-3}$	Burn-up,* Mwd/ton	Defect (diam. of hole), in.	UO ₂ diam.	Specimen dimensions, in.				Dimensional changes		Melting	
					Clearance Diam.	Axial	Tubing O.D.	Over-all length	Diam.	Length	Diam.	Center
Experiment X-1-b												
1	223	1900	0.005	0.242	0.001	0	0.304	2.5	+0.080			
2	240	1900	0.005	0.242	0.001	0	0.304	2.5	0			
3	190	1600	None	0.242	0.001	0	0.304	2.5	0			
4	240	1900	None	0.242	0.001	0	0.304	2.5	0			
Remarks: This experiment was the first in-pile loop test containing defective UO ₂ specimens. The rods contained 80% dense hot-pressed UO ₂ enriched 6.9 wt. % U ²³⁵ in total uranium. The quality of the material was somewhat dubious. From the very beginning of the test, high fission-product activities were noted in the loop water. After 43 days a burst of activity occurred following a shutdown and start-up of the reactor, and the test section was removed from the reactor. Postirradiation examination revealed that specimen 1 had bulged and ruptured near one end plug. Two pictures of this failure are shown in Figs. 4 and 5. The failure is postulated to have been produced by a waterlogging type of failure. (This type of failure is fully discussed in Sec. 5.3).												
Experiment X-1-c												
5F	32	50	None	0.352	0.001	0	0.402	5.438				
13S	310	320	None	0.344	0.001	0	0.402	9.880				
14S	380	390	0.005	0.344	0.001	0	0.402	3.555	+0.007			
6H	435	400	None	0.344	0.001	0	0.402	3.048				
4S	60	100	None	0.344	0.001	0	0.402	5.225				
2F	65	100	None	0.352	0.001	0	0.402	5.450				
3H	65	100	None	0.344	0.001	0	0.402	3.075				
4H	65	100	None	0.344	0.001	0	0.402	3.120				
11S	60	100	None	0.344	0.001	0	0.402	5.403				
82S	55	100	None	0.344	0.001	0	0.402	5.230				
Remarks: The primary purpose of this test was to verify whether the waterlogging type of failure observed in the X-1-b experiment was produced by the low-density UO ₂ . For this purpose a defective specimen (14S) containing cold-pressed and sintered 90% dense UO ₂ enriched 5.3 wt. % U ²³⁵ in total uranium was prepared. In addition, samples fabricated by different methods were placed in-pile without defects to determine the dimensional stability and fission-gas release rate of the fuel material. Specimens 5F and 2F contained 90% dense hot-pressed and sintered natural UO ₂ , specimens 3H and 4H contained 93% dense hot-pressed natural UO ₂ , specimen 11S contained cold-pressed and sintered 88% dense natural UO ₂ , specimens 4S and 11S contained 92% dense cold-pressed and sintered natural UO ₂ , specimen 6H contained hot pressed 95% dense UO ₂ enriched 5.3 wt. % U ²³⁵ in total uranium, and specimens 13S and 14S contained cold-pressed and sintered 90% dense UO ₂ enriched 5.3 wt. % U ²³⁵ in total uranium.												
Prior to the irradiation it was found that samples fabricated in a manner similar to that for the defective sample failed in corrosion. However, the test was started, and, although very high activities were noted in the loop water, the test was continued. After 1 week of irradiation the test was terminated because of a leak in the loop piping.												
The only change noted in any of the specimens was an increase of 0.007 in. in the diameter of the defective rod. This increase is thought to be associated with the poor corrosion resistance of the UO ₂ in the defective rod, which would permit water to completely permeate the fuel and thereby tend to increase the probability of waterlogging, producing an expansion in the cladding. (Waterlogging is discussed in some detail in Sec. 5.3.) Because of the low burn-ups, no significant data were obtained from the nondefective rods from this experiment.												
Experiment X-1-d												
78S	490	5900	0.005	0.3445	0.0018	0	0.401	3.515	0	+0.014	None	
79S	490	5900	None	0.3445	0.0015	0	0.402	3.490	0	-0.006	None	
Remarks: This test was designed to determine the release of fission products from a high-density defective UO ₂ specimen exposed in-pile to high-temperature water. Both specimens contained cold-pressed and sintered 95% dense UO ₂ enriched 5.3 wt. % U ²³⁵ in total uranium. The corrosion resistance of this material was checked prior to the irradiation and found to be satisfactory. The samples were irradiated for 100 days, and relatively low activity was observed in the loop water. Postirradiation examination revealed that, except for slight unexplained changes in the length of the samples, essentially no damage was produced as a result of the irradiation.												
Experiment X-3-3												
1	490	2000	0.005	0.3475	0.001	0	0.403	10.306	+0.002		None	
Remarks: This test was designed to ascertain the behavior of a defective full-length PWR Core 1 blanket fuel element when irradiated in a high-pressure, high-temperature loop. The specimen contained 93% dense cold-pressed and sintered UO ₂ enriched 5.3 wt. % U ²³⁵ in total uranium. The activity of the loop water was somewhat higher than that experienced in the X-1-d test, but no signs of gross failure occurred. Except for a slight increase in diameter, no changes were noted in the specimen as a result of the irradiation.												

Table 3—(Continued)

Spec. No.	Heat flux,* Btu/hr/sq ft × 10 ⁻³	Burn-up,* Mwd/ton	Defect (diam. of hole), in.	UO ₂ diam.	Specimen dimensions, in.				Dimensional changes		Melting	
					Clearance Diam.	Axial O.D.	Tubing O.D.	Over-all length	Diam.	Length	Diam.	Center crater
Experiment X-1-e												
1	391†	26	None	0.356	0.003	0.076	0.413	10.251	0	0	None	
2	485†	53	None	0.356	0.003	0.075	0.413	10.159	0	0	None	
3	682†	164	0.005	0.356	0.003	0.083	0.413	10.093	Failed		0.260	
4	502†	74	0.005	0.356	0.003	0.077	0.413	10.190	0	0	GG	
5	495†	60	Crack	0.356	0.003	0.074	0.413	10.239	0	0	GG	
Remarks: This experiment was designed to ascertain the effect of varying heat fluxes on the behavior of defective full-length PWR blanket fuel rods in high-temperature, high-pressure water loops. Specimens 1, 2, 4, and 5 contained 94% dense cold-pressed and sintered UO ₂ enriched 9.5 wt. % U ²³⁵ in total uranium, and specimen 3 contained 93% dense cold-pressed and sintered UO ₂ enriched 22.1 wt. % U ²³⁵ in total uranium.												
Three hours after the start-up of the test, an extremely large burst of activity was observed in the loop water. Although an attempt was made to shield the loop and continue operation, it was found necessary to remove the specimen train after 20 hr of intermittent operation.												
Postirradiation examination revealed that rod 3 had ruptured below the center, leaving an open section about 1¼ in. long with approximately half the Zircaloy-2 cladding missing in the center of the rupture. A picture of this failure is shown in Fig. 6. Since it is apparent that the observed rupture was produced by an excessive heat flux in rod 3, very little significant information could be obtained from this experiment.												
Experiment X-1-f												
1	426‡		0.005	0.351	0.008	0.060	0.413	10.25	0	+0.020	0.150-0.170	0.005-0.015
2	492‡		0.005	0.357	0.0015	0	0.413	10.25	+0.002	+0.076	GG-0.180	0-0.005
3	515‡	1450§	None	0.351	0.008	0.060	0.413	10.25	+0.001	+0.018	0.120-0.190	0.010-0.020
4	508‡		0.005	0.351	0.008	0.060	0.413	10.25	+0.002		0.220-0.230	0.025-0.090
5	464‡		None	0.356	0.003	0	0.413	10.25	+0.002	+0.061	GG-none	None
Remarks: The X-1-f experiment was originally intended to be a 1-year irradiation of PWR type rods to the maximum design burn-up of 11,000 Mwd/ton, but, since further calculations indicated melting in the high-diametral-clearance defective rods, the specimens were removed after 40 days of testing. Melting of UO ₂ was found in four of the five specimens. The UO ₂ was 95% dense, made by cold pressing and sintering, and enriched to 7.8 wt. % U ²³⁵ in total uranium.												
Experiment X-1-g												
1	391	3170	0.005	0.356	0.0025	0.150	0.413	10.25	0	0.024	GG-GG	
2	452	3800	0.005	0.355	0.004	0.195	0.413	10.25	0.007-0.012	0.010	0.205-0.215	0.030-0.060
3	474	4150	None	0.356	0.0025	0	0.413	10.25	0	0.037	GG-GG	
4	467	3860	0.005	0.358	0.001	0.195	0.413	10.25	0.002-0.010†	0.071	0.200-0.210	0.050-0.150
5	426	3070	None	0.356	0.0025	0.195	0.413	10.25	0	0.005	No effect	
Remarks: This experiment was to replace X-1-f as a 1-year test for PWR type fuel rods. Unusually low fission-product activity in the loop frustrated a subsidiary experiment in conjunction with this test involving tryouts of the fuel-element-failure detection system. Therefore X-1-h replaced X-1-g after 40 days of test. X-1-g was returned to the loop after X-1-h was removed and operated for 20 days, at which time high-activity bursts were first observed in the loop water. Five days later, the activity reached intolerable level, forcing removal of the X-1-g specimens. Examination revealed several cladding cracks 3 to 4 in. from the lower end of X-1-g-2 along with a relatively high diametral increment. Melting of UO ₂ was found in X-1-g-2 and X-1-g-4. The fuel was 95% dense cold-pressed and sintered UO ₂ enriched to 7.8 wt. % U ²³⁵ in total uranium.												
Experiment X-1-h												
1	408	2440	0.005	0.354	0.005	0.150	0.413	10.25	0	0.006	GG-0.140	
2	473	2820	0.005	0.351	0.008	0.190	0.413	10.25	0.001	0.006	0.200-0.220	0.040-0.170
3	494	2940	Failed	0.356	0.0025	0	0.413	10.25	0.002	0.050	0.160-0.210	0-0.010
4	487	2910	None	0.351	0.008	0.190	0.413	10.25	0	0.006	0.190-0.210	0.025-0.100
5	446	2740	None	0.354	0.005	0.150	0.413	10.25	0	0.005	GG-0.210	0-0.010
Remarks: This experiment was intended as a backup for X-1-g and was inserted into the reactor to check out the fuel-element-failure detection system. After 40 days of operation, high activity in the coolant was noticed. The specimens were removed 8 days later as originally planned. Examination revealed a cladding blister and severe hydriding of the Zircaloy-2 of the originally nondefective X-1-h-3 specimen. Center melting of the UO ₂ occurred in all five specimens. The UO ₂ was 95% dense, cold pressed and sintered, and enriched to 7.8 wt. % U ²³⁵ in total uranium.												

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Table 3—(Continued)

Spec. No.	Heat flux,* Btu/hr/sq ft $\times 10^{-3}$	Burn-up,* Mwd/ton	Defect (diam. of hole), in.	UO ₂ diam.	Specimen dimensions, in.				Dimensional changes		Melting	
					Clearance Diam.	Axial	Tubing O.D.	Over-all length	Diam.	Length	Diam.	Center crater
1	258	810	None	0.358	0.001	0.196	0.413	10.25	0	0.008	No effect	
2	297	930	None	0.358	0.001	0.136	0.413	10.25	0	0.010	No effect	
3	312	970	0.005	0.355	0.004	0.136	0.413	10.25	0	0.007	No effect	
4	308	960	None	0.357	0.002	0.166	0.413	10.25	0	0.007	No effect	
5	280	870	None	0.355	0.004	0.196	0.413	10.25	0	0.015	No effect	

Remarks: This test was intended to be a 1-year test of PWR type rods at heat fluxes below 400,000 Btu/hr/sq ft, but, because of indications that a failure might result due to lack of corrosion resistance of the I.D. of the cladding, this test was terminated after a month and replaced by similar specimens with corrosion-tested I.D.'s. No structural change was observed in the UO₂ of any of the specimens, which was 93% dense, cold pressed and sintered, and enriched to 4.8 wt. % of U²³⁵ in total uranium.

Experiment X-1-1

1	258	5500 up	None	0.358	0.001	0.196	0.413	10.25	Test in-pile since Jan. 20, 1957			
2	297	to	None	0.358	0.001	0.136	0.413	10.25				
3	312	Sept.	0.005	0.355	0.004	0.136	0.413	10.25				
4	308		None	0.357	0.002	0.166	0.413	10.25				
5	280		None	0.355	0.004	0.196	0.413	10.25				

Remarks: This test is to operate for 1 year. The Zircaloy-2 tubing of the PWR type fuel-rod specimens has been corrosion-tested on both O.D. and I.D. The UO₂ is 93% dense, cold-pressed and sintered, and enriched to 4.8 wt. % U²³⁵ in total uranium.

Experiment 25-2

L1	475	1000	0.005	0.355	0.004	0.193	0.413	10.25	0		0.160-0.190	0.025
L2	475	1260	None	0.355	0.004	0.173	0.413	10.25	0		No effect	

Remarks: This experiment was designed to ascertain the effect of irradiation cycling on rods irradiated in high-pressure, high-temperature loops. The rods contained 93% dense cold-pressed and sintered natural UO₂. The rods were cycled 533 times during the 9-week testing period. No dimensional changes were produced in the rods. The most remarkable fact noted from these rods was that the UO₂ melted in the defective rod, although neither melting nor grain growth was observed in the nondefective rod which ran at the same heat flux. In judging from the structure of the UO₂ in the center of the two rods, the temperature difference must have been at least 1200°C.

Experiments 29-1 and -2

1-1	230	860	None	0.3566	0.0035	0.161	0.413	10.25	0	0	None	
1-2	286	830	0.005	0.3566	0.0035	0.168	0.413	10.25	0	0	None	
2-1	286	750	None	0.3561	0.004	0.147	0.415	10.25	0	0	None	
2-2	286	750	0.005	0.3561	0.004	0.170	0.415	10.25	0	0	None	

Remarks: These two experiments were designed to determine the difference in the fission-product release of 93% dense and 97% dense UO₂. Rods 1-1 and 1-2 contained 93% dense cold-pressed and sintered natural UO₂, and rods 2-1 and 2-2 contained 97% dense cold-pressed and sintered natural UO₂. The rods were irradiated in the WAPD-29 loop at the MTR.

Experiments 29-3 to -5

3-1	240	~800	None	0.3565	0.004	0.174	0.415	10.25	0	0	None	
3-2	240	~800	0.005 × 2	0.3565	0.004	0.173	0.415	10.25	0	0	None	
4-1	240	~800	None	0.3562	0.004	0.169	0.415	10.25	0	0	None	
4-2	240	~800	0.005 × 4	0.3562	0.004	0.172	0.415	10.25	0	0	None	
5-1	240	~800	None	0.3563	0.004	0.175	0.415	10.25	0	0	None	
5-2	240	~800	0.005 × 3	0.3563	0.004	0.179	0.415	10.25	0	0	None	

Remarks: These experiments were designed to determine the effect of multiple defects on the fission product release from Zircaloy-2 clad UO₂ fuel elements. All the samples contained 95% dense cold-pressed and sintered natural UO₂.

* The heat-flux values are based on calorimetric values obtained from the ΔT across the loop. The burn-up values were obtained from fission monitors. Inaccuracies in the various measurements presumably produced the observed inconsistencies.
† See reference 9.

‡ Heat-flux values for X-1-f, X-1-g, X-1-h, X-1-j, and X-1-l are based on the asymmetrical neutron-flux distribution indicated in NEI-60.

§ Maximum burn-up value for test, derived from radiochemical analyses of UO₂ sections taken directly from the specimen.

¶ Large diameter change only near defective end of rod.

Table 4—SUMMARY OF DATA ON PWR CORE 1 PROTOTYPE BUNDLES IRRADIATED IN HIGH-PRESSURE,
HIGH-TEMPERATURE WATER LOOPS
(All Five Bundles Are of UO_2 Fuel Rods 0.413 in. in Diam. by 10.25 in. Long)

Bundle identity	No. of fuel rods	Defect rod	Max. heat flux, Btu/hr/sq ft $\times 10^{-3}$	Burn-up, Mwd/ton	Fuel clearance		Rod spacing ($\bar{x} \pm 36$ from 200 readings)	
					Diam.	Axial	Preirrad.	Postirrad.
15-1	9	Bent 0.160 in.	125	1200	0.001	0		
15-2	9	Bent 0.150 in. 0.015-in.-deep grooves at contact points, waterlogged with 0.16 g H_2O	315	1560	0.003	0		

Remarks: These two tests were designed to study the possibility of progressive failure in UO_2 rod bundles. The fuel was 93% dense cold-pressed and sintered UO_2 enriched to 4 wt. % U^{235} in total uranium in 15-1 and 8.4 wt. % U^{235} in total uranium in 15-2. In both bundles the center rod was made to contact two adjacent rods, but no contacting was found after irradiation. Also, the 15-2 defect rod cracked open in one of the grooves machined at the points of contact. No progressive-failure effect was found in either test.

Experiment CR-V(CT-1)

Welded	25	None	135	1950	0.003	0	0.0600 ± 0.0286	0.0651 ± 0.0264
Tube sheet								
Mechanical	25	None	135	1950	0.003	0	0.0557 ± 0.0300	0.0589 ± 0.0373
Egg crate								

Remarks: These two bundles were designed for a 6-month proof test of the PWR Core 1 bundle. The fuel was 93% dense cold-pressed and sintered UO_2 of varying enrichments to establish a heat-flux gradient across the bundles. In each bundle the UO_2 in three rows of fuel rods was enriched to 8.4 wt. % U^{235} in total uranium, in one row to 7.3 wt. %, and in the last row to 6.1 wt. %. The desired heat-flux maximum of 315,000 Btu/hr/sq ft was not achieved because of neutron-flux perturbation. Postirradiation examination indicated negligible changes in the over-all dimensions. Changes in rod spacing were found generally throughout the egg-crate bundle, although only localized changes were noted in the tube-sheet bundle. The rods of the bundles have been separated and are to be burst tested.

30-2	16	None	300	5500	0.003	0.166	0.0571 ± 0.0050	To be measured
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Remarks: This experiment was designed as a proof test of the PWR type bundle at high heat fluxes. The UO_2 is 93% dense cold-pressed and sintered, and enriched to 2.5 wt. % U^{235} in total uranium. The test loop is in an MTR reflector position, and therefore a flux gradient will occur naturally. Irradiation has just been completed.

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Fig. 4 — Schematic diagram of the X-1 loop.

3.3 Radiochemical Observations

To characterize the release of fission products from defective fuel elements, water samples were taken periodically for determination of gross beta activity and analysis for specific nuclides. Analyses were performed for Kr^{88} , Cs^{138} , Cs^{139} , Sr^{89} , Sr^{90} , Sr^{91} , Sr^{92} , I^{131} , I^{132} , I^{133} , Xe^{138} , Ba^{139} , Ba^{140} , Te^{132} , Br^{83} , Br^{84} , Cs^{136} , Cs^{135} , Np^{239} , and Mo^{99} , although many of these analyses were performed only infrequently. Similar samples withdrawn downstream of the ion exchanger indicated the performance of the ion-exchange resins for removal of specific nuclides. At intervals during the tests or at the end, the ion-exchange resins were removed from their shielded containers and mixed thoroughly, and aliquots were analyzed for longer-lived activities, such as Cs^{136} , Cs^{135} , Ba^{140} , I^{131} , Mo^{99} , Te^{132} , Sr^{89} , Sr^{90} , Y^{91} , Sr^{95} , and Ce^{144} . Sections of piping were also removed from the loop at the same time and were analyzed for many of the same isotopes. In some tests a radial-flow bed filter packed with magnetite was installed in the piping on the outlet of the in-pile test section, taking full loop flow. Analysis of pipe activity upstream and downstream of the bed permitted an estimation of the filtration efficiency of the bed. Following one test the loop was operated with flow bypassing the normal in-pile test section. Analysis of the 2.4h I^{132} activity in the loop water gave a measure of the amount of its 77h Te^{132} parent deposited on the pipe surfaces. Delayed-neutron and gamma monitors installed on the loops gave qualitative indications of relative activities and changes during the tests. During reactor shutdown, some measurements of the decay in radiation level adjacent to the loop components were obtained using portable survey meters.

3.4 Determination of Burn-up

The measurement of the actual conditions existing within a UO_2 fuel rod during irradiation is a matter of considerable difficulty. For early tests, in the MTR, the thermal flux and the subsequent temperature and burn-up values were calculated utilizing estimates of the thermal-

neutron flux that was present in the various test positions. Experience soon indicated that, because of changes in adjacent experiments, reactor loading, etc., such estimates were subject to rather wide errors, and a better method had to be devised. A suitable method of determining the amount of burn-up in irradiated fuel materials is to analyze a sample of the material for fission products and thus calculate the average burn-up. However, since it is quite difficult to obtain a representative sample of irradiated UO_2 , a small preweighed 1- to 2-mg sample of UO_2 of the same enrichment as the oxide in the sample was sealed in a small quartz capsule and was used as a fission monitor for the majority of the irradiations. The monitors were placed in either Zircaloy-2 or aluminum capsules attached to the ends of the fuel-element samples. After irradiation, these samples were analyzed for Cs^{137} , and the burn-up was calculated. However, there are several errors associated with this type of monitor. The small monitors cause very little perturbation of the thermal-neutron flux outside of the physical boundaries of the monitor and also are small enough that little suppression of flux occurs within the monitor. On the other hand, the 0.356-in.-diameter UO_2 rods, particularly when enriched UO_2 is utilized, cause considerable perturbation of the flux in the regions adjacent to the specimen and also cause considerable suppression within the specimen itself. An experimentally determined curve showing the suppression of the flux within a 7.69 wt. % enriched UO_2 pellet is shown⁸ in Fig. 5, the curve indicating that the flux decreased 24 per cent over the radius of the pellet. The monitors tend to give the neutron flux at the surface of the specimens

Fig. 5—Fission distribution in an enriched UO_2 pellet.⁸ The UO_2 is 94 per cent dense enriched 7.69 wt. % U^{235} in total uranium; the detector is 7 wt. % U^{235} —aluminum alloy.

and thus indicate a high value of the burn-up. These errors are slight for natural UO_2 specimens but become increasingly more severe the higher the enrichment.

To measure the magnitude of the errors in the burn-up values calculated from the fission monitors, all the UO_2 from one of the X-1-h rods (7.8 wt. % enriched) was dissolved, aliquoted, and analyzed for burn-up radiochemically at various laboratories. The results indicated that the average burn-up which occurred was about 70 per cent of the value indicated by the fission monitors. This value agreed quite well with the calculation of the flux depression made by S. Kushneriuk.⁹ Although this method appears least objectionable, time, equipment, and manpower limitations prevented any further measurements of this type; in the future, however, more analyses of this type are planned.

In samples irradiated in high-temperature, high-pressure water loops, an estimate of the heat generation rate per rod can be made from the temperature rise in the loop water together with the thermal characteristics of the loop and knowledge of the neutron-flux shape along the test section. The calculated heat-flux values shown in Table 3 are based on this type of estimate, and the burn-ups shown are based on fission-monitor results. The inconsistencies noted are considered to be produced by the above-mentioned factors.

3.5 Preirradiation and Postirradiation Measurements

(a) *Dimensions.* In general, the dimensions of all the samples were measured at a number of locations before irradiation and measured at the same locations after the irradiation, and the values were compared. Preirradiation measurements were made with standard micrometers, and postirradiation measurements were made utilizing a remotely operable micrometer.

(b) *Density of Uranium Dioxide.* Most of the UO_2 utilized for the various samples was in the form of centerless and end-ground pellets. The method utilized to measure the density of the majority of the samples was to weigh the samples, compute the volume from the dimensional measurements, and subsequently compute the density. The values are then reported in per cent of the theoretical density, 10.97 g/cm^3 . This value indicates the amount of pores existing in the material but does not indicate whether the pores are open or closed. As the technology of UO_2 developed, particularly in regard to fission-gas release, it became desirable to know not only the percentage theoretical density but also the distribution of open and closed pores. The method most commonly used to determine the distribution of pores is as follows:

1. Weigh the pellets in air to $\pm 0.0002 \text{ g}$.
2. Place the pellets in a pycnometer, evacuate, add mercury, weigh, and compute the volume of pellets. The mercury does not penetrate the pores; this volume therefore includes the solid UO_2 plus the open and closed pores. The volume calculated from the dimensional measurements is identical to this value, but the pycnometer value is considered more accurate because the effect of small chips and irregularities is eliminated. Also, the pycnometer is adaptable to pellets that have not been centerless and end ground.
3. Place the pellets in a vacuum system, evacuate, and add water. The water is assumed to enter essentially all the open pores. Remove the pellets from the water, at the same time starting a stop watch. Dry the surface of the pellets by air blast and blotting. Weigh the pellets at specified time intervals, plot against time, and extrapolate to zero time. This weight minus the weight in air gives a value for the open pores.
4. The value of the open plus closed pores is calculated by subtracting the volume of UO_2 as calculated from the weight of the pellets from the volume as measured with the mercury pycnometer. Subtract the volume of the open pores as established in step 3 from the volume of the open plus closed pores to obtain the volume of closed pores.

Note that all the above-mentioned steps have been performed only on nonirradiated samples. Uranium dioxide almost invariably cracks under irradiation, and postirradiation density measurements are extremely difficult. As a matter of fact, no reliable values have been obtained at the Bettis Plant on the density of irradiated UO_2 .

(c) *Macroexamination.* All samples were examined after irradiation on a Bausch and Lomb stereomicroscope having a magnification range of $\frac{1}{2}$ to $30\times$ and also equipped to take

stereopictures at the same range of magnification. All the macropictures of the samples were taken on this instrument, but only one-half of the stereo pairs are presented in this report.

To examine the UO_2 , the cladding was cut with a remotely operable tubing cutter equipped with micrometer positioning device. The locations of all the pellets were recorded prior to the irradiation and an attempt, not always successful, was made to cut the tubing at the pellet interfaces. Macrophotographs were also taken of these sections.

(d) *Metallography.* Irradiated UO_2 is quite friable, and hence the metallographic specimens were pressure mounted in Kelon plastic. Kelon is a thermosetting plastic which is quite fluid in the liquid state. The Kelon is forced into the pores and cracks of the UO_2 in a pressure chamber under 150 psi of helium. After mounting, the samples were prepared as follows:

The cladding was:

1. Ground under water on a stone lap utilizing 600-grit silicon carbide abrasive. The speed of the wheel was 92 rpm, and the grinding time was approximately 2 hr.
2. Polished on gamal cloth with Linde "B" abrasive. Generous amounts of dilute HNO_3 - H_2O solutions were added every 10 min. The speed of the wheel was 92 rpm, and the total polishing time was 45 min.
3. Etched with a 40 per cent HNO_3 -5 per cent H_2O_2 solution for 10 to 15 sec at room temperature. The etching solution was applied with a swab.

The UO_2 was:

1. Ground in a manner identical to that for cladding.
2. Polished in a manner identical to that for cladding except that the total time was 3 hr and the HNO_3 - HF - H_2O was added in small amounts every 20 min.
3. Etched with a 10 per cent H_2SO_4 -90 per cent H_2O_2 solution for 20 to 30 sec. The etching solution was applied with a swab.

Photomicrographs were taken on a Bausch and Lomb research metallograph equipped with a shielded stage.

(e) *Measurement of Fission-gas Release.* The fission-gas equipment is described in reference 10. The equipment consists of a vacuum furnace equipped with a drill for puncturing the cladding, a furnace for heating the specimen, a gas-collecting system, an aliquoting system, and a gamma-ray spectrometer for analyzing the released gas. In operation, the specimen is placed in the vacuum chamber, and the system is evacuated to less than 0.03μ with a mechanical pump and a diffusion pump. The system is then closed off, and the specimen is punctured, after which the released gas is pumped out of the in-cell section of the apparatus with a Toepler pump and adsorbed onto activated charcoal at liquid-nitrogen temperature. The pumping is continued for approximately 2 hr, after which the bulb containing the activated charcoal and adsorbed gas is sealed off and removed to a separate aliquoting system. The size of the aliquot taken depends on the activity of the gas.

The aliquots are subsequently analyzed on a gamma-ray spectrometer, and the amount of the various radioactive gases released is calculated. This value is subsequently corrected for the amount of radioactive decay which has occurred. Utilizing the burn-up values obtained from the fission monitors, the theoretical amount of fission gas produced during the irradiation is calculated, and the release values are reported as a percentage of this theoretical value. It should be noted that these release values are therefore subject to the same errors present in the fission-monitor values.

4 BEHAVIOR OF URANIUM DIOXIDE AS A FUEL MATERIAL

Those irradiation phenomena which apply specifically to the behavior of UO_2 , excluding effects arising from its manner of incorporation in a fuel element, are discussed in this section. As discussed in the introduction, most of such information has been inferred from the behavior of reference fuel-element samples; only in case of certain experiments on fission-gas release and X-ray diffraction studies have specifically designed tests been performed.

4.1 Fission-gas Release

It was surmised early in the course of development of the PWR Core 1 fuel element that two factors would cooperate to yield high rates of fission-gas release within the fuel element. One of these was that the oxide was unbonded to the metal cladding and that hence the entire surface of the fuel, including crack surfaces, could serve to contribute fission gas to the free volume within the fuel rod. The second factor was that, because of the poor thermal conductivity of the oxide and the consequent development of high operating temperatures, much higher rates of release of fission products might be noted than in the case of metallic fuels. There is considerable evidence in the literature¹¹⁻¹³ that metallic fuels retain volatile fission products to temperatures close to their melting point. However, it was surmised that, because of the more open structure of the oxide, higher rates of gas release could be encountered. For these reasons the tubing used in the Core 1 fuel was sized so as to contain the internal pressures that would be developed by complete release of the stable volatile fission products to metal atom burn-ups in excess of the maximum Core 1 fuel-element burn-ups of 1 at. %. The measurement of the amount of fission gas released from irradiated UO_2 as a function of temperature of operation and the determination of the mechanism of release were considered items of major importance. In this section the gas release within the fuel-element cladding only is considered. In Sec. 5.6 the release of fission products from defective fuel elements to the coolant will be discussed.

(a) *Mechanism of Fission-gas Release.* Since, as will be discussed later, no fine comminution or mechanical disintegration occurs during irradiation of UO_2 , only two mechanisms could be conceived which could lead to release of volatile fission products, namely, recoils and solid-state diffusion. The recoil range of fission fragments in UO_2 has been measured to be of the order of 5 to 8×10^{-4} cm; this is shown in Fig. 6 as a function of fission-fragment mass. The recoil contribution was ruled out as a major source of fission-gas release for the following reasons: Calculation of the amount of recoils on the basis of stopping power of helium in gas annuli between fuel and cladding and assumption of reasonable energy barriers against the incorporation of impinging ions in the cladding (the radiation damage theory of Keywell¹⁴ predicts a threshold energy of the order of the sublimation energy, or a few electron volts) fails to explain the observed amounts of gas release by factors of 3 to 6 orders of magnitude. Second, as shown in Table 5, there is a marked effect of temperature of operation on the amount of fission-gas release observed. In each of the cases listed in the table, the temperature of operation of the cladding is approximately the same, and therefore the observed

Fig. 6—Recoil range vs. mass of fission fragments.

Table 5—COMPARISON OF OBSERVED AND CALCULATED FRACTIONAL RELEASE OF Kr^{85} FROM IRRADIATED FUEL RODS

Specimen	Fuel diam., in.	Irradiation time, sec	Burn-up, Mwd/ton	Density (% theo.)	Radius of equiv. sphere, cm	Center temp., °C	Heat flux, Btu/hr/sq ft	Fractional release	
								Observed	Calculated
X-1-G-3	0.357	4.85×10^6	2,780	95	4.32×10^{-3}	2250	467,000	23.0×10^{-2}	32.26×10^{-2}
X-1-G-5	0.357	4.85×10^6	2,060	95	4.32×10^{-3}	1700*	404,000	16.1×10^{-2}	8.5×10^{-2}
X-1-B-4	0.242	3.63×10^6	1,650	80	1.742×10^{-4}	990	147,000	9.5×10^{-2}	3.17×10^{-2}
X-1-C-6H	0.3444	5.61×10^5	350	95	4.32×10^{-3}	1500	367,000	5.8×10^{-3}	10.4×10^{-3}
WAPD-25-L-2	0.357	1.58×10^6	815	95	4.32×10^{-3}	1600*	475,000	1.6×10^{-2}	4.7×10^{-2}
X-1-D-79S	0.3444	8.67×10^6	5,870	95	4.32×10^{-3}	1500	367,000	1.1×10^{-3}	40.8×10^{-3}
WAPD-29-1-1	0.357	2.42×10^6	860	93.7	3.16×10^{-3}	1000†	230,000	3.0×10^{-3}	1.4×10^{-3}
WAPD-29-2-2	0.357	1.7×10^6	750	97.4	14.69×10^{-3}	1000†	286,000	0.28×10^{-3}	0.26×10^{-3}
14-18-9B2	0.357		6,430	93		1400	300,000	2.5×10^{-3}	
14-18-9B3	0.357		12,400	93		>2750	900,000	13.6×10^{-2}	
14-18-10B1	0.357		12,100	93		>2750	890,000	15.3×10^{-2}	
14-21-6	0.357		6,400	95		>2750	760,000	23.2×10^{-2}	
14-21-8	0.357		3,500	95		1400	310,000	0.56×10^{-3}	
14-24-20	0.357		2,700	95		>2750	770,000	13.2×10^{-2}	
14-24-21	0.357		1,700	95		1400	310,000	1.8×10^{-3}	
14-25-F	0.357		3,260	95		>2750	1,030,000	32.6×10^{-2}	
14-25-O	0.357		2,100	95		1600	430,000	5.6×10^{-3}	

* This center temperature was assumed because metallographically no grain growth was noted.

† These center temperatures were assumed to be consistent with WAPD-25-L-2.

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amounts of gas released indicate directly the average temperature of the oxide fuel. It is difficult to imagine a recoil mechanism that would predict a strong dependence of gas release on temperature.

The final evidence that solid-state diffusion controls the release of the major fraction of the fission products is afforded by data, listed in Table 5, which indicate that gas release is sensitive to the fabricated density of the oxide even at high oxide densities. Again it is considered unreasonable to anticipate a strong effect of bulk density on release by a recoil mechanism.

It has therefore been considered for the purposes of the subsequent discussion that the observed amounts of gas released arise from a bulk diffusion mechanism and that gas release should therefore be sensitive to those operational and structural features, such as temperature, diffusion distance, time, concentration, defect structure, etc., which affect normal diffusion processes.

(b) *Surface Area of Sintered Oxide.* All the experiments to be discussed subsequently have been performed on UO_2 powder compacts sintered at temperatures of 1725°C or below. As discussed by Belle and Lustman,⁴ Padden has found that the interconnected porosity as measured by water absorption decreases rapidly, apparently to zero at sintered densities over 93 to 94 per cent of theoretical density. However, measurements performed by Aronson utilizing krypton adsorption techniques at low densities and butane adsorption at high densities indicate that, even at densities above 95 per cent of theoretical density, surface areas which are orders of magnitude greater than the geometric surface persist. His measurements of variation of surface area with oxide density are plotted in Fig. 7. These data have been utilized to calculate the radius of an equivalent sphere of the same ratio of surface area to volume by the relation:

$$a = \frac{3d}{S} \quad (1)$$

where a = radius of equivalent sphere, cm

d = fraction of theoretical density

S = surface area, cm^2/cc

They indicate rather surprisingly that the radius of the equivalent 100 per cent dense sphere with the same ratio of surface area to volume as a sintered pellet 0.36 in. in diameter by 0.36 in. high at, for example, 95 per cent density is only 4.3×10^{-3} cm. It is apparent therefore that

Fig. 7—Surface area vs. density for cold-pressed and sintered UO_2 .

the surface area available for release of diffusing substances is far greater than that anticipated from the geometric surface of the specimen. Thus for all subsequent observations the surface area was estimated from Fig. 7 by use of the measured values of sintered density. It is believed that these measurements serve to explain the marked effect of density on fission-gas release discussed subsequently. Note that Fig. 7 was derived from measurements performed upon cold-pressed and sintered MCW oxide pellets. It is quite conceivable that this curve would be invalid for bodies prepared from different sources of oxide or by different fabrication techniques.

(c) *Experimental Measurements.* Three types of experimental measurements have been utilized to derive information on noble-gas mobility in UO_2 . The first type of measurement has been performed in-pile in apparatus described by Markowitz, Koch, and Roll.¹⁵ In this apparatus volatile fission products are swept from the surface of specimens contained within a furnace located in the Brookhaven pile to external liquid-nitrogen-cooled charcoal traps by means of a circulating helium carrier gas. The trapped fission-product gases are subsequently aliquoted, and the release rate is determined on the basis of trapping time and gamma spectrometric analysis of 78m Kr^{87} and 9.13h Xe^{135} .

Experiments have also been performed in which samples of UO_2 after irradiation are heated at known temperatures and the evolved gas is trapped, aliquoted, and counted. Such experiments have been performed at low temperatures by Susko at Bettis and at elevated temperatures by Booth and Rymer¹⁶ at Chalk River. The isotope detected in these experiments is Kr^{85} . A final series of measurements is being performed by Bostrom at Bettis, who is measuring the solubility and subsequent rate of diffusion of rare gases in UO_2 by saturating the samples at elevated temperatures with the gas, followed by prolonged pumping at room temperature to remove adsorbed gas and that collected in fine voids. Solubilities are measured by dissolving the oxide in acid and collecting the evolved gases. Diffusion rates are determined on identical samples by heating the samples and collecting the gases evolved as a function of time. Analyses are performed mass spectrometrically with a sensitivity of about 2×10^{-6} cc/g. Results obtained from each of these experiments are discussed below.

Experiments conducted by Markowitz are subject to the objection that the emanation rates measured are summations of the rates due to recoils plus those due to diffusion. Elimination of the recoil contribution could be difficult because this may consist not only of recoils stopped in the carrier gas but also those entrapped within the surrounding furnace structure. The first effect was proved to be negligible by measurement of the change of emanation rate with change in pressure of the helium carrier gas; results obtained indicated that such contributions could be neglected. To determine the magnitude of the latter effect, specimens of the same geometric surface area but fabricated to different densities were measured over a series of temperatures. The results obtained are plotted in Fig. 8 and are tabulated in Table 6. It is apparent that, even though the geometric surface area and hence the recoil contribution remained constant as the oxide density was varied from 92 to 97 per cent, the emanation rate increased approximately linearly with surface area (as determined from Fig. 7). To correct for recoil contributions, it was assumed that the emanation rate from diffusion varied directly in proportion to the real surface area and that, for each of the temperatures and densities investigated, a subtractive factor of emanation rate due to recoils should be determined such that the diffusion emanation rate will be directly proportional to the surface area. The subtractive factor for each temperature was found by comparing the emanation rates for lower densities with that of specimen 5 of 97.5 per cent density. The recoil contributions thus estimated are listed in Table 5. Diffusion coefficients were calculated from these data from the relation:

$$D = \frac{1}{\lambda} \frac{\gamma a^2}{3} \quad (2)$$

where D = diffusion coefficient, cm^2/sec

γ = emanation rate (amount of nuclide released/amount of nuclide present $\times$ sec)

λ = decay constant, sec^{-1}

a = radius of equivalent sphere in cm

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Table 6—IN-PILE FISSION-GAS-RELEASE EXPERIMENTAL DATA

Spec. No.	% U ²³⁵	Density (% theo.)	Mass, g	Surface area, cm ²		Powder type
				Geom.	BET	
5	8.19	97.5	6.26	4.49	70*	EUR ball milled
6	8.19	96.5	3.76	3.24	150	EUR as received
7	8.19	94.2	3.64	3.24	365	EUR as received
8	8.26	91.8	3.70	3.32	565*	EUR reoxidized
9	8.26	93.1	3.84	3.39	410*	EUR reoxidized
Isotope	Temp., °C	Spec. No.	R ⁰ × 10 ⁻⁵ , sec ⁻¹	R ⁰ /M × 10 ⁻³ , g ⁻¹ sec ⁻¹	ν × 10 ⁹	ν × 10 ⁹ (recoil)
Kr ⁸⁷	100	5	0.26	4.15	3.70	1.081
		6	0.469	12.5	11.2	
		7	0.344	9.45	8.45	
		8	1.94	52.4	46.6	
		9	0.663	17.2	15.2	
	350	5	0.324	5.16	4.66	1.871
		6				
		7	0.473	13.0	11.6	
		8	1.57	42.4	37.7	
		9				
	550	5	0.712	11.4	10.6	5.8
		6	2.01	53.5	48.3	
		7	0.818	22.1	19.7	
		8	1.93	52.1	46.4	
		9				
Xe ¹³⁵	100	5	1.65	26.4	1.45	0.8
		6	1.25	33.2	1.865	
		7	1.035	28.4	1.56	
		8	6.45	174	9.67	
		9	3.1	80.7	3.95	
	350	5	1.45	23.1	1.29	0.605
		6				
		7	1.078	29.6	1.62	
		8	6.14	166	9.20	
		9				
	550	5	2.53	40.4	2.26	1.444
		6	1.64	43.6	2.44	
		7	1.29	35.4	1.94	
		8	5.32	144	8.00	
		9				

* Estimated from Fig. 7.

It may be noted from Fig. 8, as additional evidence for the minor recoil contribution, that the emanation rate differs quite markedly for xenon and krypton, whereas this factor, which is corrected for the amount of each nuclide formed, should be constant if direct recoils were the source of release.

The experimental observations of Booth and Rymer and of Susko on release of Kr⁸⁵ from irradiated UO₂ specimens heated at elevated temperature for a given length of time are listed in Table 7. The data of Booth and Rymer were obtained from specimens prepared from ammonium diuranate precipitated powders, whereas those of Susko were derived from measurements performed on sintered MCW oxide pellets. Again, as in Tables 5 and 6, the marked effect of sintered density on rate of release may be noted. The diffusion coefficients were calculated from the data in Table 7 utilizing the expression for diffusion from a sphere of

Table 7 — ANALYSIS OF FISSION-PRODUCT RELEASE DATA (Kr⁸⁵)
FROM IRRADIATED UO₂

Density (% theo.)	Radius of equiv. sphere, cm	Temp., °C	Heating		D, cm ² /sec
			Time, hr	Fractional release	
75.2	9.45×10^{-5}	1400	4	0.24	3.59×10^{-15} *
85.3	3.97×10^{-4}	1400	4	0.29	9.65×10^{-14} *
89.9	9.35×10^{-4}	1400	4	0.22	2.89×10^{-13} *
96.4	7.29×10^{-3}	1400	4	0.06	1.062×10^{-12} *
96.7	8.2×10^{-3}	1400	4	0.02	1.312×10^{-13} *
97.2	1.039×10^{-2}	1400	4	0.02	2.11×10^{-13} *
85.3	3.97×10^{-4}	1600	4	0.50	3.39×10^{-13} *
89.9	9.35×10^{-4}	1600	4	0.36	8.75×10^{-13} *
95.4	4.54×10^{-3}	1600	4	0.16	3.43×10^{-13} *
80	1.74×10^{-4}	250	2	0.00026	2.28×10^{-20}
		600	5	0.00027	0.985×10^{-20}
		1000	5	0.00094	1.183×10^{-19}
91	1.28×10^{-3}	250	1.5	0.000071	1.22×10^{-19}
		600	6	0.00073	3.23×10^{-18}
		1000	6	0.00076	3.51×10^{-18}
91	1.28×10^{-3}	370	2.5	0.0003	1.3×10^{-18}
		600	8	0.0003	9.07×10^{-19}
		1000	5.5	0.0026	4.46×10^{-17}
95	4.32×10^{-3}	250	100	0.0000033	4.72×10^{-22}
		600	24	0.000091	1.391×10^{-19}
		1000	24	0.00051	4.37×10^{-18}
91.8	1.52×10^{-3}	1000	48	0.0003	0.94×10^{-19}
92.6	1.88×10^{-3}	1000	48	0.0005	3.97×10^{-19}
92.2	1.67×10^{-3}	1000	48	0.0004	2.02×10^{-19}
91.7	1.51×10^{-3}	1000	48	0.0002	4.15×10^{-20}

* Data from reference 16.

constant initial concentration,¹⁷ the sphere size being chosen for each particular specimen density from Fig. 7. Note that at each temperature the effect of density could be reasonably well accounted for on the basis of this assumption.

The diffusion coefficients for each of these experiments were averaged at each temperature and are plotted in Fig. 9 as the logarithm of diffusion coefficient vs. $1/T^\circ\text{K}$. Although the scales on both abscissa and ordinate are quite condensed, reasonable agreement may be noted between the various types of experiments. It may be noted that the data appear to indicate two activation energies for the release of fission gases, those at high temperatures showing an activation energy of about 100,000 cal/mole and those below 1000°C showing a very low activation energy of less than 1000 cal/mole. It is unfortunate that none of the sets of data included the 1000°C range so that the reality of this break could be more firmly established.

(d) *Solubility of Noble Gases in Uranium Dioxide.* The inference was drawn from these data that, if xenon and krypton were indeed mobile in the UO₂ lattice, it might be possible to observe solubility of the rare gases in UO₂ by heating specimens of the latter at elevated temperatures in rare-gas atmospheres. Such experiments have been performed by Bostrom as indicated above with the noble gases helium, neon, argon, krypton, and xenon. The preliminary data obtained by Bostrom are listed in Table 8, and it may be noted that, both for sintered pellets and for UO₂ powder 0.15 μ in diameter prepared by ammonium carbonate precipitation of ammonium diuranate, the solubility of helium and neon was measured. Precautions taken in these experiments included pumping for long periods at low temperatures after gas absorption at high temperatures and conducting measurements in equipment different from that in which the gas absorption was conducted, to ensure that the results would not be confounded

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Fig. 8—Emanation fraction as a function of surface area.

Fig. 9—Diffusion rates of oxygen, xenon, helium, uranium, and krypton in UO₂. O, Kr⁸⁵ (Booth and Rymer; postirradiation). ○, Kr⁸⁵ (Susko; postirradiation). Φ, Kr⁸⁷ (Markowitz; in-pile). Δ, Xe¹³⁵ (Markowitz; in-pile). Δ, helium (Bostrum; solution).

Table 8a—SOLUBILITIES OF VARIOUS GASES IN UO_2 POWDER (0.15- μ DIAMETER)

Gas	Temp., °C	Time, hr	Pressure, atm	Measured gas content, $\text{cc/g} \times 10^{-4}$
Helium	800	4	1	1.2
	800	8	1	2.3
	800	16	1	2.4
	800	24	1	2.4
	800	36	1	2.5
	800	64	1	2.3
	800	16	$\frac{1}{2}$	0.45
	800	64	$\frac{1}{2}$	0.79
	1000	4	1	1.1
	1000	8	1	1.1
	1000	16	1	1.1
	1000	40	1	1.1
	600	48	$\frac{1}{2}$	0.18
	600	64	1	0.15
	600	48	2	0.52
Neon	1000	24	1	~0.03
Argon	1000	24	1	0
Krypton	1000	24	1	0
Xenon	1000	24	1	0

Table 8b—GAS RELEASE RATES FROM SAMPLES ANNEALED IN GAS
(24 Hr at 1000°C + 24 Hr in Vacuo at 300°C)

Gas	Sample	Temp., °C	Time, min	Gas evolved, cc/g	Remarks
Helium	5 5-g pellets	1100	1000	$\sim 5 \times 10^{-6}$	
	5 5-g pellets	1100	1000	$\sim 1 \times 10^{-5}$	Pellets cracked after 400 min
	0.15- μ powder	1100	420	$\sim 0.5 \times 10^{-4}$	
	0.15- μ powder	1100	865	1.0×10^{-4}	$D = 1.2 \times 10^{-15} \text{ cm/sec}$
Neon	5 5-g pellets	1100	650	$\sim 2 \times 10^{-6}$	
	5 5-g pellets	1100	400	$\sim 1 \times 10^{-5}$	
	0.15- μ powder	1100	560	1×10^{-5}	Approx. $\frac{1}{2}$ of total neon in sample; evolution rate is 0 at 560 min

by adsorption of gases, their inclusion in voids, or their absorption in glass parts which had been exposed to the noble gases at elevated temperatures. The data indicate solubility of about 10^{-6} mole fraction for helium at 1000°C and about double this amount at 800°C. The data further indicate that the solubility of helium is approximately proportional to the pressure, at least at 800°C. The rate of diffusion, which was measured at 1100°C, followed with a high degree of exactness the diffusion kinetics from a sphere 0.15 μ in diameter and of constant initial concentration. Neon also appears to be soluble in the powder to an estimated amount of about $\frac{1}{30}$ that of helium. Experiments conducted in similar fashion using xenon, krypton, and argon indicated no measurable solubility.

These observations would appear to be at variance with the experiments of Rayleigh,¹⁸ who was unable to observe permeability of noble gases through crystals such as quartz, mica, calcite, fluorite, rock salt, selenite, and beryl. Most of these crystals are compounds of elements capable of assuming only one valency state, and their homogeneity range would be ex-

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pected to be very restricted compared with that of UO_2 . The ability of UO_2 to dissolve noble gases may therefore be a specific property of this lattice structure and related to the existence of UO_2 over a wide homogeneity range.

The one value of diffusion coefficient obtained from these measurements is plotted in Fig. 9 and may be noted to be in fair agreement with diffusion rates of xenon and krypton in irradiated UO_2 .

In a fuel-element geometry such as that of the PWR Core 1 fuel rod, the released gas would exist at a relatively low partial pressure, at least under conditions of low burn-up and low gas release rates; but, in fuel-element geometries of less stable configuration such as an unbonded plate in which the cladding could exert system pressure upon the released gas, it might be anticipated that the gas pressure developed might be large enough to increase the solubility of the gases in the oxide and hence decrease the release rates. However, if the solubility measurements for helium reported in Table 8 are representative of those which might be encountered in the case of fission gases, it can be seen that the increased solubility due to increase of pressure would be insignificant compared with the concentration of gas formed at any appreciable amount of burn-up and that hence the increased pressure would be expected to exert only a negligible effect on volatile fission-product release.

(e) *Discussion.* In an earlier publication¹⁹ the variation of diffusion coefficient with temperature for fission gases was presumed to be that shown by the dotted line in Fig. 9. This assumption yielded fairly satisfactory agreement between calculated amounts of fission-product release in experimental fuel rods and those actually observed. However, the more accurate data of Markowitz, as well as a better correlation of the actual temperatures encountered during in-pile operation in experimental fuel rods, revealed that this initial assumption was probably seriously in error. Therefore, utilizing the curve for variation of diffusion coefficient with temperature shown in Fig. 9 with activation energies of 100,000 cal/mole above 1000°C and 850 cal/mole below 1000°C, a recomparison was made of the amount of fission-gas release calculated on the basis of a diffusional mechanism of evolution with that experimentally observed by puncturing fuel rods after their irradiation and collecting the Kr^{85} evolved. Because of the relatively large size of these samples and the relatively high fluxes at which they were exposed, a considerable temperature gradient existed from the center to the outside of the fuel pellets. This temperature gradient was calculated from the known values of heat flux utilizing values of thermal conductivity of UO_2 listed in reference 20. The fuel-rod diameter was then divided into five equal-volume segments, and the temperature was considered constant through each segment. The fraction of fission-gas release was calculated for each segment from the D values of Fig. 9 by utilizing the following formula derived by J. M. Markowitz for diffusion from a sphere with a constant distributed source:

$$F = 1 + \frac{6}{\pi^2 \gamma^2} \sum_{n=1}^{\infty} \frac{1}{n^4} (e^{-n^2 \pi^2 \gamma^2} - 1) \quad (3)$$

where F = the fractional release

$$\gamma = \sqrt{Dt/a^2}$$

t = time, sec

a = radius of sphere, cm

D = diffusion coefficient, cm^2/sec

Again the sphere of equivalent radius was estimated from Fig. 7 utilizing the measured density of the oxide compact. In Table 5 are tabulated the available measured fractional releases of Kr^{85} together with the calculated values for those experiments in which independent checks of heat flux or center temperature were possible. Note that the agreement for all except specimen 79S was within a factor of 3, which is considered very reasonable in view of the uncertainties connected with the values of thermal conductivity, heat flux, diffusion coefficient, and the measurement of the experimental amounts of release.

It may thus be concluded that the experimental observations appear to be quite consistent with a diffusional mechanism of fission-product release. If this mechanism is correct, the

amounts of fission gases released will be very sensitive to the density of the oxide, since this will control the length of diffusion path (from Fig. 7), time of irradiation, and temperature of irradiation.

The variation of diffusion coefficient with temperature shown as a dotted line in Fig. 9 had originally been assumed primarily on the basis of measurements made of the diffusion coefficient of oxygen ions in UO_2 both by surface oxidation and by isotopic exchange techniques. These measurements are discussed by Belle and Lustman⁴ and are shown plotted in Fig. 9. Although it appears tempting to correlate the mobility of fission gases with that of oxygen ions, primarily because of the fluorite structure of the oxide and the consequent large interstitial gap at the center of the unit cell which appears structurally highly suitable for mobility of excess ions, it may be seen from Fig. 9 that the experimental data do not lend themselves to this assumption. On the other hand, experimental measurements⁴ of the self-diffusion coefficient of uranium ions in UO_2 appear to correlate much better with the high-temperature leg of the Arrhenius plot. It may thus be tentatively concluded that at elevated temperatures fission gases have the mobility of cations and diffuse by a similar mechanism, whereas at temperatures below 1000°C other diffusional mechanisms operate.

Additional light is shed on these observations by measurements of emanation of thoron from alpha Al_2O_3 by Gregory and Moorbath²¹ and by additional measurements reviewed by Jost.²² In these experiments, mixtures of the oxides under investigation with radiothorium were made, and the emanation rates of radon isotopes were correlated with the diffusion coefficient of radon in the oxide following the treatment of Flugge and Zimens.²³ Such experiments do, in fact, reveal a variation of diffusion coefficient with temperature entirely similar to that shown in Fig. 9. The breaks in the curves shown by Gregory and Moorbath coincide for a number of different oxides with the "Tammann" temperature given by 0.51 times the melting temperature. Although a temperature of 1000°C is appreciably less than this value for UO_2 , the data are consistent with such an explanation, considering their varied origin and scatter.

Jost²² has related the high-temperature portion of the curve with diffusion under conditions where an equilibrium rate-of-disorder characteristic of the temperature of diffusion is maintained. The activation energy for diffusion therefore consists of both the energy required to secure mobility and the energy required to form defects (in the case of UO_2 , apparently cation defects). The low-temperature leg of the curve has been correlated with the mobility of foreign substances through defects frozen in at the Tammann temperature, and the activation energy therefore consists only of the energy barrier for mobility. Gregory and Moorbath show a difference between the activation energies for thoron in many oxides almost as great as that shown for fission gases in UO_2 in Fig. 9.

If the low-temperature activation energy indeed consists only of the energy required to diffuse foreign atoms and if the rate is controlled by, and the actual value of diffusion coefficient is hence sensitive to, the number of structural defects present in the material, one would anticipate an appreciable effect of irradiation at low temperatures on the diffusion rates observed. However, as noted in Fig. 9, the in-pile data of Markowitz appear to be entirely consistent with those obtained by Susko by heating samples out-of-pile after their irradiation. It appears probable, therefore, that the defect concentration introduced into the latter samples by the prior irradiation was sufficiently stable that agreement between the two sets of values was obtained. The inference may be drawn from the relative positions of the xenon and krypton diffusion rates that their mobility is a function of atom size and that the smaller krypton atom diffuses at a higher rate than the larger xenon atom.

As discussed by Belle and Lustman,⁴ Padden has shown that, in spite of the observations of extended surface area in high-density compacts, most of the porosity is closed and entirely contained within the solid oxide. In the 95 per cent dense oxide the average pore diameter (based on mean area of pore) is approximately $2\ \mu$. The surface area of such pores is, in a compact of 95 per cent density, approximately equal to that measured in Fig. 7 by gas-adsorption techniques. It is therefore to be expected that if such pores are not connected to the external surface of the compacts, the rate of release of gas to the closed pore volume should be approximately equal to the rate of release of gas from external surfaces. Additional

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light is thrown on this possibility by consideration of experiments by Barnes and Mazey,²⁴ who found that natural crystals of thorianite containing large volumes of helium released by natural radioactive decay decrepitated quite violently when heated to temperatures of about 950°C. It can be estimated, if the diffusion rates of helium in thorianite are similar to those of xenon and krypton in UO_2 , that practically all the helium produced will have collected in flaws between the fragments of the sizes shown by Barnes and Mazey and that the decrepitation upon heating would consequently be caused by expansion of the gas upon heating. The observation that irradiated UO_2 samples, even when exposed at temperatures close to the melting point, do not fragment may be related to the much lesser amounts of gas produced even at quite high burn-ups and to the shorter exposure times. Likewise, if equilibrium solubility exists between the gas and the matrix, it would be anticipated that, within the fuel-element cladding, the gas pressure over the external surface will tend to equalize with that contained within the closed pores. If such an explanation is correct, it may be possible to increase the gas-retention properties of UO_2 bodies by providing a structure in which the free surface is quite small and the volume of closed porosity is relatively large.

The question may be raised as to whether the mobility properties of fission gases with UO_2 are indeed material properties or whether the release of gases occurs by mechanisms independent of the particular nature of the matrix. Some preliminary information on this was obtained by Markowitz in the Brookhaven in-pile experiment in which he compared the release rates from UO_2 with those obtained from compacts of the same gross density of Al_2O_3 -21 wt. % UO_2 and ZrO_2 -13 wt. % CaO -17 wt. % UO_2 . The Al_2O_3 and ZrO_2 are two-phase systems with, in the first case, 9 vol. % UO_2 dispersed as small particles in a matrix of pure Al_2O_3 and, in the second case, approximately equal volumes of ZrO_2 -rich and UO_2 -rich phases. The results of this investigation are shown in Fig. 10. It may be noted first that the emanation rate from each of the oxides Al_2O_3 and ZrO_2 is greater than that from UO_2 , maximum emanation being shown by the ZrO_2 -base ceramic. It may further be noted that the apparent temperature coefficient of release is largest for the ZrO_2 -base ceramic, intermediate for the Al_2O_3 , and

Fig. 10—Emanation of Kr^{87} from various oxide fuel materials.

least for the UO_2 . It should finally be noted that, if the recoil range is assumed inversely proportional to density and proportional to the square root of atomic mass, the emanation rates observed should be almost the same for these materials or, if anything, in almost inverse relation to that shown in Fig. 10. It can therefore be concluded that fission-product release is indeed a material property and therefore susceptible to treatment by diffusion-theory systematics.

(f) *Application of Fission-product-release Data.* If indeed it will be possible eventually to establish that the mechanism of gas release is by diffusion and if the pertinent material properties are firmly established, it should be possible to apply such data to prediction and design of fuel elements, at least with respect to those properties sensitive to gas release, on a sounder foundation than empirical test observations. An attempt is made below to utilize such reasoning in the calculation of pressures developed at extended burn-ups in the fuel-element geometry shown in Fig. 1. For these calculations the variation of the diffusion coefficient at temperatures shown as the dotted line in Fig. 9 was assumed. The calculations were performed for two oxide densities, namely 94 per cent (PWR Core 1 reference density) and 96 per cent (showing from Fig. 7 twice the equivalent spherical radius of a 94 per cent dense pellet). It was assumed in this calculation that no free volume was available for containment of the gases and that they accommodated themselves within the tubing by plastic deformation of the tubing. Two cases were calculated, namely, that existing under the condition of operation of 2000 psi external pressure and that occurring during system depressurization and an assumed fuel-element temperature of 750°F. The amount of fission gas released was calculated for each of the several cases considered by dividing the oxide volume into five equal regions of varying temperatures as was done previously in comparing the experimental and calculated values of fission-gas release; where temperatures above the melting point of UO_2 resulted, it was assumed that all gas was released from molten regions. The results of the calculations of the pressures developed are shown in Fig. 11, whereas the cladding strains are plotted in Fig. 12 for the two densities considered and for UO_2 burn-ups of 3000, 10,000, and 50,000 Mwd/ton.

It may be noted in Fig. 11 that with increasing surface heat flux, the pressures first decrease. This arises from the fact that less time is required to achieve the burn-ups noted with increasing surface heat flux, and therefore less gas is evolved. As the heat flux increases still further, the rise in fuel-element temperature increases both the average temperature of the gas and the diffusion rate of gases in the oxide. Hence the pressures developed increase. As the heat flux rises still further, the weakening of the cladding, because of its increased diameter, becomes sufficiently marked that the internal pressures again decrease. Note that the internal pressures in the depressurized condition are, as would be expected, about 2000 psi below those in the pressurized condition except at high amounts of cladding strain.

The variation of cladding strain with heat flux shown in Fig. 12 is similar to that of internal pressure except that the strains vary to a relatively minor extent between cold depressurized and hot pressurized conditions. Furthermore, after the initial decrease in strain with increasing surface heat flux, the cladding strains continue to increase as more and more gases are evolved and as the gas temperature is increased with increasing surface heat flux.

The internal pressures developed under all conditions are well below the bursting pressures of 8300 to 11,000 psi found by internal pressure bursting tests on Zircaloy-2 tubing at 700°F (note that the effective bursting pressure of the tubing is the difference between internal and external pressures). However, although fuel-element performance does not appear to be pressure limited, strains in the cladding may well limit the ultimate performance capabilities of the fuel element. If the limit of strain to which a thin-walled cylinder under internal pressure can be subjected is chosen as half the uniform strain at the ultimate tensile strength,²⁵ it may then be noted in Fig. 12 that, at a 50,000 Mwd/ton burn-up, a PWR Core 1 type fuel element would be limited to a surface heat flux of about 300,000 Btu/hr/sq ft or a burn-up rate of less than 1 Mwd/ton/hr. Of course, such burn-up capabilities are far in excess of those required by the present PWR core design.

It may be observed in both Figs. 11 and 12 that, at the same heat flux, appreciably lower pressures and strains are developed the higher the oxide density. This arises solely from the

Fig. 11—Pressure developed within PWR fuel rods (no expansion space).

Fig. 12—Plastic strain developed in PWR cladding (no expansion space).

decreased interconnected porosity and hence increased diffusion path illustrated in Fig. 7. In fact, the density of 96 per cent was chosen for calculation to illustrate the effect of doubling the diffusion path encountered with the PWR Core 1 reference density of 94 per cent. The pressures and plastic strains developed can, of course, be markedly decreased by providing within the fuel-element cladding free space into which the gases evolved can expand. It can be estimated that, in order to keep the pressures within the fuel element to less than 5000 psi, a maximum free space during hot operation of 0.0016 in. per $9\frac{1}{2}$ in. of length is required for 3000 Mwd/ton operation, 0.096 in. at 10,000 Mwd/ton burn-up, and 0.81 in. for 50,000 Mwd/ton burn-up. By provision of such free expansion space, the limitation on performance of cylindrical oxide fuel elements imposed by release of gaseous fission products can be reduced to any desired extent.

4.2 X-ray Effects of Irradiation

(a) *Introduction.* Considerable work has been reported on the effects of irradiation on the structure of ionic, covalent, and metallic crystals. Such work was reviewed by Crawford and Wittels²⁸ and by Billington²⁷ at the Geneva Conference. On fast-neutron irradiation of non-fissionable ionic solids, marked decreases are reported in density, and the relative lattice parameters of noncubic crystals change appreciably. These changes were correlated by the observation that the following cation-oxygen bonds were decreasingly less stable under irradiation and also decreasingly ionically bonded in the following order: (1) BeO₂, (2) AlO₂, (3) ZrO₂, and (4) SiO₂. Wittels and Sherrill²⁸ have recently found that monoclinic ZrO₂ reverts to the cubic fluorite form upon fast-neutron bombardment. The formation of the "metamict" state in zircon crystals by alpha-particle bombardment in radioactive deposits has long been noted. Likewise, natural fluorite crystals deposited in the neighborhood of secondary uranium minerals have been shown by Berman²⁹ to exhibit appreciable line broadening and other property changes which can be annealed out at temperatures beginning at 175°C. The observations, particularly on irradiation of oxides, indicate that relatively permanent damage could be produced by fast-neutron irradiation, which can be annealed out only at elevated temperatures, and that, depending on the particular components of the crystals, the severity of damage could vary widely. For these reasons Roof and Eichenberg³⁰ have compared the X-ray structural changes occurring in uranium oxides upon fissioning.

(b) *Experimental Methods.* Four types of oxides were prepared: MCW UO₂, which exhibits relatively fine particle size and coarse crystallite size; high-pressure steam oxidized UO₂ made by reaction of uranium and steam at 343°C and 2200 psi, which exhibits relatively large particle size but quite fine crystallite size; U₄O₉ prepared by controlled oxidation of MCW UO₂ at 160°C and subsequent annealing for 2 weeks at 800°C; and finally U₃O₈ prepared by oxidation of MCW UO₂ at 800°C followed by a 2-week anneal at this temperature. Samples were examined as prepared, as annealed for 2 weeks at 400°C to simulate the thermal effects of irradiation, and as irradiated in the MTR to a maximum thermal-flux exposure of about 3×10^{19} nvt. Two levels of irradiation were examined; one was at 50 to 60 Mwd/ton, and the other was at 90 to 100 Mwd/ton.

Samples were examined after irradiation on the double-crystal spectrometer using $K_{\alpha_1+\alpha_2}$ irradiation. The X-ray results were interpreted in terms of changes in lattice parameter, changes in temperature coefficient of intensity (which can be correlated with the average displacement of an atom due to bulk temperature), and change of diffraction-peak half width. The latter was accomplished by Fourier analysis of the diffraction peaks.

(c) *Experimental Results.* The results of this analysis are listed in Table 9. It may first be noted that a small but quite definite change in lattice parameter was noted upon irradiation of the powders having the fluorite structure. The lattice-parameter increase appeared to amount at the most to about 0.05 per cent at these irradiation levels and to show no marked dependence upon irradiation level. The temperature coefficient, or the average thermal displacement derived from this term, appeared in each case to diminish. The most marked effects were noted in comparison of line broadening. By comparing Figs. 13 and 14 for MCW UO₂ before and after irradiation, respectively, with Figs. 15 and 16 for the U₃O₈ samples before and

Table 9—SUMMARY OF DATA ON URANIUM OXIDE POWDER SAMPLES

Material	Sample	Condition	Burn-up Mwd/ton	Calcu- lated average temp., °C	Lattice constant, A	Average thermal displacement, A	Crystallite size, A
MCW UO ₂	MR-2A	Control			5.4676 ± 0.0009	0.093 ± 0.005	900 ± 115
	3	Heat-treated*			5.4685 ± 0.0009	0.092 ± 0.006	1000 ± 140
	2	Irradiated	60	65	5.4677 ± 0.0005	0.081 ± 0.009	255 ± 40
	1	Irradiated	104	80	5.4697 ± 0.0006	0.074 ± 0.008	250 ± 35
High-pressure, steam-oxidized UO ₂	NOH-20	Control			5.4667 ± 0.0032	0.118 ± 0.018	180 ± 18
	13	Heat-treated*			5.4686 ± 0.0017	0.092 ± 0.007	155 ± 15
	12	Irradiated	52	60	5.4709 ± 0.0009	0.052 ± 0.013	255 ± 40
	11	Irradiated	90	75	5.4706 ± 0.0021	0.074 ± 0.008	330 ± 60
UO _{2.23}	MO-23A	Control			5.4429 ± 0.0009	0.128 ± 0.006	360 ± 75
	23	Heat-treated*			5.4426 ± 0.0009	0.123 ± 0.006	300 ± 50
	21	Irradiated	60	65	5.4459 ± 0.0011	0.115 ± 0.011	147 ± 12
	22	Irradiated	104	80	5.4456 ± 0.0012	0.128 ± 0.007	140 ± 12
UO _{2.67}	M3A	Control			a, 6.7033 b, 11.9344 c, 4.1375		380 ± 80
	33	Heat-treated*			a, 6.7232 b, 11.8661 c, 4.1380		180 ± 20
	31	Irradiated	52	60	None available		120 ± 10
	32	Irradiated	90	75	None available		125 ± 10

* Heat-treated control samples were sealed in helium-filled Zircaloy-2 capsules, identical to the capsules utilized for the irradiated samples, and heat-treated for 2 weeks at 400°C.

Fig. 13—Typical UO_2 diffraction peak obtained on the double-crystal spectrometer. Full line is slow-traverse (5 min/ 1° 2θ) trace; points represent statistical count with 1.2 per cent error. Unirradiated MCW UO_2 , 531 reflection.

Fig. 14—Typical UO_2 diffraction peak obtained on double-crystal spectrometer. MCW UO_2 irradiated to 104 Mwd/ton exposure, 531 reflection. For damage caused by exposure to neutron bombardment, compare with Fig. 13.

Fig. 15—X-ray diffraction pattern of U_3O_8 prior to irradiation; obtained on the double-crystal spectrometer.

Fig. 16—X-ray diffraction pattern of U_3O_8 after irradiation corresponding to 84 Mwd/ton. For damage caused by neutron bombardment, compare with Fig. 15.

after irradiation, note that the latter was much more profoundly affected than the former. The more expanded 2θ scale used for plotting the UO_2 results, as well as the higher reflection angles examined, should be borne in mind in comparing these figures. No diffraction peaks could be resolved for irradiated U_3O_8 at high 2θ angles, and for this reason no conclusions can be drawn concerning change in lattice parameter.

(d) *Discussion.* By comparison of the crystallite sizes before and after irradiation in Table 9, it is apparent that, irrespective of initial crystallite size, the materials tend to approach the same size after irradiation. This effect may be related to the disordering of the lattice by fission or displacement spikes and subsequent reordering upon the matrix lattice. It can therefore be anticipated that the crystallite sizes shown should be related in some constant manner to the size of the fission or displacement spike as well as to the ability of the material to reorder upon cessation of the fission event. In this way the increase in crystallite size of the initially finely crystalline steam oxidized UO_2 could be correlated with the diminution of crystallite size observed in the other oxides. Note that the disordering effect of even such slight exposures should be quite profound in fissionable materials; thus it is reported³¹ that an irradiation of as little as 19 Mwd/ton is sufficient to homogenize metal-concentration gradients in transformed gamma-phase uranium-molybdenum and uranium-niobium alloys over 3000 Å spacings.

The changes in lattice constant and average thermal displacement are considered to be too large and too sensitive to exposure to be accounted for by a fission-product contamination effect. It is believed more likely that the effects observed are due to atom displacements similar to those noted previously upon fast-neutron irradiation of nonfissionable oxides. If this is indeed the explanation, the much smaller magnitude of the effects noted here than those reported by Crawford and Wittels²⁶ should be noted and cited as evidence for the high degree of stability of the fluorite structure materials.

However, on the same basis, the apparent low degree of radiation stability of orthorhombic U_3O_8 should be noted. Warren and Averbach³² showed that, by plotting the Fourier coefficients of the real terms of the diffraction peaks against the term number, the damage may be interpreted in terms of particle-size reduction if the early portion of the curve is linear or in terms of microstresses if the early portion of the curve is concave. In the former case the mean particle size may be related to the slope of the line, and in the latter case the initial curvature may be related to the mean square strain. As shown in Figs. 17 and 18 for steam oxidized UO_2 and for U_3O_8 , respectively, the line broadening appears by this interpretation to be due in the former case to reduction of crystallite sizes and in the latter case to microstresses.

It appears, from these results and from the observations on the reversion of monoclinic ZrO_2 to the fluorite structure upon fast-neutron irradiation, that the fluorite structure possesses a high degree of irradiation stability and that little extensive permanent damage is to be anticipated. On the other hand, U_3O_8 with its orthorhombic structure is readily damaged even at slight irradiations. This increased stability of UO_2 is clearly evident from its chemical properties; UO_2 can be reduced only with difficulty to lower oxidation states, indicating the considerable stability of the U^{+4} -oxygen bond. On the other hand, U_3O_8 can be readily reduced at temperatures above 650°C in 1 atm oxygen pressure.

4.3 Microstructural, Dimensional, and Property Changes upon Irradiation

No microstructural changes have been noted upon irradiation of UO_2 other than those which could be interpreted by purely thermal effects. Thus grain growth is noted, as will be discussed later, at temperatures in-pile corresponding to those which have been noted out-of-pile. Gross thermal fracture of specimens has been noted under conditions anticipated from the imposed thermal gradients and physical properties of the oxide. No additional voids, microcracks, etc., have been observed which can be unambiguously attributed to irradiation or to fission-product contamination at the exposure levels explored. Likewise, no additional sintering has been observed beyond that anticipated from temperatures obtained in-pile.

No physical-property measurements that have been conducted either during or after irradiations are known to the writers. The marked effect of irradiation on the thermal conductivity

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Fig. 17 — Fourier coefficient $\beta_{R(n)}$ vs. coefficient number n for pure diffraction peak of MCW UO_2 . x, control. o, heat-treated. □, 60 Mwd/ton. Δ, 85 Mwd/ton.

Fig. 18 — Fourier coefficient $\beta_{R(n)}$ vs. coefficient number n for pure diffraction profile of U_3O_8 . x, control. o, heat-treated. □, 48 Mwd/ton. Δ, 84 Mwd/ton.

of ceramics has been reported by Oak Ridge investigators,³³ and it is tempting to believe that failure to correlate the metallographic observations of temperatures attained, discussed in Sec. 5, with fuel-material values may be related to a decrease in thermal conductivity upon irradiation. However, the relatively minor effect of irradiation upon X-ray structure effects discussed above would appear to argue against a major effect of irradiation. Considerably more investigation is required in this field, and experiments are presently being planned to measure in-pile changes in thermal resistance of UO_2 fuel elements upon irradiation.

Likewise, no dimensional changes have been noted in fuel elements irradiated to high burn-ups (of the order of 25,000 Mwd/ton). Such measurements, based upon changes in external dimensions, were relatively gross and would not reveal small density changes. The lattice-parameter changes shown in Table 9 corresponded to density changes of, at the most, 0.006 per cent at 100 Mwd/ton exposure. The difficulty of performing measurements on porous samples remotely has thus far hindered such measurements on high-exposure specimens. However, the gross observations made thus far indicate that changes of density far less than the values of 1 to 4 per cent per at. % burn-up noted in metallic fissionable materials are obtained upon irradiation of UO_2 .

4.4 Thermal Fracture

As shown by experiment WAPD-14-14 (Table 1), it has been noted that UO_2 irradiated to burn-ups up to 25,000 Mwd/ton showed no decrepitation or physical disintegration even though operating temperatures beyond the melting point were tested. It may be inferred from this observation that not only are fission gases released in a mechanically and structurally innocuous manner but also that no degradation of mechanical properties occurs such as to lead to fragmentation by the severe thermal stresses imposed during fuel-element operation. As shown in Figs. 23 and 24, radial cracking is noted in cross sections of pellets irradiated at any appreciable flux. Circumferential cracking may also be noted in Fig. 24. This in general is observed at the border of regions where grain growth is noted and may be caused by increased densification of the center of compacts at this high operating temperature and consequent shrinking of the center from the exterior of the pellets. A certain amount of axial cracking is also observed. However, the amount of cracking appears to be independent of burn-up.

These same fracture patterns are noted in oxide samples thermally cycled between 500 and 1500°F by quenching in molten metal baths, i.e., predominant radial cracks and some axial cracks. Such cracking is usually obtained during the first quenching cycle and appears to be stable thereafter for test cycles up to 10,000, pellets of the dimensions shown in Fig. 1 cracking into four or five pieces. It is inferred, therefore, that thermal stresses, after the initial cracking, are insufficient to cause extensive further fracture.

It can be shown, following the treatment of Timoshenko,³⁴ that the axial and circumferential normal stresses at the surface of a cylindrical pellet (of infinite length), exposed at a uniform heat generation rate q , are related to material and operational factors by the relation:

$$\sigma_t = \sigma_z = \frac{E}{1 - \mu} \frac{\alpha q b^2}{8K} \quad (4)$$

where σ_t = transverse stress

σ_z = axial stress

E = modulus of elasticity

μ = Poisson's ratio

d = coefficient of thermal expansion

q = heat generation rate

b = pellet radius

K = thermal conductivity

Substituting modulus-of-rupture values for UO_2 reported by Belle and Lustman⁴ of 13,000 psi, $\alpha = 5.6 \times 10^{-6}/^\circ\text{F}$, $b = 0.015$ ft, $K = 1$ Btu/hr/ft/°F, $\mu = 0.3$, $E = 21 \times 10^6$ psi, the heat generation rate required to initiate fracture is about 0.3×10^7 Btu/hr/cu ft or about $1/20$ of a reasonable

maximum heat generation rate corresponding to a flux of 500,000 Btu/hr/sq ft in a PWR Core 1 rod. Thus the thermal fracture of pellets is anticipated and has been observed in practically all the tests reported in Sec. 3. That further cracking has not been noted at prolonged burn-ups beyond the gross cracking noted in Figs. 23 and 24 can be cited as evidence for absence of a severe mechanical property damage by irradiation.

It is interesting to note in Figs. 27 and 29 that the thermal fracture observed occurs primarily at grain boundaries, whereas sintered compacts fractured at room temperature show both grain-boundary and transcrystalline fracture.

5 FUEL-ELEMENT PHENOMENA

In this section will be reviewed those phenomena which were revealed as a result of the fuel-element testing program discussed in Sec. 3. Although many of the findings discussed are specific to the PWR Core 1 materials, reactor environments, and fuel-element geometry, it is believed that sufficient information has been generated to permit estimation of performance of unbonded oxide fuel elements under more general conditions of reactor design and operation.

5.1 Heat-transfer Bond Between Clad and Oxide

Early during the development of the conceptual design for the PWR Core 1 blanket fuel element, considerable attention was devoted to the nature of the heat-transfer bond between cladding and oxide. Because of the high melting point of the oxide (discounted to a large extent because of its poor thermal conductivity), consideration could be given to heat-transfer bonds that would be unsuitable in elements containing metallic fuels. Serious consideration was given to radiant heat transfer alone, liquid- or solid-metal conduction, and gas conduction. The first two bonds were rejected in the first case because of the resultant high fuel temperatures and in the second case because of the anticipated difficulty and expense of fabrication and the possible reactions of feasible bonding media with steam and fuel during operation of defective fuel elements or during fuel-element fabrication. A 1-atm pressure helium-gas heat-transfer bond was selected as the best compromise primarily because of the relatively high thermal conductivity of this gas and secondarily because of its ease of incorporation into the fuel element during fabrication processes.

A different approach is reported by Hoenig, Handwerk, Kittel, and Breden,³⁵ who investigated the use of a lead heat-transfer bond between the cladding and $\text{ThO}_2\text{-UO}_2$ pellets and recommended the use of such a heat-transfer bond; the latter recommendation appears to be based primarily on a comparative test at a surface heat flux of 505,000 Btu/hr/sq ft, in which clad failure was noted in the case of fuel elements fabricated with an annulus of 80 per cent helium and 20 per cent argon but no failure with a similar element containing lead in the void space. Failures in all other cases occurred irrespective of the material used in the void space.

Since, as will be shown later, the nature of the bond and the type of gas in void spaces affect profoundly the thermal behavior of fuel rods, it appears appropriate to examine the heat-transfer conditions in a cylindrical fuel-element geometry as affected by the following heat-transfer bonds:

1. Helium at 1 atm pressure in the void space between oxide and fuel.
2. Helium and fission gases released by fuel in the void spaces.
3. Steam.
4. Lead.
5. Lead and fission gases.

(a) *Heat Transfer Through Bond.* To explain the effects of various filling gases, as well as the thermal performance of the fuel elements, a model has been assumed (see Sherman and Sherba³⁶) in which the pellet is centrally located within the cladding surrounded by the gas annulus. This model cannot be physically correct for gas-bonded fuel elements since, as will be discussed further later, there is no trace of asymmetry of heat-affected zones in the pellet

such as surely would be noted due to shift of position of the pellets within the container. Furthermore, since pellets exposed at reasonable heat fluxes all show thermal fracture, during operation the pieces are probably uniformly distributed through the cross section of the fuel element and touch the external cladding, irrespective of initial assembled clearance. It is probable that the qualitative agreement between the assumed model and the experimental observations arises from permeation of the gas in voids, cracks, and gaps in the fuel during operation and that the heat-transfer situation, in the latter case, of random distribution of gas annuli is approximated by the model used, wherein the gas is assumed to be collected between fuel and cladding. This difficulty with the assumed model does not, of course, arise in the case of the solid bond.

The thickness of the heat-transfer gap during operation depends not only on the nature of the heat-transfer medium but also on the initial clearance and operating heat flux; this arises from the change in gap thickness due to thermal expansion of the oxide. It can be shown that, for the case of uniform heat generation in a cylindrical pellet of constant thermal conductivity, the radial gap, C_f , between fuel and cladding during operation is related to the gap, C_i , existing when fuel and cladding are at the same temperature by the relation:

$$C_f = \frac{2C_i - \alpha q b^2 \left(\frac{l}{K_1} + \frac{b}{4K_3} \right)}{2 + \frac{\alpha q b^2}{K_2}} \quad (5)$$

where K_1 , K_2 , and K_3 = thermal conductivities of cladding, heat-transfer gas, and oxide, respectively

α = coefficient of thermal expansion

b = fuel radius

l = clad thickness

q = heat generation rate per unit volume

This relation is shown plotted in Fig. 19 for various initial clearances and use of steam vs. helium as a heat-transfer bond such as might be encountered in defective fuel elements. It is evident that the gap is quite sensitive to each of the factors listed and is, to a large extent, self-rectifying, in that the final clearance tends to become constant irrespective of initial clearance. The self-rectifying nature of the bond is an advantage of the gas bond which is not shared by a solid bond; a particularly unhappy situation can be envisaged in the latter case if gross volumes of the annulus are unbonded and other areas are bonded. Under such conditions, local strains are likely to be developed in the cladding owing to local high fuel temperatures. It is physically unlikely that the gap in Fig. 19 ever completely closes; it is more likely that the thermal resistance due to permeation of gas in pores and cracks approaches some minimum value represented by an annular gap 0.0002 to 0.0005 in. in thickness.

The temperature drops through a 1-mil gap of the various heat-transfer bonds likely to be encountered at a heat flux of 500,000 Btu/hr/sq ft are listed below, estimating the thermal conductivities at 400°C from the values listed in Table 10.

He, 288°F	50% He + 50% (Xe + Kr), 900°F
He + Kr, 5400°F	H, 278°F
Steam, 1490°F	Pb, 2.1°F

Thus, if the thermal performance of the fuel element is considered to be limited by a central temperature at the melting point of the oxide (5000°F) at a surface heat flux of 500,000 Btu/hr/sq ft with an initial radial gap of 0.001 in., an apparent decrease of about 4 per cent in thermal output capabilities would be shown with a helium gap as compared with a solid bond, and a decrease of almost 30 per cent would be shown with a steam gap. This decrease is, however, fictitious because of gap closure, and it can be seen in Fig. 19 from the curves of melting temperature vs. heat flux as a function of clearance that there is little decrease in thermal capabilities of a helium-bonded fuel element with diametral clearances below about

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Fig. 19—Effect of surface heat flux on radial gap between fuel and cladding.

Table 10—THERMAL CONDUCTIVITY OF GASES

Gas	Temp., °F	K, Btu/hr/sq ft	Reference
He	582	0.138	38
Ne	582	0.043	38
A	582	0.017	38
Kr	582	0.0094	38
Xe	582	0.0056	38
H ₂	80	0.10	38
H ₂ O	750	0.029	39

0.005 in. and of an element containing a steam gap below about 0.004 in. Note that this conclusion is valid only if the model upon which Fig. 19 is based is correct and that evidence will be presented below to indicate that it is inapplicable to this situation.

However, as pointed out by Sherman and Frazier,³⁷ it is also obvious from this figure that a heat-transfer medium must be provided to overcome the poor thermal conductivity of the evolved fission gases, xenon and krypton, particularly if, as is probable, the thermally effective gap at operating temperatures does not close completely but corresponds to a value of 0.0002 to 0.0005 in. Under such conditions, it appears probable that marked reductions in thermal capabilities can be realized. Use of helium initially within the fuel-cladding annulus will render the reduction in allowable heat flux somewhat less severe because of the dilution of the poorly conducting fission gases evolved with the better-conducting helium (the thermal conductivity of helium is reduced by argon appreciably more rapidly than is predicted by the rule of mixtures).³⁸ However, in cases where a solid bond is used, no dilution of the evolved gases is possible, and, at least in unbonded areas, if such exist, serious increases in temperature might result. By the same token, it is important in helium-bonded fuel elements to take particular precautions that void spaces are filled with helium during fuel-element fabrication. Sufficient xenon and krypton are evolved from a PWR Core 1 rod at 1 at. % burn-up and 1 per cent gas release to dilute the helium by 50 per cent.

(b) *Cladding Strain.* As discussed in Sec. 4, excessive internal pressures and cladding strains are developed by fission-gas release only at quite high burn-ups and can easily be provided for by increase of free volume within the fuel-element cladding. Likewise, at any suitable heat flux, the differential expansion between fuel and cladding should not lead to excessive strains. In a gas-bonded fuel element, as noted in Fig. 19, initial clearance serves to take up part of the diametral fuel expansion, whereas the longitudinal expansion is uniformly applied to the cladding through load on the end caps shown in Fig. 1. In the Core 1 fuel rods, sufficient axial free space is provided to take up any such longitudinal expansion. In solidly bonded fuel elements, such expansion is applied to the cladding both longitudinally and diametrically; it is considered, therefore, that the use of gas bonding subjects the cladding to less severe service.

One of the factors militating against selection of solid or low-melting bonding layers for PWR Core 1 was the fear of redistribution of the bonding medium through melting and subsequent solidification or by creep under the action of pressure or expansion stresses; note in Eq. 5 or in Fig. 19 that differential expansion leads either to reduction of annulus or to cladding strain. Such redistribution may lead to the application of excessive strains locally in the fuel element; circumferential failure of cladding reported by Hoenig et al.³⁵ for lead-bonded fuel elements may well have resulted from such an effect.

(c) *Eccentricity of Temperature Distribution.* It may be feared that, in a gas-bonded oxide fuel element, shifting of fuel closer to one side of the cladding than to the other could result in an unsymmetrical temperature distribution, excessive local heat fluxes, or deformation of the fuel element by the application of off-center thermal-expansion strains. The magnitude of this effect has not been worked out for cylindrical fuel elements. However, the relation between asymmetrical thermal barriers and the shift of the position of maximum fuel temperature can readily be derived for a flat slab cooled on both sides and is given by the expression:

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$$k^2 \left(\frac{r_1}{2K_3} \right) + k \left(\frac{r_3}{K_1} + \frac{lr_2}{K_2} \right) - \left(\frac{r_3}{K_1} + \frac{r_2}{K_2} + \frac{r_1}{2K_3} \right) = 0 \quad (6)$$

where K_1 , K_2 , and K_3 = thermal conductivities of cladding, heat-transfer gas, and oxide, respectively

$r_1(1 + k)$ = oxide thickness

r_1 = distance from one surface of oxide to point of maximum temperature

r_3 = thickness of cladding

r_2 = thickness of gas bond on one side of plate

lr_2 = thickness of gas bond on other side of plate

Using the various thermal-conductivity values shown in Table 10 and Fig. 19, assuming a heat generation rate in the flat slab corresponding to that in a PWR Core 1 rod operating at a heat flux of 500,000 Btu/hr/sq ft, and substituting 0.0024 in. for r_2 , 0.024 in. for r_3 , and 0.18 in. for r_1 , it is found that, with helium in the gap and a difference of 10 to 1 in gap width on either side of the slab, the maximum-temperature position is shifted from the center line about 4 per cent and that a 7.5 per cent higher heat flux is withdrawn from one side of the plate than from the other. With steam in the gap, the position of maximum temperature is shifted 20 per cent, and 41 per cent higher heat flux is withdrawn from the side with the thinner gap. A change in gap ratio from 10/1 to 2/1 changes the latter values to 9 per cent and 18 per cent, respectively.

Such asymmetrical effects might well be serious in high power density fuel elements; however, as will be shown later, no trace of an asymmetrical temperature distribution has ever been noted in fuel-rod samples even though initial clearances ranging up to 0.008 in. in the diameter have been tested. It is believed that this is further evidence that the redistribution of oxide due to thermal cracking "homogenizes" the fuel through the fuel-element diameter at least on a gross scale and that the thermal properties of the oxide within the fuel element are controlled by gas collection in gaps, cracks, and voids rather than gas conduction through an annulus. Thus one possible major advantage of using a solid rather than a gas bond, namely, centering of fuel, appears to be unnecessary at least in the PWR Core 1 geometry.

(d) *Release of Fission Products.* In a gas-bonded fuel rod, release of fission products from the fuel will exert a uniform internal pressure upon the cladding as discussed in Sec. 4. Since such gases are insoluble in metals, the use of metallic solid bonds will probably not prevent release of fission products from external surfaces. On the contrary, there would appear to be some danger that the use of solid bonds will result in the channeling of evolved gases to preferred regions and the imposition of excessive local pressures.

In defective rods it would appear that the use of a solid bond would offer a real advantage in preventing fission-product release generally from the oxide surface into the coolant. However, as will be shown later, even in gas-bonded rods, fission-product release appears to occur from local regions near the defect except during reactor start-ups and shutdowns and except under conditions of multiple defects such that passage of coolant can occur at least partially through the fuel rod. More restricted release of fission products, however, can certainly be anticipated from the use of solid bonds if such bonds can be maintained during fuel-element operation.

In summary, therefore, it is believed that the use of a helium-gas heat-transfer bond between oxide fuel and cladding possesses many inherent advantages over solid bonds with respect to maintenance of fuel-element integrity. Probable restricted release of fission products from defective fuel elements solid-bonded to the cladding is a major advantage of the latter fuel-element design.

5.2 Thermal Capabilities

It has been possible, by postirradiation examination of certain of the samples in Tables 3 and 4 in which melting or other structural changes occurred in the center of UO_2 fuel rods, to define the limits of thermal performance (based upon centerline melting) of UO_2 under irradiation as a function of fabrication and operation variables. These structural changes were found to occur at heat fluxes lower than those predicted during the initial PWR core design by calcu-

lations based on the Kingery and Vasilos⁴⁰ values for UO_2 thermal conductivity corrected for 95 per cent dense material. The results of these tests correlated better with data from Armour Research Foundation,⁴¹ which indicated lower values for the thermal conductivity of UO_2 .

The specimens involved in these tests were the PWR Core 1 type of blanket rods described in Sec. 3.1 and listed in Table 3. In the specimens under consideration, the original diametral clearance between the pellets and Zircaloy tube was varied from 0.001 to 0.008 in. The cladding of some of the specimens was intentionally made defective by drilling a 0.005-in. hole $\frac{3}{4}$ in. from the end, thus allowing introduction of water (converted to steam in rods at the higher heat fluxes) into the fuel-rod annulus during operation. The normal atmosphere in the fuel rod is helium, introduced during the welding operation. Both the initial diametral clearance and the ambient atmosphere were found to be important in determining fuel-rod center temperatures and center melting.

Most of the specimens involved here were irradiated in the CR-IV X-1 loop located in the NRX reactor operated by AECL at Chalk River, Canada, as part of a joint AECL-USAEC program. This facility was described in Sec. 3. In the X-1-e, X-1-f, X-1-g, X-1-h, X-1-j, and X-1-l tests, five fuel-rod specimens were suspended vertically in a 0.623-in.-I.D. stainless-steel pressure tube. Fission-monitor containers located between the fuel-rod specimens are finned to center the specimens in the pressure tube. The maximum perturbed thermal-neutron flux expected in the X-1 loop is about 3×10^{13} neutrons/cm²/sec. Specimen arrangement and a typical X-1 flux gradient during steady operation are shown in Fig. 20, and operating conditions for individual specimens are listed in Table 3. During reactor start-ups the position of maximum flux shifts upward from the position of specimen 4 to that shown in Fig. 20.⁹ Thus specimens 4 and 5 in each test are subjected to higher fluxes (of the order of 10 to 20 per cent) during reactor start-ups than those shown in Table 3.

For a comparison of natural UO_2 and that enriched to 7.8 wt. % U^{235} in total uranium used in the X-1-f to X-1-l tests, the results of the MTR WAPD-25-2 test are of special interest. This test consisted of two natural UO_2 specimens irradiated in the L-42 position in the MTR at a maximum perturbed thermal-neutron flux of 3×10^{14} neutrons/cm²/sec. Test loop conditions are similar to those for the X-1 tests, except that the specimens were cycled in and out of the high-flux regions. This particular test was designed primarily to study the effects of cycling on the specimens, but the metallographic observations of these specimens are of particular aid in interpreting the results of the X-1 tests.

(a) *Selection of Center Melting as a Thermal-design Limitation.* As may be noted by examination of Table 3, many fuel-rod specimens operated with extensive melting at the center apparently without detriment to the integrity of the fuel element even though deliberate defects were present in the cladding. The question may therefore be raised as to why center melting is taken as a fuel-element design limitation. Various considerations led to selection of this temperature as a valid criterion. Most important of these is the observation of failure directly attributed to center melting in the case of specimens 14-15-100S, 14-15-101S, and X-1-e-3. Of these, the most significant is the behavior of the last specimen which, as shown in Fig. 21, failed in a gross manner shortly after reactor start-up. The volume of molten zone in this specimen may be judged from Fig. 22 and Table 3 to be about 53 per cent. Other specimens, such as X-1-f-4, did not fail even with 42 vol. % molten zone and much longer irradiation times. It thus appears that a critical dimension of molten zone will lead to gross fuel-element failure; no physical basis is known upon which to select a safe amount of melting. It should further be borne in mind that (1) accelerated fission-gas release from elements operating with molten centers (see Table 5) and (2) possible effects arising from dilution of helium with poorly conducting xenon and krypton, as outlined in Sec. 5.1, may lead to an increase of the molten zone with continued irradiation and hence failure sometime during reactor life.

It was initially feared that fuel-element failures would result because of the unknown and possibly high amount of volume expansion of UO_2 upon melting. However, measurements of the volume of the solidification craters (shown in Figs. 23 and 24) compared with measurements of the volume of the melted zones indicate that this expansion is in the range of 1 to 7 per cent. Since, even in 95 per cent dense fuel, sufficient free (pore) volume is present to accommodate such volume expansions without dimensional change, failures upon melting would not be anticipated from this cause.

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Fig. 20—Specimen arrangement and flux gradient in the X-1 loop.

Fig. 21—X-1-e-3 failure.

Fig. 22—Cross section from the lower end of X-1-e-3. (Magnification 6.7 $\times$.)

Therefore, on the basis of failures that have been encountered in cases in which extreme melting was noted, the inability to assign a limit to the amount of melting tolerable, and the deleterious and possibly progressively more serious consequences from the attendant large amounts of fission-gas release, adoption of center melting as a valid limit to fuel-element performance is considered justified until more test and performance data are accumulated.

(b) *Determination of Experimental Heat Fluxes.* The heat fluxes listed in Table 3 are those obtained from calorimetric measurements of the temperature rise of the water through the test section. The total heat output of the loop is proportioned among the various specimens according to their location with respect to the reported neutron-flux gradient. An additional

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Fig. 23—Molten zones and solidification craters in the UO_2 at various locations of the X-1-h-4 specimen. (a) Pellet 1, high-flux end. (b) Pellet 3, high-flux end. (c) Pellet 26, low-flux end. (Magnification 6.6 $\times$.)

Fig. 24 — Molten zones and solidification craters in the UO₂ at various locations of the X-1-h-2 specimen. (a) Pellet 1, low-flux end. (b) Pellet 25, high-flux end. (c) Pellet 26, high-flux end. (Magnification 7.4x.)

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weighting is necessary when the test train contains specimens of differing enrichment, as in X-1-e. Such heat-flux distributions were reported for the X-1-e test by Horsman and Howieson.⁹

Heat-flux values may also be derived from the fission monitors positioned between the specimens in the test train. These monitors consist of 1 to 2 mg of the fissionable material sealed in quartz and contained in a Zircaloy-2 casing. After irradiation the analysis of these monitors for Cs^{137} and Ce^{144} provides a measurement of the integrated number of fissions from which the burn-up, neutron flux, and heat flux at the various locations can be calculated (Table 3).

However, the heat-flux values obtained from the monitors do not directly represent the heat flux from the specimen because of the neutron attenuation that occurs through the cross section of the fuel specimens. In order to determine the magnitude of the suppression for the 7.8 wt. % enriched samples, specimen 4 from the X-1-h test was dissolved in its entirety in the high-level radiochemical facilities at Oak Ridge National Laboratory. An entire nondefective specimen was selected to avoid errors resulting from possible loss due to fractionation of the fission products from the molten zone. Quantitative aliquots of the resulting solution were submitted to three different laboratories for analyses of four representative fission products, Sr^{89} , Y^{91} , Cs^{137} , and Ce^{144} , in order to determine the mean burn-up to which this particular specimen had been subjected in-pile. The mean value for this parameter was based on the results of 26 individual analyses (Table 11). The values of the neutron fluxes correspond to a 40-Mw power level of the NRX. An estimate of the over-all suppression of the neutron flux within the specimen can be made from this result. Assuming that the flux at the surface of the specimen is equal to the flux at the monitors, an average suppression of about 30 per cent was determined from the experimental values (Table 11). Although the fission-product analyses for duplicate specimens were quite consistent within each laboratory for the same nuclide, considerable scatter may be noted between the results both for the various laboratories and for the different nuclides. Therefore, although the results (particularly for cesium and cerium) can be used for comparison with similar analyses performed on fission monitors and hence can indicate correct magnitudes of flux suppression (subject to the objection that

Table 11—TOTAL FISSIONS PER FUEL ROD AND NEUTRON FLUXES
CALCULATED FROM ANALYSES OF IDENTICAL SOLUTIONS
OF X-1-h-4 FUEL

Nuclide	Values used for		Fissions ($\times 10^{-20}$)		
	Fission yield, %	Decay constant, sec^{-1}	ORNL*	NSEC†	Bettis (CTA)*
Sr^{89}	4.8	1.52×10^{-7}	6.82	6.65	7.58
Y^{91}	5.9	1.38×10^{-7}		7.38	11.0
Cs^{137}	6.3	8.14×10^{-10}	9.21	7.84	10.7
Ce^{144}	6.1	2.83×10^{-8}	13.5‡	6.82	9.86
Neutron flux, neutrons/ cm^2/sec					
		Mean§ ($\bar{\phi}$)	From fission monitors (ϕ)	Ratio ($\bar{\phi}/\phi$)	
Flux suppression in X-1-h-4		2.11×10^{13}	3.26×10^{13}	0.65	

* Average of two samples.

† Average of three samples.

‡ This value was not used in averaging.

§ Used fission cross section of $\text{U}^{235} = 504 \times 10^{-24} \text{ cm}^2$, UO_2 weight of 148.5 g, and corrected for an estimated 3% fuel depletion.

fission-monitor values may not represent specimen-surface heat generation values), their use for comparison with calorimetric heat fluxes is considered incorrect because of their wide scatter. Hence the metallographic measurements are referred to the calorimetric values in Table 3 as a basis for comparison. The suppression value for X-1-h-4 compares favorably with previous radiochemical determinations made on individual UO_2 pellets taken from the various X-1-f specimens (Table 12), with the measurements reported in Fig. 5, and with calculations performed by S. Kushneriuk.⁹

Note that fission-monitor and calorimetric measurements yield average values of heat flux over the test duration. If transient heat-flux conditions existed during these tests, they would certainly affect the correlation between nominal heat flux and metallographic indications of melting. The observed melting is thus a record of the highest flux achieved in the test. On the other hand, phenomena such as grain growth are less dependent on transient conditions.

An approximate check on heat-flux values was made by studying the ZrO_2 films formed on the internal cladding surfaces of defective rods. By correlating the thickness of these ZrO_2 films with weight-gain data for Zircaloy-2, particularly in the breakaway portions of the curves, an interface temperature of operation was estimated. With the water temperature and

Table 12—SUMMARY OF HEAT-FLUX VALUES
(All Values Are Expressed in Btu/hr/sq ft $\times 10^{-5}$)

	Experimental values			Calculated values		
	Monitor	Maximum calorimetric	ZrO_2 thickness ^a	Grain growth ^b	Macro-melt ^c	Micro-melt ^d
X-1-f-1	4.05 ^e	4.26	5.9		4.7	6.0
X-1-f-2	3.73 ^e	4.92	6.15	4.35	5.5	
X-1-f-3	3.68 ^e	5.15			6.0	
X-1-f-4	4.05 ^e	5.08	6.15		6.1	7.9
X-1-f-5		4.64		2.92		
X-1-g-1	4.03	3.91	5.32	3.35		
X-1-g-2	4.82	4.52	6.15		6.75	14.0
X-1-g-3	5.27	4.74		3.22		
X-1-g-4	4.90	4.67	6.15		6.4	
X-1-g-5	3.90	4.26				
X-1-h-1	4.11	4.08	5.5		4.45	
X-1-h-2	5.07	4.73	5.0		5.75	
X-1-h-3	5.62	4.94	5.30		5.7	
X-1-h-4	5.50 (3.8 ^f)	4.87			6.95	
X-1-h-5	4.80	4.46			5.85	
25-2-L1	4.52	4.75	5.15		5.5	5.4
15-2, bent rod		3.15	5.32	1.30		
14-19-A						11.8
14-25-2-j						

^a Determined from measurement of oxide thicknesses on the inside of Zircaloy cladding and correlation of these thicknesses with exposure time to obtain internal cladding temperatures. Heat fluxes were estimated from these temperatures by using a surface temperature of 630°F and a zirconium thermal conductivity of 7.2 Btu/hr/sq ft/°F.

^b Calculated from center temperatures in Table 13 and observed diameter of grain-growth region.

^c Calculated from diameter of melted zone shown in Table 3.

^d Calculated from distance between diameter of melted region (2750°C) and diameter of grain-growth region (1700°C).

^e Determined from fission-product analysis of small UO_2 sections. The remaining values in this column are determined from flux-monitor results.

^f Determined from fission-product analysis of entire rod.

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flow conditions used in these tests, a maximum cladding surface temperature of 630°F is expected. Disregarding any external fouling or crud formation, this results in the heat fluxes listed in Table 12, which compare favorably with the calorimetric measurements obtained for X-1-h and 25-2 (Table 12). The higher values for X-1-g can be at least partly explained by the thick crud formation found on the external cladding surfaces of these specimens after irradiation. Detracting from the accuracy of heat-flux estimates from ZrO_2 thicknesses is the possibility of higher thicknesses than would be expected because of radiation-accelerated corrosion due to fission recoils at the cladding interior, and the difficulty of achieving the desired quality of surface preparation of the inner tube wall, which would also tend to increase the corrosion rate.

Also listed in Table 12 are estimates of heat flux desired from: (1) center temperature as calculated from the grain growth (Table 13) and diametral position where no grain growth was observed and was assumed to be at a temperature of 1700°C; (2) position of the melted rim from photographs such as Figs. 22 to 24 assumed to be at 2700°C; and (3) relative position of the melted rim (2700°C) and the edge of the grain-growth region (1700°C). Heat fluxes were calculated from these positions using the corrected Armour data in Fig. 25. The agreement between these various estimates is poor except for specimen 25-2-L1 and possibly the X-1-h and X-f-2 specimens.

(c) *Experimental Results.* (1) *Macroscopic Observations.* The X-1-f, X-1-g, X-1-h, and 25-2 tests were the experiments primarily used to define the heat fluxes required to initiate melting in the PWR rods. Of the 17 specimens in these tests, nine showed melting throughout their length, three displayed melting on one end and grain growth at the lower flux end, three showed some grain growth, and the remaining two were not affected metallographically. Figure 26 shows the effects observed in the UO_2 as a result of irradiation in the X-1-f, X-1-g, and X-1-h tests.

Table 3 lists the observed diameter of molten zones and center craters as measured from stereocamera photographs of cut sections taken at 5 to 7.5 $\times$. The scatter of the data does not permit differentiation of molten diameters between the ends of the specimen exposed at high and low fluxes, and therefore the most typical value is used for comparison of the specimens.

The smallest molten diameter found was 0.120 in. or about $\frac{1}{3}$ the pellet diameter (X-1-f-3), and the largest except for the X-1-e-3 specimen (Fig. 22) was 0.240 in. or about $\frac{2}{3}$ the pellet diameter. A 0.260-in. molten zone was observed in the X-1-e specimen that failed. Also, increased molten zones tended to accompany larger shrinkage craters. These larger values are listed separately in Table 3.

Only the specimens with the larger molten zones have shrinkage craters of any magnitude. Within one specimen the largest craters are generally at the top of the specimen. Since the specimens are exposed in a vertical position, it is only to be expected that larger shrinkage cavities would appear at the top of the samples.

It is not conclusively proved that the macroscopic observations (Figs. 23 and 24) as well as the microstructures (Fig. 27) actually denote melting of the fuel. The formation of columnar grains, the observations of "solidification" craters at the center of "melted" zones (Figs. 23 and 24), and the grain growth in the UO_2 regions adjacent to the "melted" zones are strong evidence for such melting, and it is not clear that any other mechanism could produce these same effects. Therefore, in the subsequent report, the edge of the columnar zone has been considered to be at the melting point of UO_2 .

(2) *Metallographic Observations.* Metallographic examination of molten UO_2 pellets reveals the existence of radial temperature gradients by showing normal unaffected grains at the pellet-cladding interface, a transition grain-growth region farther inward, and a central columnar region usually with a center void (Figs. 27 and 28). Columnar grains that tend to extend across the entire zone of melting were observed in X-1-h-2 (Fig. 27) and X-1-f-4. These defective rods with 0.008-in. diametral clearances were exposed at the highest flux positions, and thus the center temperatures in these specimens would be higher than those for other specimens in the X-1-f, X-1-g, and X-1-h tests. The typical width of columnar grains in these specimens is about 60 to 70 μ . Shorter and wider columnar grains were observed in the X-1-h-3 specimen, in which the center temperature is expected to be lower. The

Table 13—CENTER TEMPERATURES AND HEAT FLUXES ESTIMATED FROM UO₂ GRAIN
GROWTH IN IRRADIATED PWR TYPE RODS

	Location of section	Center grain diameter		In-pile days	Temp., °C		Radius of affected grain region, in.	ϕ , Btu/hr/sq ft $\times 10^{-5}$	
		Mean	Range		Based on grain size	Calculated*		Calculated	Calorimetric
X-1-f-2	Low-flux end	80	40-150	40	2600	2750	0.105	4.35	4.60
X-1-f-5	High-flux end	50	6-70	40	2300	2150	0.105	2.92	4.40
X-1-f-5	Low-flux end	16	4-40	40	1700	1700	0		
X-1-g-1	Low-flux end	34	4-54	65	2050	1980	?		
X-1-g-1	High-flux end	96	30-130	65	2700	2650	0.120	3.35	4.40
X-1-g-2	High-flux end	77	18-140	65	2550	2750			
X-1-g-3		54	35-120	65	2300	2370	0.100	3.22	4.67
X-1-g-5	?	5	1-16	65	1700	1930 1400	0		
X-1-h-1	Low-flux end	28		48	2000	2100	?		
X-1-h-1	High-flux end	155	40-270	48	2750	2750			
X-1-h-3		120	70-200	48	2750	2750			
X-1-h-5	Low-flux end	17 85	4-40 40-140	48	2250	2180	?		
15-2, bent rod	Apex at center	31	12-80	30	2000	1900	0.110	1.30	3.15

* Based on corrected Armour data.

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Fig. 25—Thermal conductivity of UO_2 vs. temperature.

Fig. 26—Effects in the UO_2 in the X-1 loop tests. $\circ$, 0.005-in.-diameter defect hole. Center temperatures are estimates made from observed grain sizes. Melt diameters are measured from stereocamera photographs.

typical width of the grains in this specimen is about 60 to 120 μ , and the length-width ratio is approximately 5. Such observations are consistent with the behavior of other crystalline materials upon solidification. More extensive columnar growth would be expected under conditions of "adiabatic" crystal growth, which would appear to be more likely in superheated melts, particularly in the presence of impurities. Specimen X-1-g-2 displayed a central region of large equiaxed grains surrounded by short columnar grains (Fig. 28). A molten UO_2 structure

Fig. 27—Uranium dioxide columnar structures in the X-1-h-2 and X-1-h-3 specimens. Photo series are not composite. (Original magnification 100 $\times$; reduction factor $\frac{2}{3}$.)

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Fig. 28 — Uranium dioxide structures in the molten zones of the X-1-g-2 and X-1-e-3 specimens. Photo series are not composite. (a) X-1-g-2 (original magnification $250\times$, reduction factor $\frac{2}{3}$). (b) X-1-e-3 (original magnification $50\times$, reduction factor $\frac{2}{3}$).

at center temperatures that are probably considerably higher than those observed in the X-1-f, X-1-g, and X-1-h tests is provided by the X-1-e rod that failed (Fig. 28), whose structure is similar to, but more exaggerated than, that of specimen X-1-g-2.

Specimens showing only grain growth in the UO_2 also showed the structural gradation expected from the temperature gradient across the fuel pellet, with the largest grain size in the center of the specimen. At the regions showing grain growth, voids were preferentially distributed in the grain boundaries (Fig. 29). Similar void distribution has been noted in samples heated out-of-pile to 2200 to 2300°C in order to cause grain growth after sintering (Fig. 30).

Grain growth observed in the various specimens has been reported in terms of estimated operating temperatures required to produce the increased grain size. These estimates are based on experimental data obtained for grain growth in UO_2 at temperatures up to 2300°C for holding times of 5 to 40 min. These data could best be correlated by assuming that the grain diameters varied with the heat constant temperature by the relation, $\text{diameter} = Kt^{0.1}$, and that the K varied with temperature according to an Arrhenius equation with an activation energy of 23,000 cal/mole. The data from these relations were thus extrapolated to the conditions existing during fuel-element operation (Fig. 30) to obtain the estimated center temperatures shown in Fig. 31 and listed in Table 13.

(3) *Details of Individual Tests. X-1-e.* The first UO_2 melting in specimens tested in pressurized-water loops occurred in the X-1-e test, in which a cladding burn-out occurred after 2 hr of operation in a 19.5 per cent enriched UO_2 defective specimen in the hottest position of the loop (Fig. 21). This failure has been attributed directly to extensive melting of the fuel and has been confirmed by metallographic evidence of high temperatures in the cladding in the vicinity of the failure. More specifically, the failure seems to have occurred when a jet of molten UO_2 escaped through a crack in the outer solidified rim of UO_2 surrounding the molten zone and impinged on the internal wall of the cladding. Also, the cross-sectional structure of the UO_2 is somewhat different from the molten zones observed in later X-1 tests in having a central crystalline area of porous character, possibly indicating a molten zone of considerable superheat. The two defective specimens in this test, of lower enrichment, displayed only grain growth in the UO_2 , whereas the UO_2 in the two nondefective specimens was not affected (Table 3).

X-1-f. The X-1-f test was designed primarily to test rods with assembled fuel diametral clearances up to 0.008 in. Melting occurred not only through the entire length of the three large-clearance rods but also in the high-flux end of the defective low-clearance rod. Uranium dioxide melting diameters and estimated center temperatures (from grain growth) for the X-1-f test are shown in Fig. 26. Specimens 1 and 4, defective specimens with 0.008-in. diametral clearance, were molten throughout their length with specimen 4, being in a higher flux region, showing more severe melting along with large shrinkage craters. Specimen 2, a defective specimen with 0.0015-in. diametral clearance, was molten at its lower (high-flux) end and suffered grain growth indicative of a center temperature of 2600°C at the upper end. Specimen 3, a nondefective specimen with 0.008-in. diametral clearance, was molten along its entire length. Specimen 5, a nondefective specimen with 0.003-in. diametral clearance, showed grain growth estimated to have occurred at 2300°C at the high-flux end and no change of the as-sintered grain size in the lower end of the specimen.

X-1-g. The X-1-g test consisted of rods with maximum diametral clearances of 0.004 in. Melting occurred in two of the three defective rods, with only indications of UO_2 grain growth in the remaining defective rod and one of the two nondefective rods (Fig. 26). A cladding cracking failure which occurred in the No. 2 rod is considered to be unrelated to the melting and is discussed in Sec. 5.5.

Specimen 1, a defective specimen with 0.0025-in. diametral clearance, showed grain sizes corresponding to center temperatures ranging from 2050 to 2700°C. Specimens 2 and 4, defective specimens with 0.004- and 0.001-in. diametral clearances, respectively, were molten throughout their length. Specimen 3, a nondefective fuel rod with 0.0025-in. diametral clearance, showed a grain growth corresponding to 2300°C, whereas specimen 5, of similar design but at a lower flux position, was found to have suffered no changes in the UO_2 .

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Fig. 29—Uranium dioxide grain growth in the low-flux ends of the X-1-h-1 and X-1-h-5 specimens. (Original magnification 250 $\times$, reduction factor $\frac{2}{3}$.)

Fig. 30—Grain size and temperature relation for UO_2 (experimentally derived for 15 min of holding time and extrapolated to longer times by use of the equation $D = Kt^{0.1}$).

Fig. 31—Experimental observations of UO_2 melting diameters and grain growth. Temperature in loop-operated PWR type fuel rods plotted against reported calorimetric heat fluxes. Calculated curves of heat fluxes vs. center temperature, using corrected Armour data for UO_2 thermal conductivity, are superimposed. Dotted curves compare the Kingery data and show the effect of suppression on the Armour curve when the UO_2 is in contact with the cladding.

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X-1-h. The X-1-h test resulted in melting in all five rods of the test (see Fig. 26). A failure occurred in the No. 3 rod, but this has been attributed to cladding effects that are discussed in Sec. 5.5.

Specimen 1, a defective rod with 0.005-in. diametral clearance, displayed melting at the lower end and grain growth indicative of 2000°C center temperatures at the upper end. Specimens 2 and 4, a defective and a nondefective specimen, respectively, each with 0.008-in. diametral clearance, were molten throughout their fuel length and showed large solidification craters near the top of the molten zones. Specimen 3, which developed a cladding defect during testing, had a diametral clearance of 0.0025 in. and was molten throughout the fuel length. Specimen 5, a nondefective rod with 0.005-in. diametral clearance, was molten at its upper end and exhibited a grain size corresponding to a center temperature of 2250°C at the lower end.

X-1-j. The X-1-j test was designed to operate at a maximum heat flux lower than 40,000 Btu/hr/sq ft. Calorimetric measurements indicated a heat flux of 312,000 Btu/hr/sq ft. Calculations based on the Armour thermal conductivity values indicated a possible structural change only in the single defective rod in the test (X-1-j-3), with a calculated central temperature of 1850°C. However, metallographic examination revealed no grain growth in this specimen or in the four nondefective rods in this test.

WAPD 25-2 Cycling Test. Specimen L1, a defective rod with 0.004-in. diametral clearance, was molten throughout the fuel length, and specimen L2, a nondefective specimen with 0.004-in. diametral clearance, showed no melting or change in grain size in any of the UO₂ sections examined. Details of this test are given in Report WAPD-167.⁴² Note that in this test the fuel is natural UO₂ and hence is not subject to the flux suppression effects noted in the enriched tests.

WAPD 15-2 Test. The defective rod in a bundle irradiated in a pressurized-water loop (Table 4) suffered grain growth in the UO₂ at a heat flux of 315,000 Btu/hr/sq ft. The UO₂ contained 8.3 wt. % U²³⁵ in total uranium, and the assembled diametral clearance was 0.003 in.

(d) *Parameters Affecting Temperature-Heat Flux Relations.* The equation for the heat generation required to produce a center temperature which would initiate melting in the UO₂ of a PWR type fuel rod is expressed by

$$\frac{Q^* R_0^2}{4} = \int_{T_1}^{T^*} k(T) dT \quad (7)$$

where Q^* = volumetric heat generation required for initiation of melting

R_0 = radius of the UO₂ pellet

T^* = melting point of UO₂

T_1 = pellet surface temperature

$k(T)$ = thermal conductivity of UO₂ as a function of temperature

The basic assumptions used in deriving Eq. 7 are that (1) heat transfer takes place in the radial direction only and (2) heat generation is constant across the pellet radius. The second assumption is certainly invalid for the X-1 test specimens as outlined below and as can readily be seen from Fig. 5 and Table 11.

There is a direct proportionality between volumetric heat generation and the heat flux at the cladding surface. Since the pellet radius is fixed according to PWR reference dimensions, the heat flux required to produce melting in PWR type fuel rods is primarily dependent on the thermal conductivity and melting point of UO₂ and on the UO₂ pellet surface temperature. For the sake of discussion, Eq. 7 can be simplified to the following:

$$(q/A)^* = C k_{\text{UO}_2}^{\text{mean}} (T^* - T_1) \quad (8)$$

where C = appropriate constant, which includes the square of the pellet radius and conversion from heat generation to heat flux

$k_{\text{UO}_2}^{\text{mean}}$ = thermal conductivity of UO₂ averaged up to the melting point

$(q/A)^*$ = surface heat flux to obtain melting in the original design

(1) *Thermal Conductivity of Uranium Dioxide.* In the original design the Kingery and Vasilos data for the thermal conductivity of UO_2 corrected to 95 per cent theoretical density have been used in the form of an empirical equation, $1855 T^{-0.9}$ Btu/ft/hr/sq ft/°R, for calculations of temperature distributions in PWR fuel rods, where T = temperature in °R. These experimental values were measured with a comparative linear-flow apparatus on 1-in.-cube samples of UO_2 cast from a suspension and fired at 1980°C *in vacuo* to a theoretical density of 73.3 per cent. Recent data from Armour Research Foundation, measured by a radial heat-flow method on 3-in.-diameter disks of UO_2 made by pressing at 20 tsi and sintering in hydrogen and steam at a maximum of 1500°C to 75 per cent of theoretical density, indicate lower thermal conductivity values. The testing furnace contained helium, and the pellets were found to be badly cracked after test. Therefore the physical condition of the pellets is similar to that of the UO_2 in irradiated rods, and the values obtained may thus be considered an effective thermal conductivity for UO_2 in its condition within a fuel rod, rather than a material property.

The latter data were corrected for density by assuming the full density correction at 400°F and no density correction at 2200°F and above; at intermediate temperatures the correction for density was decreased linearly between 400 and 2200°F. This step was taken on the basis of data presented by Jakob⁴³ which indicate that the thermal conductivity of powders is independent of density above 1000°C. At temperatures above 2200°F it was assumed that the thermal conductivity remained constant at 0.84 Btu/hr/ft/°F to the melting point at 5000°F. Kingery⁴⁴ has pointed out that, in single-phase ceramics, lattice thermal conductivity may, under suitable conditions of elevated temperature or lattice disturbance by irradiation, be reduced to a minimum value set by photon scattering at mean free paths of the order of the lattice spacing; in the case of UO_2 , such a minimum value would correspond to about 1 Btu/hr/ft/°F.

(2) *Melting Point of Uranium Dioxide.* A variety of values for the melting point of UO_2 is available in the literature.⁴ The latest determination, a value of $2750 \pm 40^\circ\text{C}$ (4982°F) by Wisnyi, is employed for the calculations in this report. The effect of impurities on the UO_2 melting point is not known, but the low values were reported for a residual impurity content in the UO_2 of 0.5 per cent. The material used in the specimens of this report contains a maximum of 0.05 per cent impurities in the unirradiated condition.

(3) *Pellet Surface Temperature.* The equation for the pellet surface temperature may be expressed as follows:

$$T_i = T_s + \Delta T_{\text{clad}} + \Delta T_{\text{gap}} \quad (9)$$

where T_s = temperature at the external cladding surface

ΔT_{clad} = temperature drop across the cladding

ΔT_{gap} = temperature drop across the gaseous gap between the cladding and the fuel pellet

ΔT_s and ΔT_{clad} are relatively constant for the specimens considered in this report, while ΔT_{gap} will vary considerably according to the diametral clearances, the thermal conductivity of the gas in the annulus, and the operational heat flux. These relations for ΔT_{gap} can be stated according to the following equation, which is based on the assumption that the gap is thin enough to be considered a flat plate in heat transfer:

$$\Delta T_{\text{gap}} = \frac{\Delta X_{\text{gap}}}{k_{\text{gap medium}}} \left(\frac{q}{A} \right)_{\text{mean}} \quad (10)$$

ΔX_{gap} is the radial clearance in the PWR rod at operating temperatures and necessarily depends on the original assembly clearances as indicated in Fig. 19 and outlined in Sec. 5.1.

(e) *Heat Fluxes Required To Produce Melting.* The experimentally observed changes in the UO_2 fuel of the various specimens are plotted against their corresponding calorimetric heat fluxes in Fig. 31. Note that the plot consists of two parts, one for the observed molten diameters and the other showing the estimated center temperatures required to produce the observed changes in grain size.

The typical molten diameters listed in Table 3 were used for plotting. These range from 0.140 to 0.230 in. For rods molten throughout their fuel lengths, the same value of melt diame-

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ter was used for both high- and low-flux ends since the measurements made from stereo-camera photographs indicated a fairly uniform molten zone in these specimens. This longitudinal uniformity in a flux gradient may be indicative of some axial heat transfer, which was not considered in the heat-transfer calculations. Note that three specimens, X-1-f-2, X-1-h-1, and X-1-h-5, showed melting in the high-flux end and only grain growth in the low-flux end.

The estimated grain-growth temperatures listed in Table 13 were used in the other portion of the plot. Superimposed on this portion of the plot are two curves of heat fluxes vs. center temperature calculated with corrected Armour data for UO_2 thermal conductivity. The lower curve represents the center temperatures expected in defective PWR type fuel specimens with an operating gap of 0.005 in. for steam. This agrees favorably with experimental data obtained for the defective specimens X-1-g-1 (0.0025 in.), X-1-h-1 (0.005 in.), and the WAPD-25-2-L1 (0.003-in. diametral clearance) as well as the nondefective large-clearance X-1-h-5 specimen. The upper curve represents center temperatures expected in PWR type rods in which the UO_2 pellets would expand into contact with the Zircaloy-2 cladding at operating temperatures. This curve agrees with experimental data obtained for nondefective rods with low diametral clearances.

The following listing summarizes the experimental observations plotted in Fig. 31 for the minimum heat fluxes at which melting or grain growth occurred.

	Diametral clearance, in.	Heat flux, Btu/hr/sq ft		Grain-growth temp., °C
		Melting	Grain growth	
Defected	0.005 to 0.008	370,000	340,000	2000
Defected	0.001 to 0.004	425,000	330,000	2050
Nondefective	0.005 to 0.008	422,000	360,000	2250
Nondefective	0.001 to 0.004	530,000 (est.)	430,000	2300

(f) *Discussion.* Superficially, the points plotted in Fig. 31 and the values listed above appear to be in fair agreement with the assumptions that the mean thermal conductivity of UO_2 (derived from the integrated mean value of the corrected Armour data plotted in Fig. 25 from 750 to 5000°F) is 1 Btu/hr/sq ft/°F, that the effect of the gas atmosphere is equivalent to a gap thermal resistance, and that heat is generated uniformly through the specimen. Actually, none of these assumptions are justified. Thus the discussions in Secs. 3 and 5.1 certainly indicate the presence of flux suppression in all the enriched samples exposed in the X-1 tests and hence the lack of uniform heat generation; the differences observed in Fig. 31 between 5- to 8- and 1- to 4-mil initial diametral gaps can certainly not be reconciled with the assumption of a gas thermal barrier (see Fig. 19); and the data from the 25-2 nondefective sample correlate better with Kingery and Vasilos' data in Fig. 25 than with Armour data. It is thus necessary to examine in detail not only the assumptions but also the accuracy and reliability of the various measurements.

(1) *Microscopic Measurements.* Grain-growth data are considered intrinsically most reliable as an index of steady-state operating conditions primarily because of the apparent (time)^{0.1} relation. Unfortunately, the out-of-pile data substantiating this relation are rather sketchy, and the lack of sensitivity to temperature changes results in the possibility of relatively large errors. Melting observations record only the maximum temperature attained during test and not steady-state conditions. There is some possibility that microscope measurements of the extent of molten zones are in error because of nucleation of columnar grain growth in the solid from the liquid-solid interface and hence indicate a larger apparent zone of melting than is actually achieved. However, the large release of fission gas from those specimens in which melting is observed (see Table 5) argues either that the melting persisted during exposure or that the melting occurred late in life.

(2) *Thermal Conductivity Measurements.* As a measurement of a material property, there appears to be little reason to doubt the Kingery thermal conductivity data; certainly, as stated by Hedge,⁴¹ the Armour data are compounded by the presence of cracks in the test

specimens. Certain of the test data obtained from measurements on natural oxide rods appear to correlate well with Kingery data as listed below:

Specimen	Clearance, in.	Heat flux, Btu/hr/sq ft	Center temp., °C		Observations
			Kingery-K	Armour-K	
25-2-L2	0.004	475,000	1700	2350	No metallographic change
14-24-19	0.003	710,000	2830	>>2750	Grain growth
14-24-20	0.003	770,000	3240	>>>2750	Melted (0.175-in. diameter)
14-15-104S	0.0015	760,000	3180	>>>2750	No melting
14-16-114S	0.0015	790,000	3370	>>>2750	No melting
14-1-1	0.001	537,000*	1700	2750	No melting
14-19-24B2	0.008	670,000	2490	>2750	Melted (0.325-in. diameter)

* Converted to 0.357-in. diameter.

Thus, for those natural UO_2 specimens with small clearances operating with helium gas within the rod, there is fair agreement between Kingery data and melting observations. Unfortunately, a check with measures of heat flux other than those afforded by fission monitors and nominal reactor neutron fluxes is not possible in the last six specimens because they were irradiated in capsules. However, the first specimen listed above was exposed in a loop and showed good agreement between fission-monitor and loop calorimetric estimates of heat output. The agreement between the Kingery-K and the irradiation results does not appear to hold even for rods containing natural UO_2 irradiated with large initial clearances (specimen 14-19-24B2).

It is therefore tempting to consider that the cause for the differences between natural and enriched samples is some impurity or other physical effect in the enriched samples resulting either in reduction of melting point or decrease in conductivity. However, neither chemical analysis nor metallographic examination has ever revealed a detectable difference between enriched samples prepared in the laboratory from enriched uranyl nitrate solution and natural samples prepared from MCW UO_2 . Although no direct comparison has been made between enriched and natural UO_2 samples at reasonable heat fluxes, the diameters of the melted zones in 6.24 per cent enriched specimens 14-18-9B3 and 14-18-10B1 irradiated at 900,000 and 890,000 Btu/hr/sq ft are similar, for example, to those in natural UO_2 specimens 14-14-83S, 14-14-84S, 14-21-5, 14-21-6, and 14-25-J, and 14-25-F irradiated above the melting point at similar high heat fluxes. Therefore, although the evidence is not unambiguous, it appears doubtful that the laboratory process used to secure enriched specimens lowers thermal capabilities by a chemical effect.

The data presented in Sec. 3 have been critically examined to reveal whether or not the deviations from nominal thermal conductivity values could be explained by an irradiation-induced depression of the conductivity. Marked effects have been reported for various non-fissionable oxides.³³ However, examination of the data in Tables 1 to 3 reveals no effects that can be attributed to decrease in thermal conductivity. Note that the results for enriched samples presented in Fig. 31 are correlated by a mean conductivity of about 1 Btu/hr/ft/°F, which is about the minimum conductivity expected from crystalline UO_2 even after prolonged irradiation. Furthermore, as pointed out in Sec. 4.2, there is no X-ray evidence of widespread lattice damage in UO_2 . The only evidence that irradiation may adversely affect thermal performance is afforded by comparison of results from specimens X-1-e-1, X-1-e-2, X-1-e-4, and X-1-e-5 in Table 3 with those of the other X-1 specimens. These specimens, enriched to 9.5 wt. % U^{235}/U , were exposed for only a short time because of the failure of the X-1-e-3 specimen (Fig. 21). The heat fluxes listed for these specimens were estimated by Horsman and Howieson.⁹ The fact that no macroscopic evidence of changes was noted in nondefective specimens X-1-e-1 and X-1-e-2 is not in serious disagreement with the results for other enriched non-

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defective samples of small clearance which are plotted in Fig. 31 and which are best correlated by the Armour conductivity data. However, the fact that defective specimens X-1-e-4 and X-1-e-5 show no melting but only grain growth is in marked disagreement with results from other defective rods run at comparable heat fluxes. This effect may possibly be related to radiation-induced reductions in thermal capabilities.

Aside from this assumption, it is concluded that irradiation-induced physical effects are not responsible for the limited thermal performance revealed by many of the samples and that the effective thermal conductivity in a PWR fuel rod is affected primarily by the following factors:

1. Enrichment.
2. Initial clearance.
3. Atmosphere within the fuel rod.

Some consideration was given to explanation of the observations on the basis of depression of UO_2 melting point by fission-product accumulation and by reaction of UO_2 with steam. The latter is discussed in Sec. 5.5. Reduction of melting point by fission-product accumulation is considered highly unlikely, particularly since the occurrence of melting in Tables 1 to 3 can be correlated with operating heat flux and not with burn-up. Even at the highest burn-ups tested, 25,000 Mwd/ton, the contamination by fission products is considered insufficient to cause serious melting-point reduction.

If, indeed, it is true that enrichment per se affects the thermal performance as proposed above, it is difficult to conceive a mechanism whereby such an effect operates. In Fig. 32 are

Fig. 32—Temperature distribution and heat generation rate vs. radius for various flux depressions (surface heat flux and surface temperature constant). Pellet surface heat flux = 500,000 Btu/hr/sq ft. $K_{\text{UO}_2} = 1855/T^{0.9}$. Surface temperature = 750°F. —, temperature vs. radius. ---, heat generation rate vs. radius.

plotted temperature profiles through a PWR fuel pellet for various flux suppressions at constant surface heat flux and surface temperature. Note that all factors such as temperature, temperature gradient, etc., which may be considered to detract from thermal capability are improved in flux-suppressed (enriched) pellets. If enrichment does decrease thermal performance, the only effect which can be held responsible in Fig. 32 is the higher surface fissioning rate in enriched samples; this would imply that the thermal performance of UO_2 is sensitive to fissioning rate. This is unreasonable since it may be estimated from the maximum fissioning rate shown in Fig. 31 that the "relaxation time" for fissioning, based upon the time required to "melt" in a fission spike all the UO_2 molecules, is some 15 orders of magnitude greater than the relaxation time for thermal conductivity. Thus it is not clear that a physical basis for postulating an effect of enrichment exists, and it appears essential to check this postulate experimentally.

(3) *Assumed Heat-transfer Model.* It has already been pointed out in Sec. 5.1 that physically the model assumed in heat-transfer calculations of a pellet uniformly surrounded by a gas annulus cannot be correct both because of thermal fracture and because, experimentally, no anisotropy of melted zones has been noted. W. B. Lewis,⁴⁵ on examination of data presented in Table 3 and Fig. 31, independently concluded that "the melting had as much connection with the initial diametral clearance as with the surface heat flux." The assumed heat-transfer model fails completely to explain the differences in melting behavior between 1- to 4- and 5- to 8-mil nondefective samples in Fig. 31 as well as the profound effect of a steam vs. a helium atmosphere. The latter is more strikingly illustrated by the behavior of specimens 25-2-L2 (nondefective) and 25-2-L1 (defective) shown in Fig. 31, which were natural UO_2 specimens exposed alternately to the identical flux in a hot-water loop. It is considered most probable that, by some physical mechanism as yet unexplained, but related to initial clearance and hence to the permeation of the atmosphere in cracks, gaps, and voids, the effective thermal conductivity is reduced from Kingery's values to some much lower figure and that steam is much more effective than helium in securing such reduction.

(4) *Heat-flux Measurements.* The measurements of heat fluxes and the reconciliation of various such measurements are serious uncertainties in the experiments described in this section. Calorimetric measurements of heat fluxes in the X-1 loops and their correction for neutron-flux distribution are described by Horsman and Howieson.⁹ Lewis⁴⁶ has pointed out several factors that may elevate the apparent calorimetric flux, namely, heating of loop structural parts by neutron and gamma radiation and fission energy transferred nonthermally from the specimens, and has indicated that the magnitude of such effects may be as high as 10 per cent of the measured heat input to the loop. However, to within an accuracy of 10 per cent, it is believed that the calorimetry reveals the true heat output from the samples; this is confirmed at least roughly by the observations of ZrO_2 film thicknesses on the inside of defective rods listed in Table 12. Also, the observations relating the location of the melting temperature at the edge of the columnar zone in melted pellets with heat flux calculated therefrom, as listed in Table 3, are not in disagreement with the calorimetric values considering the inaccuracy of the former measurement.

However, the correlation of the calorimetric heat fluxes with other measures of specimen heat-transfer rates is far less satisfactory. Lewis,⁴⁵ on the assumption that, owing to flux suppression in enriched pellets, the heat generation rate Q varied with radius from that at the pellet center Q_0 by the relation:

$$Q = Q_0 e^{\alpha R}$$

arrived at the relation analogous to Eq. 7 for uniform heat generation:

$$Q_0 R_0^2 \left(\frac{1}{4} + \frac{\alpha R_0}{9} + \frac{\alpha^2 R_0^2}{32} + \dots \right) = \int_{T_1}^{T^*} k(T) dT \quad (11)$$

This relation is plotted in Fig. 31 for the corrected Armour data using ratios of

$$\frac{\text{Mean flux determined by analysis}}{\text{Surface flux determination by monitors}}$$

equal to 0.67 (Table 11) and 0.80. It may be noted that the center temperatures thus predicted as a function of heat flux bear little relation to the experimental observations, predicting at the same heat flux much lower center temperatures than if the flux were unperturbed. Note that the heat fluxes measured on the basis of diameter of regions of grain growth (Tables 12 and 13), which reflect the heat generation rates at the center of the pellets, yield values much lower than the calorimetric ones and thus are physical evidence of the reality of the flux suppression effect.

No means of reconciling these observations is clear to the authors. The markedly higher center temperatures attained in the X-1 tests than are predicted by the indicated flux suppression can be explained by no reasonable assumption concerning UO_2 thermal conductivity since the Armour values appear to be as low as can be attained in crystalline UO_2 ; furthermore, the more accurate Kingery values appear to hold for natural UO_2 fuel specimens of low clearance. It can only be surmised that the combination of change in physical structure and conduction characteristics discussed in Secs. 4 and 5.1 leads, at least with enriched oxide pellets, to a heat-transfer system that is not represented by Eq. 7.

(5) *Conclusions.* The following empirical conclusions were drawn from the work described above:

1. The thermal capabilities of helium-filled, low-clearance, natural UO_2 PWR fuel elements can be expressed by use of the Kingery-Vasilos UO_2 thermal conductivity values.
2. The thermal performance of helium-filled, low-clearance, enriched fuel elements is described by a thermal conductivity of the oxide of 1 Btu/hr/ft/ $^{\circ}\text{F}$.
3. The thermal capabilities of helium-filled, high-clearance natural or enriched UO_2 or steam-filled, low-clearance natural or enriched UO_2 fuel elements are described by a mean UO_2 thermal conductivity of 1 Btu/hr/ft/ $^{\circ}\text{F}$ and a gap thermal resistance of about 0.03 Btu/hr/ft/ $^{\circ}\text{F}$.
4. A steam atmosphere reduces thermal capabilities more than a helium atmosphere at the same initial clearance, and, with the same atmosphere, increased clearance increases central temperatures.
5. The thermal performance of enriched fuel rods can not be correlated with available property data.
6. A conservative maximum heat flux for nondefective PWR Core 1 fuel rods is 530,000 Btu/hr/sq ft, and for defective rods it is 425,000 Btu/hr/sq ft.

5.3 Waterlogging

A possible mechanism of failure of a Zircaloy-2-clad UO_2 fuel rod is by waterlogging. If a defect is present in the clad, water may enter the rod in the clearance spaces and interconnected voids present in the UO_2 during reactor shutdown. The amount of water entering the rod would be a function of initial clearance, density of the UO_2 fuel, and amount of interconnected porosity. Upon subsequent reactor start-up, the trapped water would flash to steam and could produce sufficiently high pressures to expand or even rupture the cladding (1) if the steam could not escape out of the original entrance hole fast enough to relieve the pressure, (2) if the original hole had become blocked by a piece of the thermally fractured UO_2 , or (3) if the water permeated connected pores in the oxide and then fractured it violently upon boiling. The possible magnitude of this effect was determined by placing 0.005-in.-diameter artificial defects in a number of samples irradiated in high-pressure, high-temperature loops. In all, 24 samples have been tested in this manner (Table 3), and, although diametral expansions up to 0.012 in. were produced in several rods, only one sample (X-1-b-1) failed by a waterlogging type of mechanism. Two views of this failure are shown in Figs. 33 and 34, and, as can be noted, the cladding bulged to a considerable extent and split in the bulged area. This sample

Fig. 33—Rod X-1-b-1, showing bulging caused by waterlogging type of failure. (Magnification 5x.)

Fig. 34—Close-up of split in cladding of rod X-1-b-1. (Magnification 15x.)

contained hot-pressed 80 per cent dense UO_2 , and therefore considerable interconnected void space was available for the entrapped water. The violence of the failure indicates that probably mechanism 3 above caused the splitting.

A diametral expansion of 0.007 in. was noted in rod 14S from experiment X-1-c after only 1 week of irradiation. Although this material was originally 90 per cent dense, the material was discovered to have poor corrosion resistance resulting from carbon pickup during argon sintering in a graphite furnace. During the preirradiation corrosion testing, attack occurred at the grain boundaries, resulting in "desintering" and thus permitting water to permeate the fuel upon reactor shutdown. The results of these two tests influenced the decision that high-density fuel pellets be used in PWR Core 1. The defect tests subsequently run have revealed no effects that could unambiguously be ascribed to waterlogging.

Diametral expansions up to 0.012 in. were noted in two of the defective rods from experiment X-1-g. Rod X-1-g-4, however, had a diametral clearance of only 0.001 in., and therefore a portion of the observed expansion was probably produced by the differential expansion of the UO_2 . The other rod (X-1-g-2) had a diametral clearance of 0.004 in., and the observed expansion may have been produced by a succession of waterlogging types of incidents. It should be noted that experiment X-1-g was in-pile for 65 days and that experiment X-1-c was in-pile for only 1 week. On the other hand, it is considered quite likely that the expansions observed resulted from hydriding of cladding as described in Sec. 5.5. In addition, the defective WAPD-25 test specimen described in Table 3 was cycled 533 times in and out of reactor flux in a hot-water loop with no signs of cladding deformation or failure.

It seems apparent from the information available that the possibility of a gross fuel-element failure occurring from a waterlogging mechanism is remote if UO_2 in excess of 93 per cent of theoretical density is utilized so that the water-to-steam phase change occurs in gaps and crevices rather than in interconnected porosity within the fuel.

5.4 Effects of Cycling on PWR Blanket Fuel Rods

When the PWR blanket rod was designed, it was apparent that a testing program was required to ascertain the behavior of such rods under various operating conditions. In particular, the dimensional stability of the rods under cycling conditions was of some concern because a "thermal ratcheting" mechanism was conceived which might cause rods to grow and fail under cycling conditions. This mechanism was postulated to operate as follows:

1. As the reactor went to power, the UO_2 could fracture as a result of thermal shock.
2. Upon cooling, void areas could be produced between cladding and fuel as a result of the differential expansion of the UO_2 and the Zircaloy-2 cladding.
3. Small pieces of the thermally fractured UO_2 could relocate into these void areas.
4. Upon further cycling, the above mechanism would repeat and hence cause the rods to deform.

The possible magnitude of this effect was first checked by cycling PWR blanket rods between 260°C (500°F) and 537°C (1000°F) in an out-of-pile thermal cycler. No deformations were noted under these conditions. More important, fracture of the UO_2 was not progressive but ceased after the first several cycles with the formation of a few gross pieces. However, since the thermal conditions existing under irradiation are much more severe than can be attained in out-of-pile thermal cycling, it was necessary to run irradiation cycling tests to ensure the absence of the postulated ratcheting effect.

The first irradiation cycling tests were run on samples canned in NaK-filled Zircaloy-2 capsules. The diametral clearances of the samples ranged from 0.005 to 0.004 in., the axial clearances ranged from 0 to 0.150 in., and the densities ranged from 81 to 96 per cent of theoretical. The results of this series are shown in Table 2, and, as can be noted, no adverse dimensional changes were produced by a maximum of 7000 cycles at an estimated heat flux of 450,000 Btu/hr/sq ft. No further fragmentation was noted in these tests than in the out-of-pile thermal cycling tests.

In addition, two rods were thermally cycled 533 times in the L-42 loop cycler at the MTR at a heat flux of 475,000 Btu/hr/sq ft and to a maximum burn-up of 1260 Mwd/ton. These two rods are of particular interest because they were tested at conditions similar to the maximum

conditions that will exist in the PWR. The results of this test are shown in Table 3, and, as can be noted, no dimensional changes were produced. It was concluded, therefore, that the probability of fuel-element failure under irradiation cycling conditions is remote and that progressive fragmentation of UO_2 as a result of thermal stress does not occur.

5.5 Environment Within the Fuel Element

As discussed earlier, it is anticipated that, within a nondefective helium-gas-bonded fuel element, the gas is, on a gross scale, uniformly distributed in cracks, pores, and crevices and, as irradiation proceeds, gradually becomes diluted with released fission gases at rates consistent with those discussed in Sec. 4. Likewise, it is anticipated that fuel elements operating in pressurized-water systems and which, because of extensive failure, have large gaps or tears in the cladding would be permeated with water or steam.

It is considered unlikely, however, that such extensive cladding failure would actually be encountered in fuel elements of the type employed in PWR Core 1. It is more likely that failures would consist of fine cracks through the cladding or small holes at the end welds. It is indeed this type of failure which has been simulated in most of the in-pile tests outlined above.

Under such conditions it is likely that during operation the environment within the fuel element does not consist of water or steam, at least during steady-state operation, but rather that it is high in hydrogen content. This conclusion is based on two observations: (1) absence of microstructural changes in defective oxide and (2) hydriding of Zircaloy cladding. This evidence is discussed further later.

The loops in which the fuel-element testing was performed operated with water conditions such that the molecular hydrogen content is about 30 cc/liter, which is the dissolved hydrogen content anticipated during PWR operation. It can be shown from data of Pray⁴⁷ that, if a steam phase is established within a fuel rod through a defect and is in equilibrium with the composition of the coolant water, an enrichment in hydrogen content by a factor of about 1000 should be noted. Under such conditions, therefore, the vapor phase within a defective fuel element would contain about 30 volumes of hydrogen to 2000 of steam (at 2000 psi system pressure). It can be shown, utilizing available reaction-rate data of Zircaloy-2 with steam, that the amounts of steam contained within a fuel rod would be gettered by the cladding within 1 day or less of operation with internal cladding temperatures in the neighborhood of 750°F. Since hydrogen is evolved during the reaction of Zircaloy-2 with steam and most of this hydrogen is released to the vapor phase, a continuous enrichment of the atmosphere in hydrogen with little net change in pressure will occur, and it appears reasonable to assume that certain regions within the fuel element will operate in the presence of relatively pure hydrogen atmospheres. Of course, during reactor shutdowns and start-ups, water will be drawn into and ejected from the interior of the fuel element, thus causing repetition of this hypothesized process.

One bit of evidence supporting this hypothesis is consideration of the oxygen contents that should be attained by UO_2 during operation in steam at temperatures above 1000°C. As shown in Fig. 35, utilizing the data of Aronson,⁴ oxygen contents in excess of $\text{UO}_{2.10}$ should be obtained during exposure of $\text{UO}_{2.0}$ to steam. Uranium dioxide of such oxygen contents, on sufficiently slow cooling, will precipitate a second phase of U_4O_9 . No trace of such second phases has been observed in microsections of defective rods upon postirradiation examination. It may be noted from Fig. 35 that a 50 per cent hydrogen-steam mixture is sufficient to reduce the hydrogen content of UO_2 to levels where such second-phase precipitation should be imperceptible. This conclusion has not been checked by oxygen analysis of oxide from defective rods after irradiation.

The second bit of evidence pointing to this hydrogen content within defective fuel elements is afforded by observations of hydriding at the Zircaloy-2 cladding. Gulbransen and Andrew⁴⁸ have shown that the corrosion film on Zircaloy-2 is permeable by pure hydrogen, resulting in formation of brittle hydride phases, at temperatures as low as 650°F. Since the hydrogen content in equilibrium with hydrogenated water of the analysis used in the loop tests is of the order of 1 atm, it might be anticipated that conversion of Zircaloy-2 to the hydride might be noted upon exposure to hydrogenated water. However, extensive tests both in-pile and out-of-pile have shown that Zircaloy-2 does not absorb molecular hydrogen dissolved in water, al-

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Fig. 35—Equilibrium pressure of oxygen with various uranium oxides.

though 10 to 30 per cent of the atomic hydrogen produced in the corrosion reaction with water is absorbed in the Zircaloy-2. Boyle⁴⁹ has recently shown that the permeation of corrosion films on Zircaloy-2 by molecular hydrogen is effectively prevented by small traces of water vapor and furthermore that, even in pure hydrogen, absorption through the corrosion film occurs primarily at discontinuities such as edges and corners of rectangular samples. It is concluded, therefore, that hydrogen pickup, which is noted in in-pile tests only in defective samples, occurs by reaction with the hydrogen-rich atmosphere within the fuel rod and occurs locally through weak points in the oxide film; in addition, excessive hydrogen contents can be built up as a result of the corrosion reaction of Zircaloy-2 with water at the interior of the cladding, particularly at poorly corrosion-resistant regions.

As a consequence of the steep temperature gradient existing through the cladding, redistribution of dissolved hydrogen is noted, with the hydrogen migrating to the exterior of the cladding as shown in Fig. 36; here the redistribution of hydrogen in the Zircaloy-2 cladding of a PWR fuel rod operated at a heat flux such that the temperature gradient in the 0.021-in. wall of the cladding⁵⁰ was about 150° is quite clear. Hydrogen, which was produced at the inside of the cladding, diffused under the thermal gradient to the colder external surfaces where it formed a solid rim of zirconium hydride. Formation of such massive brittle phases may, of course, lead to cracking and fuel-element failure and was the cause of the premature termination of the X-1-g and X-1-h tests listed in Table 3. This effect has been investigated further by Markowitz and Belle,⁵¹ who determined the magnitude of thermal-gradient diffusion in cylinders of Zircaloy-2 externally heated and internally cooled with a known, constant amount of hydrogen dissolved in cylinders prior to test. The results are shown in Fig. 37 for a specimen of hydrogen content such that, at diffusion temperature, the cylinder lay partly

within the α solid solution range and partly within the $\alpha + \text{ZrH}_{1.5}$ two-phase region and for another specimen of original hydrogen content such that it was entirely single-phase α zirconium. Note that, in both cases, hydrogen redistributed itself to the cold end of the α solid-solution region but that a further redistribution occurred in the two-phase zone. The massive hydride shown in Fig. 36 is believed to result from the precipitation of hydride at the solvus line of the zirconium-hydrogen phase diagram. Markowitz and Belle⁵¹ have estimated from the plot shown in Fig. 37 a Soret coefficient for the thermal-gradient diffusion of hydrogen in zirconium of about $5 \times 10^{-3}/^\circ\text{C}$.

5.6 Release of Fission Products into Reactor Cooling Water

(a) *Introduction.* To simulate the performance of UO_2 fuel elements in pressurized-water reactor systems, prototype elements have been irradiated in high-pressure, high-temperature circulating water systems, or loops, designed so that a portion of the piping is installed within, or adjacent to, a reactor core. Such loops, installed in the NRX and MTR reactors, have permitted simultaneous irradiation-corrosion tests of the fuel elements.

In the large number of elements (nearly 100,000) in the PWR core, it must be assumed that cladding defects would exist or develop during irradiation in some of the elements. It was necessary to determine whether the previously demonstrated stability of UO_2 to high-pressure, high-temperature water is retained also under conditions of irradiation and heat transfer and to evaluate the fission-product problems that would be encountered in the PWR from defective fuel elements. Accordingly, one or more UO_2 fuel elements that were deliberately made defective were inserted into many of the irradiation tests. Defects were, in general, 0.005-in.-diameter holes drilled through the cladding.

Investigation of the fission-product activities in the loops was directed at the following questions:

1. Distribution of activity among the various fission-product elements.
2. Amount of activity released by the fuel.
3. Determination of the mechanism governing activity release.
4. Distribution of the released activity between the coolant and the system piping and the extent of the resultant surface contamination.

Fig. 36—Hydride concentration and crack at outside diameter of X-1-g-2 cladding. (Magnification 100 $\times$.)

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Fig. 37—Redistribution of hydrogen in internally cooled Zircaloy-2 cylinder under a thermal gradient.

5. Performance of system components such as ion-exchange resins used for coolant purification.

(b) *Radiochemical Summary of the Tests.* (1) *X-1-b.* Test was begun on Nov. 4, 1954. From the beginning, high fission-product activities were noted, but these increased only slowly, remaining within operational limits until Dec. 16, 1954. At this time, following a shutdown-start-up sequence, a burst of activity occurred sending the gamma monitor off-scale and causing a reactor scram. The gamma monitor remained off-scale for several hours with the reactor down. The expectation of operating difficulties at the high activity levels led to a termination of the test and removal from the reactor on December 17.

(2) *X-1-c.* Test was begun on Mar. 11, 1955. Fission-product activity in the loop water as measured by gamma and delayed-neutron monitors roughly followed the initial stepwise start-up of the reactor, and a steady-state activity level in the coolant was reached several hours after the reactor reached steady power. Operation remained satisfactory until March 14, when a leak developed in the loop. The leak rate increased rapidly until by March 19 it was 4 kg/hr (0.075 system volume/hr). The test was terminated on this date because of the potential hazard from escape of activity through the leak.

(3) *X-1-d.* Irradiation began on May 12, 1955. A stepwise start-up of reactor power was paralleled by corresponding rises in gamma and delayed-neutron activities, but to lower levels than in the X-1-h and X-1-c tests. Operation was satisfactory to the end of the test on Nov. 7, 1955. During the period from July 20 to September 9, the loop was operated without irradiation, the NRX reactor being shut down for repairs. Delayed-neutron and gamma activities rose slowly by about a factor of 3 throughout the test.

(4) *X-1-e.* Irradiation was begun on Dec. 15, 1955. Three hours after start-up, with the reactor at steady power, a large surge of activity scrambled the reactor. Water samples showed increases in cesium activities of a factor of 1000. Subsequent reactor start-ups and scrams resulted in increased gamma-monitor and individual isotopic activities to such levels that the test was terminated on December 16. This was the first test that exhibited activity increases following reactor shutdown.

(5) *X-1-f.* This test began on Feb. 16, 1956. Activity levels were high and reasonably uniform during the test. Scheduled for only a short irradiation, the specimens were removed from the loop on March 20.

(6) *X-1-g.* Irradiation commenced on May 19, 1956. Fission-product activity levels were extremely variable, short-lived activities showing fluctuations of a factor of 100 with the reactor at steady power. On June 18, all activities decreased to levels found in loops containing no defects. Attempts to increase the fission-product release rate by varying flow, pH, pressure, and reactor power being unsuccessful, the specimens were removed from the loop on July 11. Following reinsertion of the test on September 12, short-lived activities were again observed, and the test continued normally until October 1, when the gamma monitor began to show prolonged off-scale readings on reactor start-ups, as well as peaks on shutdown. Concurrently, short-lived activities showed an increase by a factor of 10. Following a reactor start-up on October 4, the gamma monitor continued to rise after steady reactor operation was reached, and the delayed-neutron monitor also recorded extremely high activity. The test was terminated on October 5.

(7) *X-1-h.* This test was begun on July 24, 1956. Operation at high fission-product activity levels continued satisfactorily until August 30, when all activities began to rise, the increase being a factor of 5 to 10. Peaking of gamma-monitor activity at shutdown was observed after September 1, and delayed-neutron and gamma-monitor peaks at start-up increased in severity. The test was terminated as planned on September 10.

(8) *X-1-j.* Irradiation began on Dec. 14, 1956. Activities were normal until December 18, when periodic decreases and increases were observed, activities fluctuating by a factor of 1000 over a period of 3 to 7 days. The test was terminated on schedule on Jan. 14, 1957.

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(9) *X-1-l*. This test began on Jan. 18, 1957. Similar periods of activity fluctuation as found on previous tests were again observed, decreases in activity usually occurring during periods of steady reactor operation. Following one or more shutdowns and start-ups, the activity levels usually return to expected values and then sometimes decrease during steady operation. The test has proceeded satisfactorily and is scheduled for removal in February 1958.

(10) *MTR-25-2*. Irradiation began on July 28, 1956. During periods of slow cycling (12 hr in flux, 12 hr out of flux), long-lived activity was observed to peak following each change in rod power. The test was terminated as scheduled on Sept. 24, 1956.

(11) *MTR-29-1*. This test began on Dec. 1, 1956. Activity levels were high and reasonably uniform during the first cycle of reactor operation and were lower during the second 3 weeks at the same reactor power. After an additional cycle of operation at reduced heat flux, the specimens were discharged on Jan. 30, 1957.

(12) *MTR-29-2*. Irradiation began on February 1. Activities remained constant for the first cycle at high flux. For the first part of the second reactor cycle, the element was operated at low power and then was reinserted to the high-flux position. Steady-state activities were lower than during initial high power operation, paralleling the decrease observed during the 29-1 experiment. Activity levels did not fall to those expected from a nondefective element, however, as they have done repeatedly in the X-1 loop tests. Since the change in activity observed in the course of the individual tests was of the same magnitude as that observed between the 29-1 and 29-2 tests, no significant difference between the fission-product release rates could be determined from loop activity data which could be attributed to the different densities of UO_2 employed in these tests.

(13) *MTR-29-3, -4, -5*. Irradiation of 29-3 began on Mar. 15, 1957. Since operation was at low temperature during the test and the fuel element was in a low flux position most of the 2 cycles, few radiochemical data were obtained. The rod was removed on April 21.

The 29-4 test began on Apr. 24, 1957. Activity in this four-defect test was fairly uniform during the test, about the same as in previous 29-1 and 29-2 tests containing only single defects. Delayed-neutron activity was appreciably higher. The test was removed on May 12, 1957.

Irradiation of the 29-5 single-defect test began on May 15. Loop activity fell by a decade within the first 4 days of the test and remained level thereafter. The steady-state levels were about a factor of 12 lower than those observed in the 29-4 test. Delayed-neutron activity also was lower than in the 29-4 test. The element was removed from the reactor on June 2.

(c) *Rate and Mechanism of Escape*. Under constant reactor power conditions, there are three basic mechanisms by which fission products can escape from a defective UO_2 fuel element: (1) small UO_2 fragments can be eroded or corroded from the fuel and escape from the element, (2) fission fragments can penetrate the fuel surface by recoil escape, and (3) fission products can diffuse from the UO_2 matrix and escape to the external system. During power transients the rate of evolution of fission products can be increased by (4) the so-called "waterlogging" effect and related phenomena.

(d) *Escape by Erosion-Corrosion*. A possible mechanism of fission-product escape from a defective element is the erosion-corrosion of small fragments of UO_2 from the fuel and their escape to the external system carrying with them their associated fission products. The first defect test (X-1-b) is the only test in which there was any indication that this mechanism contributed to the fission products in the system.⁵³ In this test, relatively large amounts of uranium were found on the ion-exchange resins and on the surfaces of pipe specimens from the loop. Moreover, the distribution of fission-product activity on the pipe specimens was heterogeneous, indicating gravitational separation of particulate matter (see Sec. 5.6d). The release of particulate UO_2 in this test has been attributed to the low density of the fuel pellets (~80 per cent of theoretical density). Out-of-pile erosion-corrosion tests on high density UO_2 have shown that this mechanism will not release significant amounts of fuel except in the presence of high dissolved oxygen concentrations in the coolant.^{53,54}

(e) *Recoil Escape*. Under irradiation, fission fragments will penetrate any fuel surface S because of the finite range l_f of the fission fragments in the fuel material. The probability that a fission fragment originating in the element of volume Sl_f will penetrate the surface of the fuel is 0.25. The UO_2 fuel pellets are surrounded with a sheath of Zircaloy-2. Fission fragments that penetrate the surface will come to rest in the gas space surrounding the fuel or will penetrate the cladding. The rate at which fission fragments penetrating the fuel surface come to rest in the gas space is given by⁵⁵

$$\frac{dN}{dt} = \frac{fYSl_f}{4} \left[\frac{h}{l_s} \left(2 - \frac{h}{l_s} \right) \right] \quad (12)$$

where f = fissioning rate per unit volume, fissions/sec/cm³

Y = fission yield

l_f = recoil length of fission fragment in fuel, cm

h = clearance between fuel and cladding, cm

l_s = recoil length of fission fragment in gas or steam surrounding fuel, cm

$h/l_s \leq 1$

This equation, however, does not give the rate at which fission products escape through a defect into the external system since an isotope must diffuse to the defect from the end of its recoil path in the gas space. The differential equations for the steady-state rate of diffusion out of various-sized and -shaped defects in the cladding have been solved.⁵⁶

The results of irradiation tests on defective UO_2 elements indicate that recoil escape is important for short-lived fission products. Because of the half life, the radiochemical determination of short-lived isotopes in the loop water during a test is extremely difficult. In most cases it is impossible because of a preponderance of the long-lived fission products. Consequently, there is very little direct evidence to verify the theoretical equations. The only real evidence comes from the results of the (X-1-h) defect test during which the rates of escape of the 54s Br^{87} and 22s I^{137} delayed-neutron emitters were investigated. This investigation was conducted because the fuel-element-failure detection and location system of the Pressurized Water Reactor, Shippingport, Pa., must monitor short-lived fission products in the primary coolant if a significant number of defective elements are to be located.⁵⁷

During this test (X-1-h) the specific delayed-neutron activity in the coolant was investigated by passing a sample of the primary coolant through a special delayed-neutron monitor.⁵⁵ This monitor consisted of a coil of 0.5-in.-I.D. aluminum tubing surrounded by eight BF_3 tubes suspended in a tank of water for neutron moderation. The flow through this monitor could be interrupted so that decay data could be obtained in order to determine the relative abundances of 54s Br^{87} and 22s I^{137} . An example of these decay curves is given in Fig. 38. The specific activities of Br^{87} and I^{137} obtained from the analysis of these decay curves corresponded to rates of escape from a 0.005-in. hole in the cladding of 10.7×10^5 and 12.4×10^5 atoms/sec per rod for Br^{87} and I^{137} , respectively. The calculated rates of evolution from the above equations gave 9.69×10^5 and 8.85×10^5 atoms/sec per rod for Br^{87} and I^{137} , respectively. However, the agreement is probably fortuitous to some degree since at constant reactor power there were rather large variations in the specific delayed-neutron activity during the test. Moreover, the test conditions were not really at steady state since there is an unavoidable pressure cycle of approximately 50 psi imposed by the pressurizer on the system pressure with a frequency of about 10 min. It would be expected that this would result in a continuous change in the mass of steam within the element. This could give a greater rate of escape than that given by the steady-state diffusion equation.

(f) *Diffusion*. This undoubtedly is the primary mechanism for the escape of the longer lived fission products from defective UO_2 elements. Isotopes formed in fission diffuse through the UO_2 matrix to the free surface as outlined in Sec. 4 and then along the free surface to the external system. The diffusion through the UO_2 matrix to the free surface is believed to be the rate-controlling step. Consequently, it is ordinarily assumed that the UO_2 is composed of a large number of equivalent spheres of radius a which is related to the density of the bulk

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Fig. 38—Decay of delayed neutrons in loop water. Eight-BF₃-tube monitor 0130, Aug. 4, 1956.

UO₂. The latter assumption is probably unjustified for relatively short-lived fission products. The total number of atoms of an isotope formed directly in fission which are external to the equivalent sphere is given as a function of time by

$$N_i = 4\pi a^3 f Y \left\{ \left[\sqrt{\frac{d}{\lambda}} \frac{\cosh \sqrt{\lambda/d}}{\sinh \sqrt{\lambda/d}} - \frac{d}{\lambda} \right] (1 - e^{-\lambda t}) + \frac{2}{\pi^2} e^{-\lambda t} \sum_{n=1}^{\infty} \frac{1 - e^{-n^2 \pi^2 d}}{n^2 (n^2 \pi^2 d + \lambda)} \right\} \quad (13)$$

where N_i = total number of active atoms external to the equivalent sphere at any time t

a = radius of equivalent sphere, cm

f = fissioning rate per unit volume, fissions/sec/cm³

Y = fission yield

$d = D/a^2$, sec⁻¹

$D = D_0 e^{-E/RT}$ diffusion coefficient, cm²/sec

E = energy of activation for diffusion, cal/mole

T = absolute temperature, °K

R = gas constant, cal/mole/°K

λ = radioactive decay constant, sec⁻¹

$n = 1, 2, 3, \dots, \infty$

This equation is applied to the fission-product escape from a defective fuel element by assuming that the UO₂ pellets are radially divided into i constant temperature regions with m_i spheres in each region. The total number of atoms in the external system at any time t is then given by

$$N_T = \sum_i m_i N_i \quad (14)$$

where the summation is carried out over the constant-temperature regions. This procedure was followed in Sec. 4 for xenon and krypton diffusion. However, the diffusion equation is not used to evaluate the nonvolatile fission-product release rate obtained from the irradiation tests in the pressurized-water loops. The reason for this is that the energy of activation for diffusion of fission products in UO_2 must be known and in only a few cases has this been determined. In practice, a parameter in an empirical equation is evaluated from the test data so that the rates of escape of fission products can be compared from test to test.⁵⁸ This parameter, the escape-rate coefficient ν , is defined as the proportionality constant relating the total amount of an isotope in the fuel to its rate of escape to the external system, i.e.,

$$\frac{d(N)_T}{dt} = \nu(N)_f \quad (15)$$

where ν = probability per unit time that an isotope will escape from the defective fuel element, sec^{-1}

$(N)_T$ = total amount of isotope in external system, atoms

$(N)_f$ = total amount of isotope in fuel element, atoms/rod

At steady-state conditions ($\lambda t > 1$), the escape-rate coefficient ν is related to the diffusion coefficient D as follows:

$$\nu = 3\sqrt{\lambda} \sum_i \frac{m_i}{m_T} \sqrt{d_i} \quad (16)$$

where m_T = total number of equivalent spheres in UO_2 rod

m_i = number of spheres in i th temperature region

$d_i = D/a^2$

According to this equation, the value of ν for a given element should vary with the temperature distribution across the UO_2 pellets and directly with the square root of the isotopic decay constant.

The values of ν calculated from the isotopic activities found in various parts of the test systems, e.g., loop water, ion-exchange resins, and pipe surfaces, are given in Table 14 for various irradiation tests on UO_2 elements containing 0.005-in.-diameter holes in the cladding. Also given in this table are general discussions of each test. The values of ν were calculated from the isotopic concentrations in the loop water by the following equation:

$$[N]_s = \frac{\nu \epsilon Y}{W(\nu + \lambda)(\beta + \lambda)} - \frac{\nu}{W(\beta - \nu)} \left[\frac{\epsilon Y}{\nu + \lambda} - (N)_f^0 \right] e^{-(\nu + \lambda)t} + \left\{ [N]_s^0 + \frac{\nu \epsilon Y}{W(\beta + \lambda)(\beta - \nu)} - \frac{\nu(N)_f^0}{W(\beta - \nu)} \right\} e^{-(\beta + \lambda)t} \quad (17)$$

where $[N]_s$ = isotopic concentration in loop water, superscript 0 indicates isotopic concentration at zero time, atoms/g

ϵ = fissioning rate, fissions/sec/rod

Y = fission yield, atoms/fission

W = total weight of loop water, g

$\beta = \xi v_p/W$, purification constant, sec^{-1}

ξ = efficiency of ion-exchange resins

v_p = mass flow rate through ion-exchange resins, g/sec

λ = radioactive decay constant, sec^{-1}

t = time, sec

$(N)_f^0$ = total amount of isotope in UO_2 rod at zero time, atoms/rod

The values of ν from the total amount of an isotope on the ion-exchange resins were calculated from the following equation:

$$(N)_R = \frac{\beta \nu \epsilon Y}{\lambda(\nu + \lambda)(\beta + \lambda)} + \frac{\beta}{\nu} \left[\frac{\epsilon Y}{\nu + \lambda} - (N)_f^0 \right] e^{-(\nu + \lambda)t} + \left[(N)_T^0 - \frac{\epsilon Y}{\lambda} \right] e^{-\lambda t} - \left[(N)_s^0 + \frac{\nu \epsilon Y}{(\beta + \lambda)(\beta - \nu)} - \frac{\nu(N)_f^0}{(\beta - \nu)} \right] e^{-(\beta + \lambda)t} \quad (18)$$

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where $(N)_R$ = total amount of isotope on ion-exchange resin, atoms

$(N)_T^0 = (N)_f^0 + (N)_s^0 + (N)_R^0$, total amount of isotope in fuel and system at zero time, atoms

The values of ν calculated by the above equations represent only that fraction of the released activity which is in the loop water at any time or that fraction which is transported to and deposited on the ion-exchange resins. For elements that have low deposition rates on the system surfaces, these values of ν will represent the total amount of a given isotope that escapes from a defective UO_2 element. For elements that have high deposition rates, the value of ν represents only a small fraction of the activity that escapes.

(Text continues on page 702.)

Table 14—RADIOCHEMICAL DATA FOR IN-PILE LOOP EXPERIMENTS

X-1-b (NRX)			
Escape-rate coefficients (ν) calculated from isotopic activities on ion-exchange resins (HOH form)			
Isotope	ν , sec ⁻¹	Isotope	ν , sec ⁻¹
Cs ¹³⁷	1.5×10^{-8}	Sr ⁹⁰	1.1×10^{-9}
Ba ¹⁴⁰	1.3×10^{-9}	Zr ⁹⁵	1.7×10^{-12}
Sr ⁸⁹	9.6×10^{-10}	Ce ¹⁴⁴	9.2×10^{-13}

This was the first irradiation test on a defective UO_2 fuel element. The activities in the loop water during this test were high. This is attributed to the low density (~80% of theoretical) and poor quality of the UO_2 . During irradiation, the cladding on specimen 1 swelled and split, releasing large amounts of activity into the system, which resulted in the termination of the test. The failure of this element has been attributed to the waterlogging effect.

X-1-c (NRX)			
Escape-rate coefficients (ν) calculated from isotopic activities on ion-exchange resins (HOH form)			
Isotope	ν , sec ⁻¹	Isotope	ν , sec ⁻¹
I ¹³¹	6.5×10^{-7}	Ba ¹⁴⁰	1.7×10^{-8}
Cs ¹³⁷	8.4×10^{-7}	Zr ⁹⁵	6.0×10^{-11}
Sr ⁸⁹	1.6×10^{-8}	Ce ¹⁴¹	6.2×10^{-11}
Sr ⁹⁰	2.0×10^{-8}	Ce ¹⁴⁴	6.6×10^{-11}

Average specific activities in loop water and values of ν calculated therefrom

Isotope	Dis/min/ml	ν , sec ⁻¹
Kr ⁸⁸	1.0×10^7	7.3×10^{-7}
Xe ¹³³	8.3×10^5	7.3×10^{-7}

This test had a high leak rate and was run with continuous degasification of unknown efficiency. Both of these conditions will have a great effect on the specific activity of the 5.27d Xe¹³³, whereas the 2.77h Kr⁸⁸ is relatively unaffected because of the shorter half life. Since the degasification efficiency was unknown, the value of ν for Xe¹³³ was assumed to be equal to ν for Kr⁸⁸. This corresponds to a degasification efficiency of 22%, which is reasonable for the type of degasifier.

The values of the escape-rate coefficient are the highest observed in any defect test except possibly X-1-e. The values of ν for barium and strontium were a factor of 10^2 greater than what is considered normal for a UO_2 rod. The high activities are attributed to the low density of the UO_2 (88.8% of theoretical) and, most important, to the fact that during irradiation an axial hole developed through the center of at least six of the 10 UO_2 pellets in the specimen.

Table 14—(Continued)

X-1-d (NRX)					
Escape-rate coefficients (ν) calculated from isotopic activities on ion-exchange resins					
Period: Resin type:	5/12 to 6/22 HOH	6/22 to 7/6 HOH	7/6 to 7/20 KOH	9/14 to 10/9 HOH	10/9 to 11/7 KOH
Isotope	ν , sec ⁻¹				
I ¹³¹	11×10^{-8}	10×10^{-10}	6.5×10^{-10}	15×10^{-10}	7.2×10^{-10}
Cs ¹³⁷	1.3×10^{-8}	1.2×10^{-8}	0.5×10^{-8}	0.3×10^{-8}	1.3×10^{-8}
Ba ¹⁴⁰	5.6×10^{-12}	5.9×10^{-12}	0.9×10^{-12}	9.7×10^{-12}	0.3×10^{-12}
Sr ⁸⁹	16×10^{-12}	5.6×10^{-12}	0.8×10^{-12}	9.9×10^{-12}	0.2×10^{-12}
Sr ⁹⁰	7.0×10^{-12}	9.2×10^{-12}	0.9×10^{-12}	22×10^{-12}	0.3×10^{-12}
Y ⁹¹	2.8×10^{-13}				
Zr ⁹⁵	7.6×10^{-13}	9.4×10^{-13}	20×10^{-13}	18×10^{-13}	35×10^{-13}
Ce ¹⁴⁴	23×10^{-13}	14×10^{-13}	19×10^{-13}	4.1×10^{-13}	8.4×10^{-13}

Type of resin on stream: HOH, hydrogen hydroxyl form; KOH, potassium hydroxyl form.

Total isotopic activities on system surface and ion-exchange resin beds;
also, the total ν_T calculated therefrom

Total activity, dis/min at end of test

Isotope	On resins	On system surface	ν_T , sec ⁻¹
Sr ⁸⁹	1.6×10^9	1.3×10^9	4.5×10^{-12}
Zr ⁹⁵	1.3×10^9	5.6×10^9	9.3×10^{-12}
Cs ¹³⁷	1.1×10^{11}	3.5×10^8	1.1×10^{-8}
Ba ¹⁴⁰	4.4×10^8	2.6×10^9	10×10^{-12}
Ce ¹⁴⁴	2.3×10^8	2.4×10^9	7.8×10^{-12}
Y ⁹¹	4.0×10^8	1.3×10^9	1.9×10^{-12}

The system surface is based on a total system of 1.2×10^5 cm².

Average specific activities in loop water and values of ν
calculated therefrom

Isotope	Dis/min/ml	ν , sec ⁻¹
Kr ⁸⁸	$(6.5 \pm 8.0) \times 10^5$	$(1.8 \pm 2.2) \times 10^{-8}$
Xe ¹³³	$(5.2 \pm 6.3) \times 10^7$	$(1.3 \pm 1.5) \times 10^{-8}$

This is the first test that contained high-density UO₂ (95.3% of theoretical). The activities in the loop water remained at a moderate level for the entire period of the test. The values of the escape-rate coefficient observed in this test served as a basis for the evaluation of the fission-product hazard in PWR.

There is no apparent explanation for the large variation in the escape-rate coefficient during the various periods of the test. However, it should be noted that the values of ν , particularly for Ba¹⁴⁰, Sr⁸⁹, and Sr⁹⁰, show the greatest variation during those periods when the potassium hydroxyl form of the ion-exchange resin was on stream. In general, the KOH form of the ion-exchange resin is much less efficient for decontamination than the HOH form.

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Table 14—(Continued)

X-1-e Test (NRX)

The UO_2 pellets melted in this test, and the cladding failed after only a few hours of irradiation. The activity levels were excessive. In general, the values of ν were not calculated because they were considered to be meaningless. The Cs^{138} activity in the loop water reached 4.4×10^8 dis/min/ml. This corresponds to a ν of $3.3 \times 10^{-6} \text{ sec}^{-1}$.

X-1-f Test (NRX)

Escape-rate coefficients (ν) calculated from isotopic activities on the ion-exchange resins

Isotope	ν, sec^{-1}		
	First period	Second period	Third period
I^{131}	1.3×10^{-7}	9.0×10^{-9}	1.4×10^{-8}
Cs^{137}	9.3×10^{-8}	9.7×10^{-8}	2.1×10^{-8}
Ba^{140}	9.6×10^{-11}	2.2×10^{-11}	4.8×10^{-12}
Sr^{89}	1.1×10^{-10}	1.0×10^{-10}	1.4×10^{-11}
Sr^{90}	2.5×10^{-11}	6.6×10^{-12}	2.9×10^{-12}
Mo^{99}	2.8×10^{-9}	2.2×10^{-9}	5.4×10^{-10}
Ce^{144}	2.9×10^{-13}	2.2×10^{-14}	4.7×10^{-14}
Zr^{95}	2.7×10^{-13}	4.3×10^{-13}	2.6×10^{-12}

Total escape-rate coefficient calculated from the total isotopic activities on ion-exchange resins and the system surface

Isotope	ν_T, sec^{-1}	Isotope	ν_T, sec^{-1}
I^{131}	2.1×10^{-8}	Mo^{99}	4.0×10^{-9}
Cs^{137}	5.5×10^{-8}	Ce^{144}	6.4×10^{-12}
Ba^{140}	1.7×10^{-10}	Zr^{95}	7.6×10^{-12}
Sr^{89}	4.2×10^{-11}	Te^{132}	2.7×10^{-8}
Sr^{90}	2.7×10^{-10}		

Average specific activities in loop water and values of ν calculated therefrom

Isotope	Dis/min/ml	ν, sec^{-1}
Kr^{88}	1.5×10^8	3.5×10^{-7}
Xe^{133}	4.5×10^8	9.7×10^{-8}
Cs^{138}	6.1×10^8	3.7×10^{-8}

The specific activities in the loop water during this test were high. This is attributed to the fact that the UO_2 pellets melted in the center during irradiation.

Table 14—(Continued)

X-1-g (NRX)					
Total isotopic activities on ion-exchange resins (dis/min at time of removal from system)					
Period: Resin Type:	5/19 to 5/28 HOH	5/28 to 6/14 HOH	6/14 to 7/3 HOH	7/3 to 7/8 KOH	9/12 to 10/5 HOH
Isotope	Dis/min				
I ¹³¹	7.2×10^{11}	1.6×10^{13}	2.5×10^{12}	6.8×10^9	3.8×10^{12}
Cs ¹³⁶	7.8×10^8				
Cs ¹³⁷	7.8×10^8	2.0×10^{11}	1.7×10^{11}	2.6×10^8	2.5×10^{12}
Ba ¹⁴⁰	2.7×10^9	1.2×10^{10}	3.7×10^{10}	6.8×10^8	6.2×10^{10}
Sr ⁸⁹	2.4×10^9	3.8×10^9	6.2×10^9	1.2×10^8	7.6×10^{10}
Sr ⁹⁰		9.5×10^6	1.9×10^7	9.7×10^5	2.5×10^8
Mo ⁹⁹	1.8×10^{10}	7.1×10^{13}	1.5×10^{11}		
Zr ⁹⁵	1.4×10^6				1.3×10^8
Ce ¹⁴⁴		1.8×10^6	1.5×10^6	9.4×10^5	6.7×10^7

Values of ν are not yet calculated for this test.

Average specific isotopic activities in loop water and values of ν calculated therefrom

Period	5/19 to 5/28		5/28 to 6/14		6/14 to 7/3	
Isotope	Dis/min/ml	ν , sec ⁻¹	Dis/min/ml	ν , sec ⁻¹	Dis/min/ml	ν , sec ⁻¹
Cs ¹³⁸	3.0×10^5	2.3×10^{-9}	3.4×10^5	2.6×10^{-9}	4.5×10^6	3.5×10^{-8}
Kr ⁸⁸	3.0×10^6	5.3×10^{-9}	1.7×10^7	3.0×10^{-8}	3.7×10^7	6.6×10^{-8}

During the first part of this test (5/19/56 to 7/8/56) the specific isotopic activities in the loop water did not appear to be higher than those expected for a normal rod. However, there were periods when the fission-product activity in the loop water fell to levels comparable to those observed in tests that did not contain a defective element. This test was resumed after the test (X-1-h). The activity levels in the loop water remained normal until 10/1/56 when the gamma monitor showed a large increase in activity levels. Soluble activities rose rapidly, Cs¹³⁸ increasing from an average of 6.6×10^6 dis/min/ml during the period 9/17/56 to 10/1/56 to 7.7×10^7 dis/min/ml on 10/3/56, the latter activity corresponding to a ν value of 4.8×10^{-7} sec⁻¹. Examination of the defective specimen showed that the UO₂ pellets had melted in the center and that another defect had developed in the cladding during irradiation.

X-1-h (NRX)

Total isotopic activities of ion-exchange resins (HOH resin)
for the period 7/24 to 9/26

Isotope	Dis/min at time of removal from system
I ¹³¹	3.7×10^{15}
Cs ¹³⁷	2.3×10^{12}
Sr ⁸⁹	2.9×10^{11}
Sr ⁹⁰	2.9×10^8
Ba ¹⁴⁰	4.6×10^{12}
Ce ¹⁴⁴	1.3×10^8
Zr ⁹⁵	5.2×10^9

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Table 14—(Continued)

Average specific isotopic activities in loop water and values of ν calculated therefrom				
Isotope	First period		Second period	
	Dis/min/ml	ν , sec ⁻¹	Dis/min/ml	ν , sec ⁻¹
Kr ⁸⁸	3.8×10^7	9.6×10^{-8}		
I ¹³¹	1.4×10^7	Not yet calculated	5.6×10^7	Not yet calculated
I ¹³³	1.4×10^7	3.2×10^{-8}	1.2×10^8	2.7×10^{-7}
Xe ¹³⁸	1.1×10^6	1.5×10^{-8}	2.6×10^7	3.5×10^{-7}
Cs ¹³⁷	5.9×10^3	Not yet calculated	9.5×10^5	Not yet calculated
Cs ¹³⁸	6.3×10^6	5.9×10^{-8}	5.0×10^7	4.7×10^{-7}
Cs ¹³⁹	4.5×10^5	1.2×10^{-8}	1.2×10^6	3.2×10^{-8}
Cs ¹³⁶	6.1×10^4	Not yet calculated	2.1×10^6	Not yet calculated

During the second period of this test, most of the isotopic activities in the loop water increased by about a factor of 10. Postirradiation examination of the specimens showed that the cladding on one of the nondefective elements had failed. Both this element and the original defective specimen showed evidence of center melting in the UO₂ pellets.

X-1-j (NRX)

Total isotopic activities on ion-exchange resins (LiOH form)
(resin on stream 746 hr); values of ν are not yet calculated

Isotope	Dis/min	Isotope	Dis/min
I ¹³¹	2.2×10^{10}	Ba ¹⁴⁰	5.0×10^8
Cs ¹³⁷	3.2×10^9	Ce ¹⁴⁴	2.6×10^6
Sr ⁸⁹	1.9×10^9	Zr ⁹⁵	2.1×10^7

Average specific isotopic activities in loop water and values of ν calculated therefrom

Isotope	Dis/min	ν , sec ⁻¹
Kr ⁸⁸	3.5×10^6	3.3×10^{-8}
Xe ¹³³	9.7×10^7	6.4×10^{-9}
Cs ¹³⁸	1.5×10^6	3.6×10^{-8}

Activity levels in this test were normal.

X-1-1 Test (NRX)

Escape-rate coefficients (ν) calculated from isotopic activities on
the ion-exchange resins (LiOH form)

Isotope	ν , sec ⁻¹		
	First period	Second period	Third period
I ¹³¹	1.3×10^{-8}	1.6×10^{-9}	6.9×10^{-9}
Cs ¹³⁷	8.4×10^{-8}	1.0×10^{-8}	Not yet available
Sr ⁸⁹	3.3×10^{-11}	4.6×10^{-12}	4.2×10^{-12}
Zr ⁹⁵	1.6×10^{-13}	Not yet available	Not yet available
Ce ¹⁴⁴	2.4×10^{-14}	2.7×10^{-14}	1.0×10^{-14}

Table 14—(Continued)

Escape-rate coefficients (ν) calculated from the average specific isotopic activities in the loop water

Isotope	ν , sec ⁻¹		
	First period	Second period	Third period
I ¹³¹	5.7×10^{-8}		2.0×10^{-8}
I ¹³³	1.1×10^{-9}		4.9×10^{-8}
Xe ¹³³	1.7×10^{-8}		
Xe ¹³⁸	3.0×10^{-8}		5.4×10^{-9}
Cs ¹³⁶	1.5×10^{-8}		3.5×10^{-7}
Cs ¹³⁷	1.7×10^{-9}		7.0×10^{-9}
Cs ¹³⁸	4.4×10^{-8}	4.1×10^{-9}	5.5×10^{-8}
Cs ¹³⁹	5.4×10^{-8}		1.4×10^{-9}
Br ⁸³	1.0×10^{-8}		
Br ⁸⁴	2.9×10^{-9}		
Kr ⁸⁸	2.1×10^{-8}	8.0×10^{-9}	2.4×10^{-8}
Sr ⁸⁹	4.9×10^{-11}		5.9×10^{-12}
Sr ⁹¹	8.6×10^{-12}		1.5×10^{-12}
Ba ¹⁴⁰	5.1×10^{-12}		

This test, still in progress, is scheduled for a 1-year irradiation. The fission-product activity level in the loop water has never exceeded that expected from a normal rod. However, there are periods when the activity level falls to that which would be expected from only the uranium contamination in the loop, i.e., it appears that in some manner the defect becomes plugged.

WAPD-13-6 (MTR)

Average specific isotopic activities in loop water and values of ν calculated therefrom

Isotope	Dis/min/ml	ν , sec ⁻¹
I ¹³¹	3.9×10^5	4.4×10^{-8}
I ¹³³	2.2×10^6	4.6×10^{-8}
Cs ¹³⁷	262	1.3×10^{-8}
Cs ¹³⁸	5.2×10^6	1.9×10^{-7}
Cs ¹³⁹	1.3×10^5	3.6×10^{-8}
Xe ¹³⁵	1.8×10^6	3.1×10^{-8}
Ba ¹⁴⁰	2.3×10^3	1.8×10^{-10}
Sr ⁸⁹	1.4×10^3	5.1×10^{-10}
Sr ⁹¹	1.9×10^4	5.0×10^{-10}
Sr ⁹²	9.8×10^3	2.2×10^{-10}
Sr ⁹³	4.1×10^4	4.9×10^{-9}

The ion-exchange resins were not analyzed in this test. This test gave the most consistent values of ν thus far observed in any test.

WAPD-15-2 (MTR)

Escape-rate coefficients (ν) calculated from the isotopic activities on the ion-exchange resins (cycle 55)

Isotope	ν , sec ⁻¹	Isotope	ν , sec ⁻¹
I ¹³¹	1.0×10^{-10}	Sr ⁸⁹	5.2×10^{-12}
Cs ¹³⁷	1.5×10^{-11}	Zr ⁹⁵	4.7×10^{-13}
Ba ¹⁴⁰	1.1×10^{-12}	Ce ¹⁴⁴	6.9×10^{-14}
Te ¹³²	1.8×10^{-9}		

The values of ν for Te¹³² was calculated from 2.25h I¹³² in loop water after removal of the defective element.

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Table 14—(Continued)

Average specific isotopic activities in loop water and values of ν calculated therefrom				
Isotope	Cycle 55		Cycle 56	
	Dis/min/ml	ν , sec ⁻¹	Dis/min/ml	ν , sec ⁻¹
I ¹³¹	3.4×10^4	6.6×10^{-10}	5.3×10^5	7.1×10^{-9}
I ¹³³	2.4×10^5	8.9×10^{-10}	2.1×10^6	1.2×10^{-8}
Cs ¹³⁸	5.4×10^4	1.5×10^{-9}		

The values of ν for iodine and cesium appeared to be particularly low during cycle 55. However, from the very start of cycle 56, specific activity of I¹³¹ and I¹³³ increased by about a factor of 10 and remained level.

WAPD-25-2 (MTR)

The defected element in this test was cycled between two positions in the reactor. The ratio of the average thermal-neutron flux between the two positions was 8.5.

Average specific isotopic activities in loop water and the value of ν calculated therefrom

Isotope	High-flux position		Low-flux position	
	Dis/min/ml	ν , sec ⁻¹	Dis/min/ml	ν , sec ⁻¹
Ba ¹³⁹	1.2×10^5	$(6.6 \pm 2.4) \times 10^{-9}$	4.3×10^4	$(2.1 \pm 0.7) \times 10^{-8}$
Cs ¹³⁸	3.5×10^6	$(3.2 \pm 0.9) \times 10^{-8}$	1.3×10^5	$(1.0 \pm 0.7) \times 10^{-8}$

The specific activity of 85.0m Ba¹³⁹ is controlled by the direct escape and subsequent decay of the 9.5m Cs¹³⁹ parent. Consequently, the values of ν given for Ba¹³⁹ are those for Cs¹³⁹.

Theoretically, if the specific activities of Cs¹³⁹ → Ba¹³⁹ and Cs¹³⁸ in the loop water are controlled by diffusion out of the UO₂, the value of ν should vary between the two flux levels because of the effect of temperature on the diffusion coefficient. However, the values of ν between the two positions is the same within experimental error for the two isotopes. Other data on the specific activities of the relatively long-lived Ba¹⁴⁰ and I¹³¹, whose concentration in the fuel does not vary between cycles, are discussed in Sec. 5.6g.

Table 14—(Continued)

WAPD-29-1 and WAPD-29-2 (MTR)

These tests were designed to determine differences in the rates of evolution of fission products from defected UO_2 elements of different densities and at different heat fluxes. The average density of the UO_2 in the defected specimens in the WAPD-29-1 test and the WAPD-29-2 test was 93.53% and 97.33% of theoretical, respectively.

Escape-rate coefficients (ν) calculated from the isotopic activities on the ion-exchange resins (LiOH form) during the WAPD-29-1 test

Heat flux:	230,000 Btu/hr/sq ft				21,000 Btu/hr/sq ft	
Period:	12/1/56 to 12/16/56		12/21/56 to 1/6/57		1/18/57 to 1/28/57	
Isotope	Dis/min	ν , sec ⁻¹	Dis/min	ν , sec ⁻¹	Dis/min	ν , sec ⁻¹
I ¹³¹	4.8×10^{10}	4.4×10^{-10}	3.5×10^{11}	6.9×10^{-9}	6.8×10^{10}	9.5×10^{-10}
Cs ¹³⁷	2.5×10^8	6.1×10^{-10}	3.5×10^8	1.1×10^{-10}	2.4×10^9	1.3×10^{-9}
Sr ⁸⁹	2.9×10^9	5.6×10^{-11}	4.9×10^9	1.6×10^{-11}	2.6×10^9	5.6×10^{-11}
Ba ¹⁴⁰	2.6×10^8	Not yet	1.1×10^9	Not yet	5.0×10^9	Not yet
		calculated		calculated		calculated
Mo ⁹⁹			9.6×10^9	Not yet		Not yet
				calculated		calculated
Ce ¹⁴⁴	4.2×10^7	3.4×10^{-12}	1.8×10^7	1.8×10^{-13}	2.4×10^7	4.3×10^{-13}
Zr ⁹⁵	1.3×10^8	2.5×10^{-12}	8.5×10^7	2.5×10^{-13}	2.1×10^8	1.1×10^{-12}

Average specific isotopic activities in loop water during WAPD-29-1 test and the values of ν calculated therefrom

Heat flux:		230,000 Btu/hr/sq ft			21,000 Btu/hr/sq ft	
Isotope	Dis/min/ml	ν , sec ⁻¹	Dis/min/ml	ν , sec ⁻¹	Dis/min/ml	ν , sec ⁻¹
Cs ¹³⁸	1.1×10^7	2.0×10^{-7}	6.7×10^6	1.2×10^{-7}	5.8×10^4	1.1×10^{-8}
Cs ¹³⁹			4.7×10^5	2.1×10^{-8}	1.4×10^4	6.8×10^{-9}
I ¹³¹	8.7×10^4	1.0×10^{-9}			4.0×10^4	2.2×10^{-9}
I ¹³³	9.5×10^3	5.2×10^{-9}				
Kr ⁸⁸	2.6×10^7	1.1×10^{-7}	1.1×10^7	4.7×10^{-8}	1.6×10^5	7.2×10^{-9}
Xe ¹³⁸	5.4×10^6	1.3×10^{-7}				

Escape-rate coefficients (ν) calculated from the isotopic activities on the ion-exchange resins (LiOH form) from the WAPD-29-2 test

Heat flux:		286,000 Btu/hr/sq ft				26,600 Btu/hr/sq ft	
Period:	2/1/57 to 2/5/57		2/5/57 to 2/18/57		2/18/57 to 3/4/57		
Isotope	Dis/min	ν , sec ⁻¹	Dis/min	ν , sec ⁻¹	Dis/min	ν , sec ⁻¹	
I ¹³¹	3.3×10^{10}	1.9×10^{-9}	5.5×10^{10}	4.1×10^{-10}	4.0×10^{10}	2.7×10^{-11}	
Cs ¹³⁷	1.6×10^7	Not yet calculated	1.6×10^8	Not yet calculated	7.2×10^8	Not yet calculated	
Sr ⁸⁹	8.4×10^7	1.5×10^{-11}	1.5×10^9	2.1×10^{-11}	2.3×10^8	2.6×10^{-11}	
Ba ¹⁴⁰	2.4×10^8	Not yet calculated	1.3×10^9	Not yet calculated	1.8×10^8	Not yet calculated	
Ce ¹⁴⁴	1.0×10^7	Not yet calculated	5.5×10^7	Not yet calculated	9.3×10^6	Not yet calculated	
Zr ⁹⁵	1.8×10^8	Not yet calculated	3.9×10^8	Not yet calculated	2.4×10^8	Not yet calculated	

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Table 14—(Continued)

Average specific isotopic activities in loop water during the WAPD-29-2 test and the values of ν calculated therefrom

Heat flux:	286,000 Btu/hr/sq		26,000 Btu/hr/sq ft	
Isotope	Dis/min/ml	ν , sec ⁻¹	Dis/min/ml	ν , sec ⁻¹
Cs ¹³⁸	5.6×10^6	1.1×10^{-7}	6.9×10^4	1.2×10^{-8}
Cs ¹³⁹	7.5×10^5	6.1×10^{-7}		

The effect of high oxygen concentration in the loop water was studied during the last several days of the WAPD-29-2 test. At the beginning of this phase of the test, the specimen was returned to the high-flux region of the reactor, and the steady-state activities were again determined. Three days later, sufficient oxygen was added periodically to the loop to maintain the oxygen concentration at approximately 12 cc/kg. The specific activities and values of the escape-rate coefficient ν for Cs¹³⁸ and Kr⁸⁸ before, during, and after the high oxygen concentration are given below.

Average specific isotopic activities in loop water containing high dissolved oxygen concentrations and the values of ν calculated from the activities

Period	Cs ¹³⁸		Kr ⁸⁸	
	Dis/min/ml $\times 10^{-6}$	ν , sec ⁻¹ $\times 10^8$	Dis/min/ml $\times 10^{-6}$	ν , sec ⁻¹ $\times 10^8$
Before O ₂	1.24 ± 0.13	3.48 ± 0.37	1.46 ± 0.22	1.16 ± 0.17
During O ₂	1.44 ± 0.16	4.04 ± 0.45	2.18 ± 0.42	1.73 ± 0.33
After O ₂	1.4	4.0		

Total isotopic activities accumulated on ion-exchange resin (LiOH form) during period of high oxygen concentration in the loop water (period: 3/4/57 to 3/10/57)

Isotope	Dis/min	Isotope	Dis/min
I ¹³¹	5.5×10^9	Ba ¹⁴⁰	4.9×10^8
Cs ¹³⁷	7.1×10^7	Ce ¹⁴⁴	6.3×10^6
Sr ⁸⁹	1.7×10^9	Zr ⁹⁵	3.0×10^7

These results indicate that there was very little difference in the rate of evolution of fission products between the two defective elements containing UO₂ of 93.53% and 97.33% of theoretical density, respectively. However, a nondefective low-density UO₂ element accumulated during the irradiation 10 times more Kr⁸⁵ than a nondefective high-density UO₂ element. Lowering the heat flux on the defective elements in these tests appears to lower the value of ν , as theoretically it should, for the short-lived cesium isotopes. However, the values of ν for the longer lived species appear to have been relatively unaffected. The data also indicate that oxygen concentrations as high as 12 cc/kg for as long as 32 hr will not affect the rate of evolution of fission products from a UO₂ fuel rod containing a single defect.

WAPD-29-3 (Two Defects in Specimen, MTR)

Reference water temperatures were never achieved during this test owing to a malfunction of loop components. The specimen was in the out-of-flux position during most of the test. Consequently, very few radiochemical data were obtained during this test. The values of ν for Kr⁸⁸ and Cs¹³⁸ when the loop water temperature was 390°F and the specimen was in the in-flux position were 4.3×10^{-8} , 3.3×10^{-8} sec⁻¹, respectively.

Table 14—(Continued)

WAPD-29-4 (Four Defects in Specimen, MTR)			
Total isotopic activities on ion-exchange resin (LiOH form); values of ν are not yet calculated (period: 3/15/57 to 5/12/57)			
Isotope	Dis/min	Isotope	Dis/min
I ¹³¹	7.4×10^{10}	Ba ¹⁴⁰	2.3×10^8
Cs ¹³⁷	2.3×10^8	Ce ¹⁴⁴	4.0×10^7
Sr ⁸⁹	1.3×10^{10}	Zr ⁹⁵	7.1×10^8
Average specific isotopic activities in loop water and values of ν calculated therefrom			
Isotope	Dis/min/ml	ν , sec ⁻¹	
Kr ⁸⁸	4.8×10^6	3.1×10^{-8}	
Cs ¹³⁸	2.0×10^6	4.6×10^{-8}	
Cs ¹³⁹	2.6×10^5	1.8×10^{-8}	
Cs ¹³⁹ from Ba ¹³⁹	(Ba ¹³⁹) 2.5×10^4	2.1×10^{-9}	
WAPD-29-5 (One Defect in Specimen, MTR)			
Analyses on isotopic activities on ion-exchange resin have not been completed.			
Average specific isotopic activities in loop water and values of ν calculated therefrom			
Isotope	Dis/min/ml	ν , sec ⁻¹	
Kr ⁸⁸	6.0×10^5	3.9×10^{-9}	
Cs ¹³⁸	1.1×10^5	3.1×10^{-9}	
Cs ¹³⁹	2.0×10^4	1.4×10^{-9}	
Cs ¹³⁹ from Ba ¹³⁹	(Ba ¹³⁹) 2.0×10^3	1.8×10^{-10}	

The total escape-rate coefficient ν_T represents, as far as can be determined, the total amount of an isotope that escapes from a defective UO₂ element. This coefficient was calculated from the following equation:

$$(N)_T = \frac{\nu_T \epsilon Y}{\lambda(\nu_T + \lambda)} + \left[\frac{\epsilon Y}{\nu_T + \lambda} - (N)_f^0 \right] e^{-(\nu_T + \lambda)t} + \left[(N)_f^0 - \frac{\epsilon Y}{\lambda} \right] e^{-\lambda t} \quad (19)$$

where $(N)_T = (N)_R + (N)_W$, i.e., the total amount of an isotope in the system is assumed to be on the ion-exchange resins, $(N)_R$, and uniformly distributed over the system surface, $(N)_W$.

It is evident from Table 14 that fission-product halogens, alkali metals, and rare gases contribute most to the activity in the loop water from a defective UO₂ fuel element. The values of the total escape-rate coefficient ν_T for these elements have generally been in the range of 10^{-8} sec⁻¹ from a normal UO₂ rod. (A normal rod is defined as one in which there does not occur any center melting, coring, or other abnormal phenomena.) All these elements contribute very little to system contamination and are easily, except for the rare gases, removed by side stream demineralization. The values of ν_T for those elements that contribute significantly to system contamination are probable less than 10^{-9} sec⁻¹. A discussion on the isotopic rate of deposition on loop surfaces is presented in Sec. 5.6h. In tests where the UO₂ pellets have shown evidence of melting in the center, the values of ν have generally been approximately a factor of 10 higher than those observed from a normal rod.

At the present time, the use of the escape-rate coefficient ν in the empirical equations appears to be the best method for calculating the rate of release of fission products from a

defective UO_2 rod with PWR reference tolerances and heat fluxes. Theoretically, the value of ν should vary with heat flux in that it is related to the diffusion coefficient and thus the energy of activation for diffusion. However, the variation in the isotopic rates of release during any given test has been so great that the effect of heat flux on ν from test to test cannot be determined. In the WAPD-25-2 test (MTR) the heat flux from the defective element was varied by a factor of 8.5, but the value of ν for Cs^{138} and Cs^{139} remained the same within experimental error.⁶⁰ However, during the WAPD-29-1 and the WAPD-29-2 tests in which the thermal-neutron flux on the specimens was varied by a factor of 11, the values of ν for Cs^{138} , Cs^{139} , and Kr^{88} showed an apparent decrease by about a factor of 10 in the low-flux position. The relative amounts of long-lived isotopic activities accumulated on the ion-exchange resins with the defective elements in either of the two flux positions, and those values of ν that have been calculated therefrom, do not indicate a decreased rate of evolution in the low-flux position. The apparent invariance, with heat flux and thus temperature, of the values of ν derived from irradiation tests in the loops cannot be explained at the present time.

The WAPD-29-3, 4, and 5 series of tests were designed to determine differences in the rates of evolution of fission products between fuel elements having one, two, and four defects per specimen. Very few radiochemical data were obtained during the WAPD-29-3 (two defects in specimen) test due to malfunctioning of the loop. The values of ν for Kr^{88} , Cs^{138} , and Cs^{139} during the WAPD-29-4 (four defects in specimen) test were approximately a factor of 10 higher than during the WAPD-29-5 (one defect in specimen) test. However, during the WAPD-29-1 and WAPD-29-2 tests in which each specimen contained but one defect, the values of ν were greater than those obtained during the WAPD-29-4 (four defects in specimen) test. Consequently, it cannot be said, conclusively, that the rate of fission-product release increases with the number of defects per specimen.

Another apparent anomaly is the relative rates of evolution of fission products between defective and nondefective elements in the WAPD-29-1 and WAPD-29-2 tests. These tests were designed to determine the relative differences in the rate of evolution of fission products between UO_2 elements of 93.53 per cent (29-1) and 97.33 per cent (29-2) of theoretical density. The rate of evolution of fission products from the defective elements during the WAPD-29-1 and WAPD-29-2 tests did not appear to be substantially different. However, the amount of Kr^{85} accumulated in the void space of the nondefective elements was 10 times greater in the WAPD-29-1 test than in the WAPD-29-2 test.

(g) *Escape of Fission Products from a Defective Element During Power Transients.* Under steady, full reactor power conditions, the temperature at the surface of the UO_2 in a defective element is sufficiently high that the space surrounding the fuel is filled with superheated steam at system pressure. Lowering the reactor power to a certain level will drop the temperature of the fuel and permit water to fill the void space within the element. A subsequent increase in the reactor power will change this water to steam, expelling it from the element along with the fission products that have been leached from the fuel. This is the so-called "waterlogging" effect described in Sec. 5.3. This effect was investigated during a reactor start-up in the X-1-g test. Figure 39 shows a plot of the reactor power and the Cs^{138} and delayed-neutron activities in the loop water as a function of time. This effect is also shown on the traces of the delayed-neutron monitor and the gamma monitor, which regularly show two to three factors of 10 increases in the loop-water activity during reactor start-ups.

There is also a relatively large increase in the rate of evolution of fission products during reductions in reactor power. The reasons for this is not so obvious. It could possibly be caused by the fact that, as the steam density within the element falls during a reduction in reactor power, water is drawn into the element and upon hitting the still hot fuel is vaporized and expelled. This effect was discovered during the WAPD-25-2 test in the MTR.⁵⁹ The specimen in this test was mounted on a cycling mechanism which permitted the thermal-neutron flux to be changed by a factor of 8.5 by adjusting the position of the fuel specimen in the reactor. The specific activities of Ba^{140} and I^{131} were followed in the loop water after a change in the neutron flux, increasing and decreasing. In Figs. 40 and 41 are plotted the escape-rate coefficients for I^{131} and Ba^{140} vs. time from a change in the neutron flux. From these plots it is evident that

Fig. 39—Increase in specific activities of Cs^{138} and delayed neutrons during reactor start-up. X-1-g test, June 11, 1956.

an 8.5-fold decrease or increase in the thermal-neutron flux causes about a 10-fold increase in the specific activities of Ba^{140} and I^{131} in the loop water. Moreover, the increased rate of evolution from the defective element apparently persists for some time since neither the Ba^{140} nor the I^{131} activities in the loop water decayed with the period expected from radioactive decay and constant system purification by ion-exchange resins.

It is likely that the increased rate of evolution during power changes of a reactor obscures, at times, what is assumed to be a steady-state accumulation of activity on the ion-exchange resins. This is particularly true of irradiation tests in the NRX reactor, AECL, which ordinarily has many such power changes during a reactor cycle due, primarily, to the experimental program. It would be expected that the readily leachable long-lived fission products would be most affected by this effect. In fact, the experimental values of ν for Cs^{137} derived from tests in the MTR appear to be consistently lower than those obtained from tests in the NRX reactor (see Table 14). Ordinarily the MTR maintains constant power during a reactor cycle. Theoretically, the value of ν for Cs^{137} should be considerably lower than that for Cs^{138} since the value of ν for a given element should vary approximately as the square root of the decay constant (see Eq. 16). The data obtained in the MTR indicate such a relation since the values of ν for Cs^{137} are consistently lower than for Cs^{138} . This is not true of data obtained in the NRX reactor. Consequently, it appears that the total amount of Cs^{137} that escapes from defective elements during irradiation in the NRX reactor might be controlled by the number of power changes.

(h) *Fission-product Deposition on Loop Surfaces.* There are two primary mechanisms by which fission products can be deposited on loop surfaces: (1) small fragments of UO_2 with

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Fig. 40—Escape-rate coefficient ν for I^{131} vs. time from flux change.

their associated fission products can be transported to and deposited on the surfaces, and (2) fission products in the coolant can be adsorbed on the surfaces. If the first mechanism were important, it might be expected that the particulate UO_2 would eventually settle on the bottom of horizontal sections of pipe by gravitational separation. In any event the activity would be heterogeneously distributed on the surfaces. If the second mechanism were important, fission products would be expected to be more uniformly distributed over the surface.

The first irradiation test on defective UO_2 fuel elements (X-1-b) was the only test from which there were data indicating that the first mechanism was important.⁵² This test occurred early in the developmental stage of UO_2 fuel elements when low-density UO_2 pellets were being investigated. The technology of the preparation of UO_2 pellets had advanced sufficiently by the time of the third defect test that the UO_2 pellets tested were representative of Core 1 production. In Table 15 are the results of the radiochemical analyses of a horizontal pipe specimen taken from the first (X-1-b) defect test. The pipe specimen was sectioned longitudinally as indicated in Table 15 to determine heterogeneities in the fission-product distribution. Figure 42 shows an autoradiograph of a pipe specimen. For comparison, in Table 16 are the results of the radiochemical analyses of pipe specimens from the third defect test (X-1-d).⁶⁰ These data indicate a rather uniform distribution of fission products over the entire surface of the system. Consequently, it seems likely that particulate UO_2 in the X-1-h test was important in loop contamination.

In deriving an expression for the rate at which fission products are deposited on loop surfaces, it is assumed that an isotope is deposited irreversibly at a rate that is proportional to the isotopic concentration in the coolant. Although this approach might be questionable because it neglects feedback to the loop water, the results appear to be reasonably consistent. The differential equation relating the rate of deposition on the pipe wall and the isotopic concentration in the loop water is

$$\frac{d(N)w}{dt} = \beta_w(N)_s - \lambda(N)w \quad (20)$$

Fig. 41—Escape-rate coefficient ν for Ba^{140} vs. time from flux change.

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Table 15—ISOTOPIC ACTIVITIES ON 1-IN. SCH. 80 PIPE
SPECIMEN FROM X-1-b TEST

Horizontal section from upper header room, dis/min/cm ² , at end of test				
Section	U ²³⁴	Sr ⁸⁹	Zr ⁹⁵	Ce ¹⁴⁴
Top, 120°	0.62	4.6×10^4	4.2×10^4	7.4×10^3
Sides (2), 60°	0.84	8.9×10^4	9.8×10^4	2.0×10^4
Bottom, 120°	0.91	10.7×10^4	11.9×10^4	2.2×10^4
Average	0.79	8.1×10^4	8.6×10^4	1.6×10^4

Table 16—ISOTOPIC ACTIVITIES ON 1-IN. SCH. 80 PIPE
SPECIMENS FROM X-1-d TEST

Horizontal sections, dis/min/cm ² , at end of test				
Isotope	Upper header room		Lower header room	
	Lower 180°	Upper 180°	Lower 180°	Upper 180°
Sr ⁸⁹	1.09×10^4	1.19×10^4	1.11×10^4	1.55×10^4
Zr ⁹⁵	9.69×10^4	8.15×10^4	2.15×10^4	3.05×10^4
Ba ¹⁴⁰	2.13×10^4	2.97×10^4	2.09×10^4	2.67×10^4
Ce ¹⁴⁴	3.38×10^4	3.27×10^4	1.11×10^4	1.90×10^4
Y ⁹¹	1.40×10^4	1.31×10^4	1.04×10^4	9.21×10^3

Complete specimens, dis/min/cm ² , at end of test			
Isotope	Upper header room		Average of all specimens
	Vertical section	Elbow	
Sr ⁸⁹	1.52×10^4	9.43×10^3	1.23×10^4
Zr ⁹⁵	6.74×10^4	3.28×10^4	5.51×10^4
Ba ¹⁴⁰	2.91×10^4	2.25×10^4	2.50×10^4
Ce ¹⁴⁴	2.36×10^4	1.81×10^4	2.30×10^4
Y ⁹¹	1.85×10^4	9.98×10^3	1.25×10^4

where β_w is the probability per unit time (sec⁻¹) that an isotope will be deposited on a surface. It was further assumed that the fission-product activity is uniformly distributed over the entire surface of the loop. This assumption probably underestimates the isotopic activity on the surfaces since other loop components (valves, elbows, small-diameter tubing, etc.) probably have relatively greater specific activities compared with the 1-in. Sch. 80 pipe specimens. With these assumptions, the proportionality constant β_w was calculated by the following relation:

$$\beta_w = \beta_R \frac{(N)_w}{(N)_R} \quad (21)$$

where β_R is the purification constant in sec⁻¹. Summarized in Table 17 are the values of β_w derived from the various tests. All isotopes that appeared to have the same value of β_w within limits were averaged together.

Most of the data in Table 17 were obtained under high pH (~10) conditions at an average water temperature of 525°F and in a loop having a gross surface-to-volume ratio of 4.2 cm⁻¹. Since the deposition characteristics of an element would depend on pH and temperature, the values of β_w should, in principle, only be used for systems that are operated with the same water conditions. Moreover, theoretically the value of β_w should be increased for systems

Fig. 42—Autoradiograph of pipe specimen.

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Table 17—EXPERIMENTAL VALUES OF THE DEPOSITION-RATE COEFFICIENT, β_w

Isotopic members of group	No. of observations	β_w , sec ⁻¹			Standard deviation
		Average	Maximum	Minimum	
Sr ⁸⁹	4	8.8×10^{-5}	2.2×10^{-4}	1.5×10^{-5}	8.6×10^{-5}
Sr ⁹⁰	1				
Ba ¹⁴⁰	4	1.9×10^{-3}	7.1×10^{-3}	1.9×10^{-4}	1.8×10^{-3}
Zr ⁹⁵	4				
Ce ¹⁴⁴	4				
Mo ⁹⁹	1				
Te ^{132*}	1	0.11			

* Other observations indicate that tellurium is deposited so rapidly on pipe surfaces that little if any gets to the ion-exchange resin.

having larger surface-to-volume ratios than the test system. However, in the absence of specific information on the variation of β_w with pH and temperature, the values would probably give reasonable approximations for systems operated at neutral water conditions but at the same average water temperature. For systems having substantially different surface-to-volume ratios, an approximate β_w can be obtained by multiplying the value of β_w by the surface-to-volume ratio of the system and dividing this product by the surface-to-volume ratio of the test system (4.2 cm⁻¹).

In general, those elements that have the highest values of β_w have the lowest values of the escape-rate coefficient ν . Consequently, only small amounts of those fission products that contaminate the system badly would escape from a defective UO₂ element. For this reason, UO₂ appears to have a decided advantage as a fuel for power reactors compared to other economic fuels thus far developed. As far as it is known, tellurium and molybdenum are the worst fission-product isotopes from the point of view of system contamination. Both of these elements have large values of β_w , and they also have the highest values of the escape-rate coefficient compared to other elements that contaminate surfaces. Tellurium is particularly bad in that it is the precursor of iodine. The rate of deposition of tellurium is apparently so rapid that little if any is ever found in the loop water or on the ion-exchange resins. It is known to escape rapidly from a defective element because of the relatively large amounts found on the pipe specimens that were analyzed. Moreover, relatively large amounts of 2.25h I¹³² have been found in loop water samples several days after the removal of a defective fuel specimen from the system. The I¹³² in the loop water decayed with an apparent half life of 78 hr, although no 78h Te¹³² could be found in the water.

(i) *Conclusions.* The experimentally determined rates of escape of fission-product isotopes from defective UO₂ fuel elements have been expressed in terms of escape-rate coefficients. This coefficient, ν , is defined as the probability per unit time that an isotope will escape from a defective element into the external system. The values of the escape-rate coefficient have been derived from empirical equations, but they are probably related to the diffusion coefficients of fission products in UO₂. Consequently, the values of this coefficient are directly related to the diffusion process, which is probably the basic mechanism for the escape of fission products from defective UO₂ fuel elements. The erosion-corrosion of UO₂ and the subsequent escape of small fuel fragments from a defective element, carrying with them the associated fission products, have been shown to be a very minor mechanism for fission-product escape. Recoil escape is possibly important for very short-lived fission products.

Fission-product halogens, alkali metals, and rare gases have the highest rates of escape from a defective UO₂ rod. The values of the escape-rate coefficient ν for these elements have generally been in the range of 10⁻⁸ sec⁻¹ from a normal UO₂ rod. (A normal rod is defined as one in which there does not occur any center melting or other abnormal phenomena.) All these

elements contribute very little to system contamination and are easily, except for the rare gases, removed from the system by side stream demineralization. Other elements, particularly those which contaminate the system, have relatively low rates of escape from defective rods. This, coupled with the fact that UO_2 is extremely stable in high-temperature water, appears to give UO_2 a distinct advantage as a fuel for pressurized-water reactors.

At the present time, the use of the escape-rate coefficient ν in the empirical equations appears to be the best method for calculating the steady-state rate of release of fission products from a defective UO_2 rod with PWR reference tolerances and heat fluxes. The value of ν is increased by about a factor of 10 for rods in which the UO_2 melts during irradiation. There is also an increase in the rate of evolution of fission products during power transients of a reactor. To date, all defects have been in form of 0.005-in. holes drilled through the Zircaloy-2 cladding. There does not appear to be any significant difference in the values of ν rods that contain one, two, or four holes.

The deposition characteristics of various fission-product isotopes have been expressed in the form of a rate coefficient in an empirical equation. This coefficient, β_w , is defined as the probability per unit time that an isotope will be deposited on the walls of a system having a definite surface-to-volume ratio. The values of this coefficient indicate that strontium, barium, zirconium, cerium, molybdenum, and tellurium are deposited rapidly on system surfaces. In so far as it is known, tellurium and molybdenum are the worst elements from the standpoint of system contamination. These elements not only have high values of β_w , but their values of ν are probably a factor of 10 higher than other elements in the above group. Thus they escape relatively rapidly from a failed element and are deposited rapidly on the system surfaces.

The results of the irradiation tests on defective UO_2 fuel elements have served as a basis for the evaluation of the hazards associated with failed blanket rods in the Pressurized Water Reactor, Shippingport, Pa., and provided the necessary data for the final acceptance of UO_2 fuel elements in the blanket region of this reactor. The number of failed UO_2 elements which that system could tolerate with respect to hazards from leaks and radiation fields was determined from these data. They also served as a basis for the evaluation of the PWR fuel-element-failure detection and location system. The PWR waste-disposal system was also designed on the basis of the data.

6 FUEL-ELEMENT ASSEMBLIES

6.1 Progressive Failure

Some of the irradiation experiments already described resulted in the failure of individual fuel elements under test. In the PWR a number of fuel elements are assembled in a closely knit array in which the coolant flows past the elements through relatively small channels. The possibility has been advanced that a failed element could cause the failure of adjacent elements in the assembly by blockage of channels, interference with heat flow, deformation, etc., and these in turn could fail their neighboring elements to such an extent that coolant contamination would necessitate shutting down the reactor. This repetitive phenomenon has been called progressive failure. Although such an effect had not been observed and was considered unlikely to occur, its disastrous consequences required that consideration be given to the likelihood of its occurrence for the PWR assembly design.

The most likely progenitor of progressive failure would be an initially failed element in which bulging or distortion occurs, resulting in reduction or obstruction of the coolant channel. This might reduce coolant flow in this channel sufficiently to result in overheating of nearby cladding surfaces and burn-out of adjacent elements. This overheating would be aggravated if the bulging or distortion were so severe that the initial failure contacted and masked the cladding surfaces of neighboring components, producing large areas of inadequately cooled fuel-element surfaces. Rod assemblies with their open coolant channels are, of course, less subject to failure by such a mechanism than plate assemblies.

The in-pile tests designed to study progressive failure at Bettis have been performed on two small fuel-rod bundle assemblies. These bundles were tested in a pressurized-water loop

in the MTR. Their test designations were WAPD-15-1 and WAPD-15-2. The two bundles were of similar general construction, each containing nine fuel rods of the design shown in Fig. 1 and seven dummy Zircaloy-2 rods welded into tube sheets (Fig. 43), and differing only in the percentage enrichment of the fuel material and the type of artificial defect placed in the center fuel element. This artificially defective element was to initiate progressive failure.

The 15-1 bundle contained UO_2 of 3.5 per cent enrichment. The center fuel rod was bent 0.160 in. and made to contact two adjacent rods. The rods were assembled at a centerline distance of 0.468 in. The 15-2 bundle contained fuel rods with 7.4 per cent enriched UO_2 . For 15-2, not only was the defect rod bent 0.150 in. but its cladding was weakened with 1.5-in.-long V-groove slots of 0.015-in. maximum depth at the two contact points, and the fuel rod was waterlogged so as to contain 160 mg of water.

The defects were designed to simulate as realistically as possible the only previous experience of UO_2 rod failure at that time. This was the waterlogging failure of a defective UO_2 rod (Table 3, specimen X-1-b-1) at Chalk River in December 1954, which failed by bulging of the cladding. In a PWR bundle such a failure could result in a cladding-to-cladding contact between rods. An attempt to evaluate the effect of such contact was made in the 15-1 bundle. A worse case would occur if the bulged cladding were to tear open at the contact point so that exposed fuel came in direct contact with the surface of the adjacent rod. The 15-2 bundle was made in an attempt to simulate this possibility.

The 15-2 test was conducted at a flux level (average, 315,000 Btu/hr/sq ft) comparable to PWR flux levels. On the day after start-up, the MTR was shaded toward the test loop, thereby increasing the heat flux 30 to 50 per cent, but this was after the defect rod had broken open. Radioactivity in the water was detected by the counting instruments shortly after full power was reached, which was later corroborated by analysis of the loop water for soluble fission-product iodine. This radioactive seepage continued throughout the test and at a higher level during the latter part of the test. From the above history it is apparent that failure of the 15-2 rod occurred during start-up or shortly after.

Postirradiation observations of the 15-1 bundle showed that the bent rod was separated from the adjacent rods approximately 0.005 in. Before the test, contact was so firm that the bent rod deflected one of the adjacent rods by a distance of 0.020 in. Examination of the separated rods in the defect zone showed slight differences in crud formation at the points of closest approach but no clear evidence of contact during the test run.

Examination of the 15-2 bundle showed that the defect rod was not touching either of the adjacent rods after the test, although the separation from one of the rods was so small that only careful viewing showed a gap. This loss of contact is attributed to stress relief of the defect rod and lengthening of the fuel rods resulting from thermal expansion of the UO_2 . The magnitude of this fuel-rod lengthening, estimated by the increase in gap between the unwelded ends of the dummy Zircaloy-2 bundles and the tube sheet, was about 0.005 to 0.015 in. Examination of the separated 15-2 defect rod revealed a crack, in the notch nearest the reactor side, about 1 in. in length and 0.010 in. in maximum width.

Thus, in conclusion, no evidence of progressive failure was found in either the 15-1 test or the 15-2 test. Damage to adjacent rods by the defect rod was limited to minor marring of cladding surfaces.

Types of failures observed in tests since X-1-b-1, namely, the X-1-e failure (resulting from excessive heat fluxes) and the X-1-g and X-1-h failures (resulting from cladding hydriding), are not considered likely to lead to progressive failure since they are associated with little cladding deformation and hence would not seriously block coolant channels. The probability of progressive failure in an oxide rod assembly is, on the basis of these tests, considered highly remote.

6.2 Performance of Assemblies

One of the concerns in the operation of the PWR fuel-element assemblies under irradiation has been the possibility of mechanical distortion of the assemblies in a flux gradient, both radial and axial. Because of such distortions, a reduction in spacing might lead to restricted

Fig. 43—Progressive-failure bundle (bundle length is $10\frac{1}{4}$ in.).

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cooling of certain channels. For such reasons, and also to prove out the usefulness of the fuel-element and assembly design, a number of proof tests have been and are being operated in in-pile loops. The initial proof test (Table 4, experiment CT-1) consisted of two bundles tested in the Central Thimble position in the NRX at Chalk River, Canada, and a test of a rod bundle which has recently been completed in an MTR reflector loop (Table 4, experiment WAPD-30-2). All three bundles consist of fuel rods of the PWR type arranged in a square array on a 0.466- to 0.468-in. pitch, with a nominal spacing between rods of 0.053 to 0.055 in.

(a) *CR-V(CT-1)*. The tests designed for the Chalk River Center Thimble Loop, designated CR-V(CT-1), consisted of two 25-rod bundles mounted end-to-end in a Zircaloy-2 flow director. Rods in one bundle were joined by welding the ends into two $\frac{1}{4}$ -in. Zircaloy-2 end plates drilled to receive the rods in their proper array (the tube sheet design), and the other was mechanically joined by a cross array of notched and drilled Zircaloy-2 strips fitted into the cross-notched or drilled ends of the rods (the egg-crate design), Fig. 44. Three different enrichments of fuel arranged in rows and aligned in each bundle as shown in Table 4 were used to simulate the desired flux gradient across the bundle.

The bundles were tested in a pressurized-water loop with coolant at about 540°F and 2000 psi for a period of 6 months. Difficulties in predicting the proper fuel enrichment required to overcome flux perturbation (primarily in the stainless-steel pressure tube) led to a conservative estimate of enrichment. Thus the maximum heat flux was 135,000 Btu/hr/sq ft, which was only about 40 per cent of the flux desired.

Postirradiation examination revealed no detectable change in over-all dimensions. Measurements of rod spacing after irradiation were somewhat erratic due to the difficulty of remote operation of the mechanical probe used in measuring this dimension. However, general trends are at least indicated. Over-all averages indicate little change in the rod spacing of the tube sheet bundle and a general increase in the spacing of the egg-crate bundle. Local reductions in rod spacing up to 0.010 in. were observed for the outer rods of higher enrichment in the tube sheet bundle, and more severe local changes up to 0.025 in. were observed in the egg-crate bundle, particularly in the vicinity of the more highly enriched rods. Generally, significant changes in spacing were found in only several places in the tube sheet bundle. Changes in

Fig. 44—CT-1 bundles (bundle length is $10\frac{1}{4}$ in.)

the egg-crate bundle were more widespread and more severe, primarily because of the greater flexibility of the end supports in this bundle. More detailed measurements indicate that these changes in spacing are due not only to bowing of the rods but also to translatory movements of the entire rod, probably as a result of yielding in both the tube sheet and egg-crate supports.

The closest approach between rods is estimated to be about 0.030 in. in the tube sheet bundle and about 0.020 in. in the egg-crate bundle. These are approximations made from photographs, because the range of the mechanical probe was only 0.040 to 0.075 in. Although these final spacings differ greatly from the nominal 0.055 in., it must be remembered that these bundles were fabricated at an early date during the PWR development. Subsequent to these assemblies, improvements have been made in controlling the spacing dimensions, and a similar bundle which was recently irradiated had excellent tolerance limits in the spacing prior to insertion into the test reactor.

(b) *WAPD-30-2*. This is a 16-rod bundle joined by welding into end plates and tested at a higher heat flux and burn-up level than the CR-V test. The bundle was tested in a reflector position in the MTR, which has a naturally steep neutron-flux gradient. This natural gradient plus the small size of the bundle made the gradient of this assembly of uniformly enriched rods at least twice as severe as that encountered in reactor operations. The maximum heat flux obtained is estimated by calorimetry to be about 300,000 Btu/hr/sq ft. The burn-up over a 7-month period was about 5500 Mwd/ton in the hottest rod. This irradiation test has just been completed, and no postirradiation examination has been made to date.

(c) *Conclusions*. Those subassemblies which have been examined after irradiation, as well as the absence of any incidents during exposure of the WAPD-30-2 bundle, have indicated the stability of the tube sheet PWR Core 1 design under very severe operating conditions and are considered to have proved the applicability of the PWR fuel-rod design to fabrication into subassemblies.

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Irradiation Behavior of Dispersion Fuels*

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ABSTRACT

The dispersion fuel concept offers a method for minimizing irradiation-induced property changes in nuclear fuel systems by localizing fission damage into regulated domains within the system. The system is thereby provided with a structural framework, or matrix, whose properties are relatively unaffected by the dynamic and impurity effects of fission fragments. Dispersion type fuel systems whose irradiation behavior has been, or is being, investigated in the U. S. are listed.

The extent of property retention in a dispersion fuel alloy is dependent on the materials selected for the fuel-bearing and matrix phases and on their microstructural arrangement in the alloy. The consequences of varying the materials and fuel-phase particle size and volume fraction are discussed. From experimental observations it is shown that, by proper control of these parameters within the bounds of existing technology, the dispersion concept does provide improvement in property retention over alternate alloy design concepts.

However, gaining property retention by the use of the dispersion principle requires the acceptance of additional sources of stress and greater irradiation damage in localized regions. A superior fuel system is obtained only when these effects do not limit its performance. However, the flexibility in design, fabrication, and selection of materials offered by the dispersion concept serves to combat these potential limitations.

1 DEVELOPMENT OF THE DISPERSION FUEL CONCEPT

A continuing objective in the development of fuel materials for use in heterogeneous reactors is the improvement of their physical and chemical properties and the stability of these properties under irradiation. Desirable materials have sufficient strength and ductility to resist failure under the external and severe internal thermal stresses, possess good thermal conductivity to transfer heat to the coolant and to keep thermal stresses to a minimum, and will not corrode if exposed to the coolant. Many fuel materials have adequate initial properties, but these properties change severely under irradiation if the fission products become distributed homogeneously. Uranium metal, which becomes completely embrittled with only small amounts of fission-product impurities,^{1,2} provides an extreme example of such property instability.

Another objective in the development of fuel materials is to minimize dimensional and volume instability resulting from irradiation. Uranium dioxide is an example of a material with good stability in this respect, but it lacks the desirable properties and characteristics mentioned in the previous paragraph.

The dispersion fuel concept, which has been discussed by Howe and Weber,³ Weber and Hirsch,⁴ Howe,⁵ Billington,⁶ and others in the U. S., offers a potential technique for achieving both objectives by localizing the fission damage into regulated domains within the fuel system. A dispersion type of fuel alloy is a two-phase alloy with particles of the fuel-bearing phase dispersed in a well-behaved metal matrix. In accordance with the dispersion fuel concept, the

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alloy should ideally be so designed and fabricated that a continuous network of fission-product-free metal is maintained throughout its service in a reactor. In practice, however, there are fuel alloys having a two-phase, dispersion type of structure in which fission products are found throughout the matrix as a result either of their escape from the fuel-bearing phase during irradiation or of the presence of a small uranium content in the matrix phase. In order to assess fully the merits of the dispersion concept, we shall consider the behavior under irradiation of both types of alloys: those with heterogeneous and those with homogeneous distribution of fission products.

A major feature of the dispersion fuel concept is the flexibility that it offers in the selection of the constituent materials and in the microstructural arrangement of these constituents to optimize the properties and behavior under irradiation. The relation of microstructure to property stability and mechanical response of dispersion fuel systems in irradiation will be treated in detail in the next section.

The flexibility in the selection of materials for the dispersed, fuel-bearing phase is illustrated by the number of uranium compounds of potential interest which are listed in Table 1. Some of the factors in choosing a particular uranium compound for a dispersion fuel system will be brought out at various points throughout the paper. Foremost among these factors, of course, is the irradiation stability of the compound itself at high temperature.

Table 1—FISSILE MATERIALS^{4,21}

Material	Density, g/cc	V _r *	Melting point, °C
U	18.9	1.0	1120
UAl ₂	8.1	0.35	~1590
UAl ₃	6.7	0.26	1320
UAl ₄	6.0	0.22	730
UBe ₁₃	4.37	0.15	2000
UC	13.6	0.69	2350–2400
UC ₂	11.7	0.56	2450–2500
UO ₂	10.96	0.53	2750†
U ₆ Fe	17.7	0.91	815‡
UFe ₂	13.2	0.48	1235
UN	14.3	0.71	2650 ± 100
UPb	14.5	0.41	1280
U ₃ Si	15.6	0.77	930§
U ₃ Si ₂	12.2	0.59	1650
UZr ₂	10.3	0.31	600¶

*Uranium content per unit volume relative to density of uranium.

†Determined by L. G. Wisnyi and S. W. Pijanowski, KAPL.

‡Peritectic temperature.

§Peritectoid temperature.

¶Disordering.

Materials for the matrix phase are selected on the basis of their physical and chemical properties since these properties will, to a large measure, govern the properties of the bulk alloy. Such properties may include ductility, high-temperature strength, thermal expansivity, thermal conductivity, and corrosion resistance. One should also consider allotropic transformations within the temperature range of operation and whether the presence of such a transformation will have objectionable effects. Rate of reaction or interdiffusion with the dispersed phase at fabricating and operating temperatures should not be overlooked since this factor can affect properties even in the absence of irradiation. Of course, such factors as fabricability, cost, and nuclear cross section must be considered as with any reactor core material.

Table 2 lists some dispersion type fuel systems whose irradiation behavior has been, or is being, investigated in the U. S. Included in this table are two combinations representing what are commonly referred to as aluminum-uranium alloys and zirconium-uranium alloys. The

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Table 2—DISPERSION FUEL SYSTEMS

Dispersed phase	Matrix phase
UO ₂	Stainless steel (austenitic and ferritic), Fe, Nichrome, SiC-Si, MoSi ₂ , Nb, Al, Zr, Zircaloy, graphite, ThO ₂ , BeO, Al ₂ O ₃ , SiO ₂
U	Mg, Th, Zr, Zircaloy
UAl ₄	Al
UZr ₂	Zr, Zircaloy
UC	Stainless steel, Zr, Zircaloy
UN	Stainless steel, Zr
U ₃ Si	Zr
U ₆ Ni	Zr
U ₂ Ti	Zr

former, which are used in the fuel elements for the Materials Testing Reactor (MTR), consist microstructurally of a dispersion of the compound UAl₄ in an aluminum matrix.* The latter is normally comprised of UZr₂ particles dispersed in zirconium;* this is one of several fuel systems employed in fuel elements for naval reactors. Table 2 also lists graphite and some ceramic materials as matrix constituents; the dispersion fuel concept can be applied to an all-ceramic system as well as to an alloy. Many of the data and observations on the systems shown in the table are preliminary or too fragmentary to be presented in this paper. Data will be presented where they appear to be significant to the evaluation of the dispersion concept. In addition, critical use will be made of significant information on the irradiation behavior of dispersion alloys of boron and its compounds. The n, α reaction of B¹⁰ is analogous to the fission of uranium in that it creates two fragments, He⁴ and Li⁷ (with an energy release of about 2.8 Mev), which serve as counterparts of fission fragments.

The foregoing remarks on the potential merits of the dispersion fuel concept should be tempered by pointing out that there are also potential limitations. The very fact that the fission events and fission products are localized will give rise to local internal stresses. The effect of these stresses on the mechanical response of a dispersion fuel alloy in service will be appraised in Sec. 2. Volume stability may also be affected, and this possibility will be discussed later.

2 MICROSTRUCTURAL GEOMETRY AND MECHANICAL RESPONSE UNDER IRRADIATION

A basic premise of the dispersion fuel concept is that the retention of the preirradiation properties after irradiation is a desirable characteristic in a fuel element and that this objective can be accomplished by controlling the microstructure of the fuel system to maintain a continuous matrix with no fission-fragment damage. This section of the paper will consider:

1. The influence of the various microstructural parameters on fission-product distribution in a dispersion type system and, in turn, on properties of the system.
2. The properties of some irradiated systems.
3. Sources of stress in dispersion fuel systems.
4. The mechanical response resulting from the interplay between stresses and properties under conditions of fuel-element operation.

2.1 Microstructural Parameters and Fission-product Distribution

Although the fission fragments are born in the uranium-bearing particulate phase of a dispersion fuel system, some of them will recoil into the matrix phase. [The average recoil range of fission fragments in various materials is of the order of 10 μ ; for the B¹⁰(n, α)Li reaction, the alpha particles have about one-third of this range, and the lithium fragments have a still

*In these cases the matrix actually contains a small fraction of 1 per cent of uranium in solid solution.

somewhat shorter range; see Table 3.] Many of these impurity atoms are large and incompatible with most of the suitable matrix materials. Consequently, the properties of the contaminated region around particles are changed, usually in an undesirable way. In order to maintain a continuous matrix free of impurities, it is necessary to space the fuel-bearing particles far enough apart that the damaged matrix zones do not touch or overlap.

In Fig. 1 are pictured the damaged zones in an irradiated fuel system of stainless steel- UO_2 dispersion; the two UO_2 particles shown in the photomicrograph are sufficiently spaced to provide a web of undamaged stainless steel between them. This photograph also illustrates the potential improvement offered by the dispersion concept with regard to retention of chemical properties and corrosion resistance. The fission-product-free matrix region was far less sensitive to the metallographic etchant than was the contaminated zone.

Table 3 — FRAGMENT RECOIL RANGES IN VARIOUS MATERIALS

Material	Average range					
	For U^{235} fission fragments*			For alpha particles from B^{10} "fission"		
	Mg/cm^2	μ	$\text{In.} \times 10^4$	Mg/cm^2	μ	$\text{In.} \times 10^4$
U	12.6	6.8	2.7			
UO_2	10.0	9.4	3.7			
Zr	5.8	9.1	3.6			
Fe	5.2	6.7	2.6			
Al	3.7	13.7	5.4	1.22	4.8	1.9†
Cu				2.0	2.0	0.9†
Ag				1.8	1.5	0.6†
Pb				2.54	2.0	0.9†
B^{10}					5.1	2.0‡
Stainless steel					2.5	1.0‡

*Reference 4.

†Reference 22.

‡Reference 16.

The microstructure of an irradiated dispersion fuel alloy can be uniquely described by specifying the volume fraction and particle size of the fuel-bearing phase and the distances to which the fission fragments will penetrate either phase, as will be shown below. These microstructural parameters will first be related to thickness of undamaged matrix between particles. Setting this thickness at a value of zero specifies the limiting conditions for maintaining a continuous undamaged matrix.

Although the web thickness of undamaged matrix may be an important variable, particularly if this thickness is small, it is not sufficient to describe how the alloy will respond to imposed stresses. Additional measures of the extent of property change are needed. One such measure is the volume proportion of matrix remaining undamaged; this factor will be described in terms of the microstructural variables.

If it is reasoned that fractures will develop locally in the most highly damaged regions of the matrix, then the average fission-product content of these damaged regions may be a significant quantity. An average concentration per unit volume of total matrix may be equally as suitable a measure of property change if local damage is not limiting. The relation of these two factors to microstructural geometry will be presented, after we have first shown the particle-size dependence on fraction of fission fragments escaping into the matrix.

Next, the influence of particle size, particle volume fraction, and fission-fragment recoil distance on distribution of fission products in the matrix will be shown qualitatively. The significance of variations in impurity damage to the selection of matrix materials will be dis-

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Fig. 1—Irradiated UO_2 -stainless steel dispersion, showing zones of fission-fragment damage in steel matrix around UO_2 particles. (Barney and Wemple, KAPL.)

cussed. Finally, it will be pointed out how fission-product concentration is affected by the choice of material for the fuel-bearing phase and by fuel depletion or burn-up.

This analysis, the details of which are presented below, cannot be used as a precise formula for the design of dispersion fuel alloys because it is based on several simplifying assumptions. However, it may serve as a qualitative guide for optimizing property stability through the control of microstructure. Experimental observations to test the analysis will be presented later.

(a) *Conditions for Undamaged Matrix Between Particles.* Equations have been derived by Harrison,⁷ Kernohan,⁸ and others in the U. S. to describe cubical arrays of spherical particles of constant diameter. Such equations are adequate for dilute fuel concentrations, but they can be readily revised for close-packing arrays to provide relations suitable for high as well as low fuel concentrations. With a close-packing array of spherical particles of uniform diameter, the distance d between particles is

$$d = \left[\left(\frac{\pi}{3\sqrt{2}V_f} \right)^{1/3} - 1 \right] D$$

where D is particle diameter and V_f is volume fraction of the fuel-bearing phase. Depending upon the size and quantity of the fuel particles and also the distance λ_m that the fission fragments penetrate the surrounding matrix (which depends, of course, upon the particular matrix material selected), the intervening matrix may or may not be continuously damaged. This is indicated schematically in Fig. 2a for two different particle diameters, D_1 and D_2 , and graphically in Fig. 2b. The distance between adjacent particle surfaces has been subdivided into two parts: $2\lambda_m$, the thickness of the damaged matrix zones around both particles, and d' , the thickness of the intervening region free of fission products. For fixed values of fuel volume fraction and fission-fragment recoil range, interparticle distance is seen to vary linearly with

Fig. 2—Effect of particle size and spacing on undamaged distance between particles. (a) For constant-volume fraction of particle phase. (b) For various volume fractions (V_f) of particle phase.

Fig. 3—Relation between size and volume fraction of particles for a given undamaged distance between particles.

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particle diameter. Hence, specifying that there be intervening undamaged matrix ($d' > 0$) places a lower limit on permissible particle size.

These relations can be expressed in terms of the ratios $D/2\lambda_m$ and $d'/2\lambda_m$, as follows:

$$D/2\lambda_m = \frac{1 + d'/2\lambda_m}{\left[\left(\frac{\pi}{3\sqrt{2}V_f}\right)^{1/3} - 1\right]}$$

This is exhibited graphically in Fig. 3. Both Figs. 2b and 3 indicate how, for a fixed value of λ_m , particle size must be increased when volume fraction of the fuel constituent is increased, if a given thickness of undamaged matrix is to be maintained. (Note that the volume fraction occupied by spheres of equal size when they are closely packed is 0.74.)

(b) *Proportion of Matrix That is Undamaged.* The extent of property change of the dispersion alloy will be influenced by the amount of matrix becoming contaminated with fission products. The proportion of damaged matrix to total matrix is given by V_{dm}/V_m , where V_{dm} and V_m are the respective volume fractions of damaged matrix and total matrix in the alloy; the expression is related to V_f , D , and λ_m as follows:

$$V_{dm}/V_m = \frac{V_f}{1 - V_f} \left[\left(1 + \frac{1}{D/2\lambda_m} \right)^3 - 1 \right]$$

The remaining portion of the matrix, the undamaged portion, will be $1 - V_{dm}/V_m$, and its relation to particle size and volume fraction of fuel is shown graphically in Fig. 4. Again, the advantage of large particle size is observed, but with respect to undamaged matrix this advantage diminishes with increasing particle size. The points on the dashed line in this graph represent the condition for $d' = 0$. Therefore the region of interest for dispersion fuel design is to the right of this line.

Fig. 4—Effect of particle size on fraction of matrix that is not damaged.

(c) *Fission-product Content in Matrix.* Not only will the alloy properties be affected by the proportion of matrix volume becoming damaged but also by the degree of damage within the affected region. The fraction, E_{fp} , of fission fragments escaping from each fuel-bearing particle increases as particle size is reduced and as fission-fragment recoil range in the fuel phase, λ_f , is increased. The fraction changes in accordance with the following relation, reported by Weber and Hirsch⁴ of Knolls Atomic Power Laboratory (KAPL).

$$E_{fp} = \frac{3}{4} \frac{2\lambda_f}{D} - \frac{1}{16} \left(\frac{2\lambda_f}{D} \right)^3$$

which is given graphically in Fig. 5. All the fission fragments escape from the particle when the particle diameter is equal to or smaller than the recoil range ($D/2\lambda_f = 0.5$). Because of the differences in recoil range λ_f , there will be complete escape of fission fragments from UO_2 particles up to 9.4μ in diameter and from uranium metal particles less than 6.8μ , as was shown in Table 3. The fuel particles neither gain nor lose atoms when $E_{fp} = 0.5$, a value which corresponds to a $D/2\lambda_f$ ratio of about 1.4, as indicated by the dashed line in Fig. 5. The significance of this factor on irradiation stability will be discussed later.

The fission fragments escaping from the particle come entirely from within a thickness λ_f of the particle surface. The depletion from this zone, E'_{fp} , decreases with increasing particle size in accordance with the relation

$$E'_{fp} = \frac{E_{fp}}{1 - \left(1 - \frac{2\lambda_f}{D} \right)^3}$$

which is also plotted in Fig. 5. The value for E'_{fp} levels off at 0.25 for large values of $D/2\lambda_f$; it is synonymous with the value for E_{fp} when the particle radius is equal to or less than the recoil range ($D/2\lambda_f \leq 1$).

The fission-product content per unit volume of damaged matrix, M_f , is affected by two competing factors. While the number of fission fragments escaping into the matrix (for a given burn-up of all atoms in the dispersion alloy)* increases as the particle size is reduced, the volume of the matrix region in which they become distributed also increases. The net effect is given by the relation

$$M_f = \frac{E_{fp}}{\left(1 + \frac{2\lambda_m}{D} \right)^3 - 1}$$

which is represented by the solid line in Fig. 6 for the simplified case of $\lambda_f = \lambda_m$.

It can be concluded from this graph that the fission-product concentration in the damaged portion of the matrix is greater in a coarse-particle alloy than in a fine-particle alloy. However, this is offset by the greater proportion of undamaged matrix in the coarse-particle material, as previously shown in Fig. 4. A simplified measure of the net effect on property alteration of the over-all matrix phase may be the average fission-product content in the total matrix, M'_f , which is given by

$$M'_f = E_{fp} \left(\frac{V_f}{1 - V_f} \right)$$

*Although E_{fp} has been defined as the ratio of the number of fission fragments escaping to the number produced per particle, it can be readily shown to be equivalent to the ratio of the total number of fission fragments released to the matrix to the total number produced throughout the alloy.

Fig. 5—Effect of particle size on fraction of fission products escaping from particle by recoil.

Fig. 6—Fission-product concentration in matrix: relation to size and volume of fuel particles and to distance between damaged matrix zones.

This is plotted (as the dash-dot lines) against particle size in Fig. 6 for various volume fractions of fuel phase*; here again λ_f and λ_m are taken to be equal for simplicity. In contrast to the damaged matrix region, the matrix as a whole should, under the assumptions made,† suffer less property change when the fuel-bearing particles are large than when they are small. For fixed particle size and fixed recoil range, the fission-product content in the matrix increases as the volume fraction of fuel is raised.

An interesting observation is made in Fig. 6 by plotting the points corresponding to fixed thicknesses of undamaged matrix between fuel particles. For very small values of $d'/2\lambda$, the fission-product concentration reaches a maximum of $V_f = 0.3$ to 0.4 , which implies that the minimum property change ought to be encountered when the volume fraction of fuel is either above or below this range. However, this variation diminishes rapidly as $d'/2\lambda$ is increased, and its significance to dispersion fuel design is uncertain.

(d) *Distribution of Fission Products in Matrix.* The foregoing discussion referred to average fission-product concentration in the damaged matrix region or in the matrix as a whole. Actually the concentration will vary within a recoil range of the particle surface in both fuel and matrix phases, somewhat as represented in the top row of diagrams in Fig. 7. The variation in concentration from the center of the fuel-bearing particle to the extremity of the damaged matrix zone is shown schematically for three different particle sizes, when the fission-fragment range is (1) less than the particle radius, (2) greater than the radius but less than the diameter, and (3) greater than the diameter. In the latter case it will be noted that all the fission fragments escape from the particle and reach a maximum concentration in the matrix at a finite distance from the particle.

The fission-product distribution in two adjacent particles of equal diameter and in the intervening matrix phase is presented schematically in the middle and bottom rows of diagrams in Fig. 7. The middle row represents one volume fraction of fuel particles, and the bottom row represents a higher volume fraction; interparticle spacing is reduced when particle size is decreased or when volume fraction is increased (as was previously shown in Fig. 2). The significant observation to be made here is that a homogeneous distribution of fission products is not necessarily reached until the interparticle spacing becomes so very small that the range of the fission fragments escaping from the particle extends into adjacent particles as well as throughout the intervening matrix. At somewhat larger spacings the fission-product distribution varies, reaching minimum concentrations at the points midway between adjacent particles for the particle-size range down to $D = 2\lambda_f$ or slightly less. For particle diameters less than $0.5\lambda_f$, the peak fission-product concentration may be in the matrix rather than in the particles.

Although it has been assumed necessary to maintain a matrix zone free of fission products between adjacent particles to fulfill the requirements of the dispersion fuel concept, it is possible that small concentrations of impurity atoms are tolerable, depending on the particular material chosen for the matrix phase. Undoubtedly, there is a difference from one metal to another in the fission-product content that can be tolerated without extensive change in properties. For example, uranium metal has been reported to become almost completely embrittled at burn-ups as low as 0.001 per cent,¹ whereas a zirconium-7 per cent uranium alloy has been observed by R. L. Mehan (KAPL) to retain some measure of ductility at 1.5 per cent burn-up of all atoms. Therefore the criterion for dispersion fuel design should perhaps be modified to specify a continuous matrix phase not in terms of absence of fission-product con-

*These relations are not valid when the interparticle spacing is so small that the range of fission fragments recoiling from a particle extends into adjacent particles. The concentration of fission products found in either phase will then be proportional to the volume fraction and the stopping power of that phase.

†Such a criterion as average fission-product content in the whole matrix assumes that the properties of the matrix would not be radically different if the impurity atoms were distributed homogeneously rather than concentrated in portions of the matrix. The validity of this assumption will probably vary with the kind of property being measured and with the degree of inhomogeneity in fission-product distribution. The problem is quite analogous to measuring the properties of any alloy at the ingot stage, where there may be microsegregation of alloying elements, rather than after homogenization at a later stage.

tamination but rather in terms of minimum change of pertinent physical and mechanical properties. It should then be possible to select component materials which will permit closer interparticle spacing and higher volume fractions of fuel-bearing phase than would be allowed under the present design objectives. To this end, it would be very desirable to obtain experimental data on the variation in properties with fission-product content for various matrix-phase materials.

(e) *Other Factors.* The volume fraction of fuel-bearing phase in a dispersion fuel alloy depends, of course, on the uranium content specified for the fuel element and also on the particular uranium-bearing material selected for the dispersed phase. The more uranium atoms per unit volume of the dispersed material, the smaller will be the volume fraction required in the alloy, a desirable feature from the standpoint of minimizing matrix damage as previously discussed. In this respect, U^{235} metal is the optimum material as the dispersed phase because it obviously offers the highest possible concentration of fuel. The concentration, V_R , of uranium atoms per unit volume of a compound U_aX_b relative to that for pure uranium increases with density of the compound and with the ratio of a to b but decreases with atomic weight of X . Weber and Hirsch⁴ have listed values of V_R for a number of uranium compounds, and some of these are presented in Table 1. The most attractive ones from the standpoint of volume fraction required in a dispersion fuel are those with the higher V_R values. On the other hand, selection must also be based on factors such as irradiation stability, compatibility with the matrix material, melting point, and neutron economy.

In all the relations between microstructural parameters and fission-product distribution presented thus far, fuel burn-up has been held to be constant. Since some of the fission fragments recoil from the fuel-bearing particles into the matrix phase, it is to be expected that,

Fig. 7 — Distribution of fission products as influenced by particle size and spacing.

as more fuel is burned up and more fission products are produced, the properties of the system would change as a result of further contamination. However, according to the dispersion fuel concept, the rate of property change with burn-up will be less than in a system having homogeneous fission-product damage.

2.2 Property Changes Due to Irradiation

The foregoing analysis of the relation between microstructural variables and fission-product distribution in a dispersion fuel system and the implications of this relation with respect to property alteration have been based on close-packing arrays of spherical particles of uniform diameter. Such an ideal is, of course, not realized in actual practice, and the departure from ideality will vary with the care and ease of fabrication. The particles are not of uniform size but at best fall within a discrete range of particle sizes differing by 15 to 20 per cent. Rarely are the particles spherical in shape, and they often may have sharp edges or corners. It is difficult to achieve complete uniformity in particle distribution; clustering or alignment (stringering) is often a problem.

Nevertheless, the principles derived for the ideal case should apply qualitatively to the usual cases, and it is relevant to test these principles by actual measurement of properties of irradiated dispersion fuel systems and comparison of the results with microstructural parameters and fission-product distribution. One of the earliest experimental observations of a particle-size effect was made by Hunter,^{6,9,10} who measured the in-pile thermal conductivity of compacts of graphite- U_3O_8 in the temperature range of 600 to 800°C. The samples had been fabricated in two different ways; the result was a much larger U_3O_8 particle size by one method than by the other. After a relatively short exposure in the Oak Ridge graphite reactor, the samples with the fine particles were found to have greatly reduced values (an order of magnitude) of thermal conductivity, whereas the coarse-particle samples lost only one-third of their original conductivity. Subsequent extension of this work by Berggren and Primak¹⁰ to include lower irradiation temperatures disclosed larger changes in the thermal conductivity as a function of irradiation time, with the same large differences between types of samples still apparent. These studies gave qualitative evidence that particle size has an important influence on radiation damage in a dispersion type fuel.

Later, a more detailed study^{6,8,10} of the particle-size effect was made by R. H. Kernohan of Oak Ridge National Laboratory (ORNL) in cooperation with L. D. Loch, R. J. Harrison, and G. B. Treff of Battelle Memorial Institute (BMI). These investigators used samples of graphite- UO_2 , some of which were made with enriched oxide and others contained normal UO_2 . The UO_2 particle size was quite uniform within each sample but ranged among the samples from approximately 600 μ to less than 40 μ . The samples, which contained 5 wt. % uranium, were irradiated to 0.1 per cent burn-up of the uranium at a temperature not exceeding 90°C. Comparison of postirradiation properties with those in the unirradiated condition revealed that the 2×10^{18} nvt exposure to neutrons had produced appreciable increases in elastic modulus and electrical resistivity and decreases in thermal conductivity in all samples. However, in the samples having enriched UO_2 with particle sizes less than 44 μ , the changes were twofold to threefold greater than those exhibited by the other samples with larger particle size and with normal UO_2 ; this would indicate that fission-fragment escape from the UO_2 had played an important role in damaging the graphite matrix. Although the other samples did not show significant differences in property changes among themselves as irradiated, subsequent annealing produced less recovery in the samples with smaller particle size. Thus the permanent type of damage caused by fission-product contamination was demonstrated, and again the effect of particle size on fission-product content in the matrix was exemplified.

Because of their application in fuel elements for such reactors as the MTR, the LITR (at Oak Ridge), and various swimming-pool reactors, the aluminum-uranium alloys containing up to 30 per cent uranium have received considerable attention by people engaged in the field of radiation damage. Since these alloys consist primarily of a dispersion of UAl_4 particles in an aluminum matrix, it is appropriate to cite one or two pertinent observations from the data reported by Billington.^{6,10} After a burn-up of 0.2 per cent of all atoms, the electrical resistivity

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had increased by about 25 per cent for a 5.7 per cent uranium-aluminum alloy and by about 50 per cent for a 15 per cent uranium-aluminum alloy. Similarly, the increase in yield and ultimate tensile strengths and decrease in uniform elongation after a given nvt exposure were greater in the 15 per cent alloy than in the 5.7 per cent alloy. These observations are consistent with the prediction that an increase in volume fraction of the dispersed uranium-bearing phase (UAl_4 in this case) promotes greater fission-product contamination of the matrix phase.

Although the experimental observations cited thus far appear to verify the previously discussed concepts on the relation between microstructural parameters, fission-product distribution, and property retention, they (as well as numerous other observations not mentioned) were made on samples having relatively low burn-up. It is of interest to examine what happens to the properties of dispersion fuel systems at higher burn-ups. Most of the pertinent observations in this connection are to be found in work on fuel elements of stainless steel- UO_2 and on dispersion systems containing boron or a boron compound as the dispersed phase. Although the latter systems represent nuclear absorbers rather than nuclear fuels, they serve as examples of the dispersion concept.

(a) *Stainless Steel- UO_2* . In work at ORNL by Feldman and coworkers¹⁰⁻¹² dispersions of up to 30 wt. % UO_2 in austenitic stainless steel (type 304 or type 347) matrices were irradiated to high burn-up, as high as 40 per cent of the uranium in some cases. The UO_2 particle size ranged from <3 to $105\ \mu$. Definite particle-size effects on mechanical properties of the irradiated samples were noted. For example, for samples having equivalent fuel loading and irradiation history, those with the $3\text{-}\mu$ particle size showed the highest increase in hardness. The elements with small UO_2 particle size also were more brittle on postirradiation bend testing than those with large particle size. These effects are shown graphically in Fig. 8 (reported by Feldman¹²). The hardness measurements plotted in Fig. 8 were made before irradiation, after irradiation to 30 per cent burn-up of the uranium, and after postirradiation annealing for

Fig. 8—Annealing of stainless steel- UO_2 plate type fuel elements. (Feldman, ORNL.)

stainless steel-25 per cent UO_2 dispersion fuel-element samples having three different particle-size ranges. By comparing the results before and after irradiation, it is noted that there is a very definite correlation between hardness change and particle size; the largest hardness increase corresponds to the smallest particle size. Some of the hardness increase is due to neutron bombardment alone, as indicated by the change shown for the stainless-steel cladding. The differences between this change and the total changes represent the respective amounts of fission damage in the three samples.

The results shown in Fig. 8 for the postirradiation study are very interesting in that the hardnesses actually increase upon annealing at 400°C and then decrease progressively with higher annealing temperature. This behavior is suggestive of an aging phenomenon, followed by overaging at high temperature, wherein the impurity fission-product atoms may be playing the role of the alloying elements of conventional age-hardening alloys.

The ORNL workers also observed an increase in the incidence of cracking and failure during irradiation and during postirradiation bend testing with decrease in particle size and with increase in burn-up. This again demonstrated the embrittling effect of fission-product contamination of the stainless-steel matrix. A further interesting observation was that some specimens having electrolytic iron as the matrix phase showed greater tendency for cracking upon irradiation and postirradiation bending than did the stainless-steel matrix samples with equivalent UO_2 particle size, fuel loading, and irradiation history. This may possibly be another example of the differences between materials in sensitivity to the effects of fission-product contamination.

From work by W. E. Seymour, W. K. Barney, W. D. Valovage, and others at KAPL on stainless steel- UO_2 , there are also illustrations of the effect of UO_2 particle size on post-irradiation properties. Figure 9 shows bend-test curves obtained by Valovage and Siergiej¹³ for stainless steel-25 per cent UO_2 samples before and after irradiation to uranium burn-ups of 28 and 40 per cent in two cases and 10 to 20 per cent in most other cases. The bend tests were performed both at room temperature and at two different elevated temperatures, 1200 and 1400°F . The ductility differences between the large-particle (105 to $210\ \mu$) and smaller particle ($44\ \mu$) samples after irradiation are readily apparent. Even after 40 per cent burn-up the large-particle samples exhibited greater ductility than the samples with smaller particle size after 28 per cent burn-up. These differences persist at the elevated temperatures, although the actual ductility decreases with temperature both before and after irradiation, and thus an inherent characteristic of some of the stainless steels is demonstrated. Table 4, which lists tensile-test data on stainless steel-25 per cent UO_2 (105- to $210\text{-}\mu$ particle size) at three different temperatures after various burn-ups, also illustrates the reduction in ductility at higher temperatures. This observation points up a factor to be considered in the selection of a matrix material for a dispersion fuel alloy, namely, the need to take into account the properties over the entire temperature range of fuel-element operation.

(b) *Boron Dispersion Systems.* Perhaps the most striking comparison between a dispersion type alloy and a homogeneously damaged material with respect to property retention is found in the work of Anderson, Dunning, Neisz, and McKittrick¹⁴ of KAPL on zirconium-boron and titanium-boron alloys. Bend-test curves are presented in Figs. 10 and 11, respectively, for samples of these two systems irradiated to 1 to 2 per cent burn-up of all atoms. The microstructures of the melted alloys were such as to result in homogeneous distribution of fission products during irradiation, and the dispersion alloys, which were synthesized from powders, had boron particles in the size range 105 to $420\ \mu$, sufficiently large to cause relatively little matrix damage. None of the samples failed on preirradiation bend testing. After irradiation, however, the melted alloy samples failed at low deflections both at room temperature and at 600°F , whereas the dispersion alloys endured considerable deflection at room temperature before failure and exhibited no failure at 600°F . Although the irradiation conditions labeled on these curves show somewhat higher burn-ups for the melted alloys than for the dispersion alloys, it is known from other data not shown here that the embrittlement of the melted alloys occurs early in their irradiation.

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Fig. 9—Bend tests of stainless steel—25 wt. % UO₂ dispersion fuel elements at room temperature, 1200°F, and 1400°F. (Valovage and Siergiej, KAPL.)

Table 4—TENSILE TESTS OF 25 WT. % UO_2 —STAINLESS STEEL
DISPERSION ALLOYS
(Valovage and Siergiej, KAPL)

Uranium burn-up, %	Temp., °F	Ultimate strength, psi	Yield strength,† psi	Total‡ elongation, %
0	R.T.	46,000	23,000	16
3.2	R.T.	48,000	44,700	8
15.3	R.T.	46,700	42,700	4
21.3	R.T.	49,500	46,500	2
0	1000	25,050	13,800	9
6.7	1000	32,300	28,200	4
10.5	1000	33,200	31,300	3
19.4	1000	33,700	31,200	2
0	1200	20,070	12,400	11
6.6	1200	21,800	19,200	3
12.0	1200	20,900	19,100	3
18.5	1200	18,500	18,500	2
0	1400	13,800	10,400	8
6.6	1400	15,000	15,000	2
12.0	1400	9,900	8,700	6

*105 to 210- μ UO_2 particle size.

†0.2% offset.

‡Approximately 2-in. gauge length.

Asanovich et al.¹⁵ at BMI, in a study on irradiation effects in dispersion alloys of various boron-containing materials in titanium and Zircaloy-2 matrices, observed a curious effect in Zircaloy-8.4 per cent normal B_4C samples. After irradiation to 20 to 31 per cent of the B^{10} present, the ductility in bending was 25 per cent higher than before irradiation. No explanation for this behavior was apparent.

Although the studies on zirconium-base and titanium-base boron dispersions demonstrated the effect of a dispersion type structure in minimizing property alteration by irradiation, such was not the case with stainless steel-boron dispersions according to Eichenberg¹⁶ of Westinghouse Atomic Power Division (WAPD). Samples prepared with boron particle sizes and interparticle spacings that were presumably sufficient to preserve a continuous undamaged stainless-steel matrix were found to have become almost completely embrittled by irradiation, even at exposures as low as 0.8×10^{20} nvt, as evidenced by hardness, tensile, and impact results before and after irradiation. The cause for this behavior could not be explained.

(c) *Other Observations.* Evidence for the effect of large volume fraction of fuel-bearing phase in a dispersion structure is found in studies by Freshley and Last¹⁷ of a magnesium-uranium fuel element. The samples contained 50 vol. % uranium metal, in the form of large particles, surrounded by a matrix of magnesium or magnesium-silicon alloy. Obviously, with such a large fraction of uranium phase the interparticle spacings were extremely small. This condition was reflected in the observation that there was almost complete loss of ductility as a consequence of irradiation at 0.1 per cent burn-up of the total uranium atoms. However, the elements had merit even at 2 per cent burn-up from other standpoints, as will be mentioned later.

The above examples of the effects of microstructure of dispersion fuel systems on property alteration by irradiation are not meant to be exhaustive. There are other data on work done in the U. S. that could be cited, but those presented serve as highlights to exemplify one of the major features of the dispersion fuel concept.

Fig. 10—Bend-test results on Zircaloy-2-0.35 wt. % B^{10} alloys. (Neisz and McKittrick, KAPL.)

Fig. 11—Bend-test results on titanium-1 wt. % B^{10} alloys. (Dunning, Anderson, and McKittrick, KAPL.)

2.3 Sources of Stress

The mechanical behavior of any system depends upon the nature of the stresses to which the system is exposed and the response of the material to them. The principal sources of stress in a fuel element are the gross differential thermal stresses arising from the dissipation of heat from the composite element to the coolant. These stresses depend upon the power per unit length of fuel, the shape of the fuel element, and the mechanical and thermal properties of the fuel. In a dispersion type element there are additional sources of stress which must be tolerated. These are:

1. Differential thermal stresses of a local nature arising from the inhomogeneous distribution of heat sources within the system. For a fixed power per unit length of a fuel element, this stress increases with increasing particle size.
2. Differential volume changes due to mismatch in thermal expansion coefficients or thermal conductivities between the fuel and matrix phases, or due to phase transformations.
3. Differential volume changes due to the localized accommodation of fission products or the agglomeration of the rare-gas atoms to form a gas phase.

The response to the imposed stress will depend upon the mechanical properties of the component phases, the interactions between these phases, and the changes in these properties induced by irradiation. Figure 12 provides an example of interparticle cracking resulting from local stresses in a stainless steel- UO_2 dispersion fuel. In this particular sample the cracks were not observed in the irradiated condition but rather were formed in subsequent annealing. In the annealing treatment, interaction between fission-gas atoms probably produced additional stresses around the UO_2 particles.

Dispersion fuel alloys inherently have higher temperatures in the fuel constituent than do homogeneous alloys, where heat generation is uniform. The magnitude of this temperature will depend upon the thermal conductivity of the fuel phase and upon the thermal resistance at the fuel-matrix interface, which is influenced by the differential expansion between the two phases. Increased fuel temperatures are undesirable if the increased mobility of the atoms within this phase causes agglomeration of the fission gases and the development of gas pressures. However, the flexibility of the dispersion concept offers the possibility of selecting alternate constituents which may reduce this problem. Current indications are that the rate of gas agglomeration is lower in the materials of higher melting point.

Stresses caused by volume increases in the dispersed phase can be relieved by introducing porosity in and around the fuel-bearing phase. Such porosity would be advantageous provided that it does not result in higher fuel temperatures and gas atom interactions. (The advantageous use of porosity will be discussed later in connection with the volume changes in the stainless steel- UO_2 fuel element.) It is doubtful, however, that sufficient porosity could be introduced into a dispersion element to accommodate very large amounts of released gases and still derive the benefits in mechanical behavior of the dispersion alloy.

Particle temperatures can also be decreased by selecting a matrix material having a high thermal conductivity. For example, samples of magnesium-25 vol. % uranium dispersion alloy contained in stainless-steel jackets were irradiated by Hirsch and Ropitsky (KAPL) to 2.5 per cent total atomic burn-up (10 per cent of the uranium atoms); no dimensional instability was observed. The surface temperature of the samples was 300°C , and the surface heat flux was 250 watts/cm^2 . A second example would be the utilization of a ferritic rather than an austenitic matrix in stainless steel- UO_2 dispersion elements to decrease the difference in thermal expansion coefficients of UO_2 and matrix and thereby decrease the fuel temperature.

Stress concentrations may result from irregularity in particle shape and from alignment of particles in stringers. The directional cracking of a bend-test specimen at a point removed from the load is illustrated in Fig. 13, where the failure lies in a plane parallel to the neutral axis in the plane of stringering. J. G. Morgan and P. E. Reagan of ORNL observed severe cracking and cladding separation in nickel-10.3 per cent BN dispersion alloys with a badly stringered structure at about 38 per cent burn-up of the B^{10} . On the other hand, at the same burn-up of the B^{10} , only microcracking was observed in an iron-7.6 per cent CaB_6 alloy that had a more random dispersion of particles. The boron content per unit volume in these alloys was similar.

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Fig. 12—Cracks between UO_2 particles in stainless steel—25 wt. % UO_2 irradiated to 8 per cent burn-up of the uranium and annealed 500 hr at 1200 to 1650°F. (Barney and Wemple, KAPL.)

Fig. 13—Stainless steel—30 wt. % UO_2 having fine ($<3 \mu$) stringered UO_2 particles and irradiated to 9 per cent burn-up of uranium atoms. Cracks were induced by bending. (ORNL.)

An effect of localized stress may also be indicated by Asanovich et al. of BMI,¹⁵ who reported microcracking in dispersions of enriched boron and boron compounds in titanium and Zircaloy-2 matrices but none in natural boron dispersions with equivalent total atomic per cent depletions. The local stresses causing the cracking may have stemmed from the higher burn-up of the enriched particles.

2.4 Mechanical Response

The mechanical behavior of a system will depend upon the magnitude and the state of stress, the mechanical properties of the components, and the effects of environment upon these variables. Normally, through the judicious selection of the cause of failure, reasonable estimates of the life of a system can be made. However, if large changes in properties occur, such estimates are difficult. The introduction of irradiation as an environmental condition and the changes in properties caused by the fission products create new situations about which little is known. Predictions about the mechanical response of such systems are, therefore, uncertain.

Along these lines, one should observe the conflicting reports of the embrittlement^{1,2} of alloy fuel materials as indicated by postirradiation testing, and concurrently, the reports of large volume increases in these same materials. Roberts and Cottrell¹⁸ nicely resolved this anomaly in uranium metal by demonstrating experimentally that this material, which is brittle in postirradiation tests, does creep at low temperatures and at low stress levels during irradiation. Konobeevsky et al.¹⁹ also mention induced plastic behavior in alpha uranium upon the instant of irradiation. In interpreting the volume changes in zirconium-uranium alloys, Willis²⁰ has suggested that a similar plasticity is induced even in fuel materials that lack the gross crystallographic anisotropy of alpha uranium. Such a phenomenon should enhance ductility during irradiation. The absence of fission in the matrix phase of a dispersion fuel alloy might then be disadvantageous.

If strain is the significant parameter, the criterion for satisfactory performance of a material is that the maximum strain to be endured should be less than the strain to failure, or limiting strain. Inherent in the dispersion fuel concept is the assumption that this strain ratio is minimized by maintaining, as nearly as is possible, the properties of the unirradiated matrix material. Although such a conclusion is consistent with the decrease in ductility observed in postirradiation tests of homogeneously damaged alloys, it may be contradictory to the above-mentioned processes for the enhancement of ductility. However, the versatility provided by introducing porosity in dispersion fuel alloys and thereby reducing the maximum strain should also be noted as being in favor of the dispersion principle.

3 DIMENSIONAL STABILITY AND FISSION-GAS EFFECTS

Although a dispersion type design may improve the response of a fuel system to its environment, it also increases the fission-product damage in localized regions of the system. Therefore an improved material results only when these latter effects do not become limiting. Although the source of instability of selected components can be established only by direct testing, some potentially major problems that may arise should be discussed.

Generally, two types of dimensional instability have been observed in irradiated fuel materials:

1. Anisotropic changes which cause deformation but which result in little or no volume changes.
2. Volume increases associated with the accumulation and interaction of the fission-product atoms.

3.1 Anisotropic Dimensional Stability

The deformation of polycrystalline alpha uranium on thermal cycling and the irradiation growth of textured uranium and of graphite provide well-known examples of dimensional instability. Here the crystallographic anisotropy is the source of instability.

Such anisotropy in the fuel-bearing phase should not be limiting in dispersion alloys, even if uranium metal is the fuel material. The fuel particles should be randomly oriented throughout the element in a gross sense, and the matrix should constrain the growth of individual particles. The contribution of such anisotropic deformation of the dispersed phase to the matrix stresses should be small.

Excellent dimensional stability is reported by Freshley and Last¹⁷ for dispersions of 50 vol. % uranium in magnesium to 2 per cent burn-up of the uranium; their finding appears to substantiate the above conclusions.

3.2 Volume Stability

If a given crystalline structure is maintained, then volume increases should be anticipated in irradiated systems containing fissile atoms unless (1) free storage space exists in the material with which to accommodate the increased volume (e.g., as in B_4C , as indicated by Tucker and Senio²⁵), (2) chemical effects reduce the average size of the impurity atoms formed (e.g., as in UO_2 , as suggested by Howe and Weber³), or (3) there is accommodating microscopic porosity within the element so that the volume increase of the components need not produce net external dimensional changes. The typical rates of volume increase per per cent burn-up of the total atoms are: 3 per cent for zirconium-uranium alloys containing up to 40 per cent uranium,²⁶ less than 1 per cent for UO_2 ,²⁷ and 2 to 4 per cent for boron alloyed with titanium or zirconium.¹⁴

In addition, abnormally large volume increases (swelling) should be anticipated where the inert-gas atoms interact to form gas pockets. These rare gases constitute about one-eighth of the fission yield, amounting to the formation of 25 to 30 cc (NTP) of gas formed per gram of uranium fissioned. If the size of the gas pockets becomes sufficiently large that surface tension forces do not play an important role in minimizing the resulting gas volume, swelling results. The rate and magnitude of the swelling will then depend upon the creep strength of the material surrounding the gas pockets. Rates of volume increase as high as 300 per cent per per cent burn-up have been obtained under such conditions.

(a) *Sources of Instability in Dispersion Type Fuels.* In a dispersion fuel alloy where the fissionable material is confined to the dispersed phase, the fission density and the resultant impurity-atom concentration are increased locally. Both effects may alter the volume stability of the system.

From the standpoint of total volume increase of the system, the accommodation of the fission products should be no more serious a problem in dispersion systems than in homogeneous alloys. (However, the localized nature of these volume increases represents an additional source of differential stress, as previously discussed.)

Difficulties may, however, be encountered in dispersion systems because burn-up in the fuel-bearing phase is higher than in a homogeneous system. The burn-up that can be tolerated in the fissile phase should be questioned because both the high fission-product concentration and the degradation of the parent phase may lead to rare-gas atom agglomeration. Fission products are incompatible with most materials, and the effect of adding increasing amounts of these impurity atoms on the stability of materials is yet unknown. Accelerated swelling must be considered a potential problem unless it can be demonstrated that the average pore size of the gas pockets does not increase with increasing burn-up. Should the size of these gas-filled pockets increase to the point where surface tension forces do not limit the contained gas volume, swelling must be expected.

Interactions between fuel and matrix are also important in dispersion alloys. Gross dissimilarities in properties between the dispersed and matrix phases may result in higher particle temperatures and fission-gas agglomeration. Chemical reactions between the fuel and matrix phases may occur in irradiated systems even where no reaction occurs in the unirradiated system. An example of such a reaction was found by Barney and Wemple²⁷ in some irradiated stainless steel- UO_2 samples, in which the stainless-steel matrix contained silicon and manganese. The UO_2 particles in these samples were surrounded by a layer of foreign substance after irradiation; this phenomenon was not observed in samples with no silicon or

Fig. 14—Surface blistering due to subsurface boron particles in unclad titanium—1 wt. % B^{10} dispersion alloy plates. (Anderson, Dunning, and McKittrick, KAPL.) (a) 5 $\times$. (b) 18 $\times$. (c) 100 $\times$.

manganese in the stainless-steel matrix. The investigators interpreted the phenomenon to have been caused by a reaction between the oxygen released by the fissioned UO_2 and these impurities. Of course, the operating temperature must be sufficiently high for such diffusion processes to occur.

Other sources of irradiation instability which are unique to dispersion alloys may also be encountered. A dispersion alloy containing dispersed particles that have a diameter approximately equal to the fission-fragment recoil range is unique in that the total number of atoms in the fuel-bearing phase need not increase. In fact, there may be a net flux of atoms and of the fissionable phase when the ratio $D/2\lambda_f$ is less than 1.4, as was shown in Fig. 5. Such depletion in itself may lead to instability. The stability of such a fissionable phase cannot be demonstrated by irradiation in the bulk form under such circumstances. The technology of such small fuel particles may be decidedly different from that of bulk materials. With a depletion of atoms in the particles, the mobility of the contained gas atoms may be increased as a result of the increased concentration of vacancies, thereby causing swelling. On the other hand, the fission-spike-induced homogenization process postulated by Bleiberg, Jones, and Lustman²⁸ should reduce or eliminate differences in the concentration of vacancies within the recoil range of the fission events. Such a competitive phenomenon would render stable sufficiently small particles (those with about the dimensions of a fission spike). Therefore there may exist a particle-size range that leads to instability, and above and below this range the system is stable.

Anomalous swelling observed at KAPL in some irradiated zirconium-uranium alloys may provide a valid indication of such a particle-size effect. Four compositions were investigated: 7, 12, 22, and 40 per cent uranium. In this range of composition, the zirconium-uranium system is composed of two phases, UZr_2 (approximate composition of the epsilon phase) and alpha zirconium (containing about 0.3 at. % uranium in solid solution). An increase in uranium content results in an increase in the volume fraction of the uranium-rich phase, as shown in Table 5.

Table 5—VOLUME INCREASES IN IRRADIATED ZIRCONIUM-URANIUM ALLOYS

Uranium, wt. %	Burn-up, at. %	Uranium burn-up, %	% vol. change per at. % burn-up*	Calculated uranium-rich phase (UZr_2), vol. %
7	0.94 - 2.0	34-71	3-4	9
22	0.5 - 1.2	5-10	~3	35
40	1.5 - 4.5	22	2-3	73
12	2.5	49	7.8	17.4
22	3.2	33	5.3	35

*Potential error $\pm 0.5\%$.

With the exception of 12 and 22 per cent compositions irradiated to 3.2 and 2.5 per cent total atom burn-up, zirconium-uranium alloys below 1100°F have exhibited only the predictable rate of volume increase of 3 to 4 per cent for each per cent of the total atoms fissioned.²⁶ This observation is based on many experiments, which include 7 and 40 per cent alloys irradiated to burn-ups as high as 2 and 4.5 per cent, respectively.

The UZr_2 particle size (which is less than the range of fission fragments in the 7, 12, and 22 per cent alloys), as well as the volume fraction, increases with greater uranium content in the alloys. Therefore the apparently poorer irradiation stability of the alloys of intermediate composition can be interpreted in terms of the particle-size effect mentioned above. That is, the 12 and 22 per cent alloys fall in a particle-size and interparticle-spacing range that apparently leads to instability, whereas above or below this range the system is more stable. If the instability were due solely to the degradation of the uranium-rich phase, then the 7 per cent alloys, having the highest proportion of uranium atoms fissioned (50 to 70 per cent), should have been the least stable. If the number of fission-product atoms per unit volume limited stability, the 40 per cent alloy, which was irradiated to 4.5 per cent burn-up of all atoms, should have been unstable.

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(b) *Fission-gas Retention in Dispersion Type Fuels.* If the fission gases collect in pockets within the fuel-bearing phase, one is concerned with the amount of gas, the size of the pockets, and the associated swelling of the fuel element. Although the escape of these gases from the fuel phase relieves this problem, it certainly aggravates the net swelling problem unless the gases are concurrently released from the fuel element. However, interconnected porosity caused either by fabrication or interparticle fracturing during irradiation is undesirable since it increases the potential consequences of a cladding defect. Of course, the consequences of such a defect will depend upon whether the fission products freely diffuse to the coolant or whether the coolant enters the element and leaches fission products or increases the severity of the defect.

Data on the release of fission products from fuel elements are sparse and uncertain and only recently have been subjected to any rigid examination. The extent of the fission-product release will depend upon particle size and the ability of both the matrix phase and the fuel-bearing phase to retain fission-product atoms.

Neisz and McKittrick²⁹ report loss of corrosion resistance and spalling of the surface of zirconium-boron alloys and surface blistering of Zircaloy-clad dispersion alloys after irradiation. Such blistering was also observed in unclad titanium-boron dispersions and is shown in Fig. 14. These pictures were taken from the work of Anderson and Dunning, who noted that such blisters could be correlated with subsurface boron particles.¹⁴ It is evident that the thin web of titanium matrix at the surface did not provide sufficient strength to restrain local swelling of those particles.

The importance of creep strength in resisting swelling may be inferred from the results of Johnston (KAPL),³⁰ who studied swelling and fission-gas release during postirradiation annealing of zirconium-8 per cent uranium alloy samples. As shown in Fig. 15, Johnston found that the rate of volume increase is dependent on fuel burn-up as well as on temperature. The irradiated samples were annealed for 500 hr at the three temperatures noted. Less than 1 per cent of the fission gases was released from the samples at the temperatures studied. The activation energy for the swelling rate indicated that the deformation was controlled by the creep strength of the material.

The effect of interconnected porosity in allowing fission-gas release and relief of the swelling problem was observed jointly by Johnston and personnel of BMI, who conducted post-irradiation annealing tests on stainless steel-25 per cent UO_2 samples having about 8 per cent porosity. These samples, which had been irradiated to 9 to 15 per cent burn-up of the uranium, were observed to release up to 15 per cent of the fission gases at annealing temperatures as low as 900°C with virtually no volume change. These results, however, probably do not reflect fission-gas diffusion within the UO_2 particles. As indicated in Fig. 5, approximately this amount of gas would have recoiled from the particles (which were 50 to 100 μ in size) during irradiation. Furthermore, L. G. Wisnyi (KAPL) has found by postirradiation heating that fission gases are not released from bulk UO_2 until temperatures much higher than 900°C are reached. Because of the large degree of porosity in the stainless steel- UO_2 samples studied by Johnston and BMI personnel, it was not possible to deduce whether the fission gases that had recoiled from the UO_2 particles escaped from the fuel elements by permeation through interconnected voids and cracks or by diffusion through the stainless steel.

The extent of fission-gas release from stainless steel- UO_2 is greatly reduced when interconnected porosity is absent or when the UO_2 particles are sufficiently large that a significant fraction of fission fragments does not recoil from them. Reporting on fission-gas release from stainless steel-25 per cent UO_2 fuel elements during irradiation to burn-ups of 20 to 40 per cent of the uranium atoms, Barney and Seymour²⁴ observed that only small amounts of gas (less than 10 per cent) were released at irradiation temperatures of 400 to 650°C (matrix temperature). Even in elements that had purposely defective cladding and interconnected porosity, the gas release was small, indicating the retentivity of UO_2 for fission gases. However, elements irradiated at a matrix temperature of about 900°C ruptured and released large amounts of gas (45 to 60 per cent). Of course, the temperature of the UO_2 particles was considerably higher than that of the matrix.

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Fig. 15—Density changes in Zircaloy-clad zirconium-8 wt. % uranium alloys on postirradiation annealing. (Johnston, KAPL.)

There are other examples of the ability of uranium compounds in dispersion fuel systems to retain fission gases up to relatively high temperatures. Workers at ORNL found that 99.8 per cent of the generated gases in thorium-uranium dispersions containing 2.5 per cent uranium were retained at temperatures of 1840°F.³¹ M. B. Reynolds of KAPL also observed no gas release from UAl_4 particles dispersed in aluminum to about the decomposition point of the UAl_4 .

(c) *Additional Observations.* The stainless steel- UO_2 dispersion system is being investigated for several applications because of its good irradiation stability at relatively high temperatures. As a result, many of the data substantiating the dispersion concept have been obtained from investigations on this system.

Seymour, Barney, et al.,²⁴ who investigated this system with UO_2 particle sizes ranging from 44 to 105–210 μ , report excellent stability to burn-up of as high as 40 per cent of the uranium and at temperatures of 400 to 650°C. The volume expansion rate of the UO_2 was deduced to be less than 1 per cent for each per cent burn-up of the uranium atoms;²⁷ this would indicate that the stresses resulting from the accommodation of fission-product atoms should be small. In addition, swelling due to gas agglomeration was not observed, although the UO_2 particle temperature was considerably higher than the 400 to 650°C cited for the matrix.

In view of the problems that have been encountered in metallic fuel materials, UO_2 might be termed surprisingly stable. Commenting on the irradiation stability of UO_2 , Weber³² notes that the fission-product atoms should become oxidized by the released oxygen and suggests that the resultant mixed oxides may be analogous to naturally occurring mineral oxides. As such, they may be inherently more compatible and stable than mixtures of foreign atoms in a metal lattice.

Fig. 16—Stainless steel—25 wt. % UO_2 . (Barney and Wemple, KAPL.) (a) Unirradiated and unetched. (b) Irradiated to 12 per cent burn-up of uranium atoms at 450 to 600°C; lightly etched. (c) Irradiated to 30 to 40 per cent burn-up of uranium atoms at 450 to 600°C; unetched. (d) Irradiated to 14 per cent burn-up of uranium atoms at 1100 to 1700°C; unetched.

IRRADIATION BEHAVIOR OF DISPERSION FUELS

Fig. 16—(Continued)

Barney and Wemple²⁷ have observed the following irradiation effects in UO_2 particles in stainless steel- UO_2 dispersion fuels:

1. The tendency for cracks initially present in the particles to heal upon irradiation. This effect can be seen in Fig. 16 by comparing the fragmented, unirradiated particles (Fig. 16a) with the irradiated particles (Figs. 16b, c, and d). Similar observations have been made by A. E. Richt of ORNL.

2. The sintering and rounding of UO_2 particles during irradiation, as demonstrated in Fig. 17. The material shown here initially possessed a considerable amount of porosity (5 to 10 per cent), which was located principally in and around the UO_2 particles. With such a low starting density, the particles contracted away from the stainless-steel matrix on sintering. Such behavior would be expected to raise the particle temperature and accelerate further sintering. The material shown in Fig. 16 had a higher initial density than that in Fig. 17 and, therefore, exhibited less sintering.

3. The formation of pores in the UO_2 , as shown in Figs. 16b, c, and d and Fig. 17. Observe the size of the pores in Fig. 16c, which represents an irradiation to 30 to 40 per cent burn-up at 450 to 600°C, and compare these pores with the larger pores in Fig. 16d, where less than half this burn-up but a considerably higher temperature, 1100 to 1700°C, is represented.

Thus, although good irradiation stability of some stainless steel- UO_2 dispersion fuels has been demonstrated, physical changes in the UO_2 particles have also been observed. The healing of cracks initially present in the UO_2 , sintering of UO_2 particles, and the formation of pores in the UO_2 may influence this stability. The significance of these changes on the irradiation stability of the stainless steel- UO_2 dispersion system should be investigated further in order to establish more fully the limitations of the system.

(d) *Merits of Dispersion Type Fuels.* The foregoing discussion merely indicates precautions that must be considered in the design of a dispersion fuel alloy. Where irradiation instability limits the design, there is no advantage (and there may be disadvantages) in the dis-

Fig. 17—Stainless steel-25 wt. % UO_2 irradiated to 21 per cent burn-up of uranium atoms at 650 to 830°C. (Barney and Wemple, KAPL.)

persion concept. If these factors are not limiting, the dispersion concept has significant merits, particularly in the flexibility of design, since it offers the following advantages over the customary approach to fuel design:

1. A wider selection of fuel materials, many of which may be less sensitive to impurity-atom damage. Uranium dioxide is a good example of such a superior fuel-bearing material. Even though its uranium content per unit volume is less than that of uranium metal, it does offer a higher fuel operating temperature, a lower expansion rate for the accommodation of fission-product atoms, and higher fuel burn-ups (40 to 50 per cent uranium burn-up and perhaps more) without gross instability.

2. A wider selection of matrix materials and, therefore, optimization of the gross properties of the fuel system. In this respect, note that the fuel composition, particle size, and matrix composition are limited only by the conditions required for fabrication and the existence of suitable materials. Within these bounds and the limitations imposed by irradiation, any combination of fuel and matrix material is practical.

3. A convenient method for introducing porosity into the fuel material to alleviate the strains produced by fission-product accommodation and potentially to allow higher fuel burn-ups. The effect of porosity in minimizing the volume increase of the composite element appears to have been adequately demonstrated in stainless steel- UO_2 dispersions. Here, 98 per cent dense alloys exhibited some volume changes (about 1 to 2 per cent), while those having 90 to 95 per cent composite densities had none at even higher burn-ups.

4 CONCLUSIONS

The improvement of the postirradiation properties of a fuel system by the control of microstructural factors in accordance with the dispersion concept has been borne out experimentally. With such improvement in properties, contingent upon the stability of the components, the dispersion concept provides a technique for the design of potentially superior fuel elements. On the other hand, the dispersion fuel concept may not represent a unique solution to the complete loss of ductility characteristic of irradiated uranium. Measurable postirradiation ductility has been observed in some homogeneously damaged alloys. Nevertheless, maximum retention of ductility and other properties will probably be found only in alloys designed along the lines of the dispersion fuel concept.

One should observe that the dispersion concept suggests that, where strains must be tolerated, the ratio of the existing strain to limiting strain is minimized by maintaining the properties of the unirradiated materials. Although this conclusion is consistent with the comparative decreases in ductility observed in postirradiation tests, it should be noted that processes for the enhancement of ductility of fission-product-damaged materials during irradiation have also been proposed. Moreover, the localized increases in fission density and fission-product concentration that are characteristic of dispersion alloys are also potentially disadvantageous in that they may cause both local stresses and irradiation instability. The dispersion concept is practical only where these effects do not limit the stability of the alloy. Nevertheless the flexibility offered by the dispersion fuel principle both in selecting the constituent materials and in introducing porosity may combat these limitations.

The successful performance of (1) the aluminum-15 per cent uranium alloy (aluminum- UAl_4 dispersion) fuel element in the MTR at burn-ups of up to 50 per cent of the uranium in endurance tests,²³ (2) the stainless steel-25 per cent UO_2 dispersion fuels at high temperatures (650°C) for burn-ups of 20 to 50 per cent of the uranium,^{11,24} (3) the aluminum-54 per cent UO_2 fuel element in the Geneva reactor,¹¹ and (4) other systems, including boron dispersions, demonstrates the applicability of dispersion fuel systems.

Obviously a considerable amount of additional information is necessary to utilize fully the merits of dispersion elements. In an engineering sense this does not prevent one from designing an improved fuel element on the basis of the dispersion concept, but it does restrict one in establishing the optimum parameters. Further work is needed to develop fully the potentialities of the dispersion concept. To date, a majority of the investigations have been cursory,

with emphasis on the development of a satisfactory composite fuel element. Many aspects have not been adequately investigated, such as the allowable range of particle sizes, the criteria for proper selection of fuel and matrix materials plus the effect of fission-product impurity atoms on their properties, and the importance of porosity in and around the fuel-bearing phase or in the matrix. There is need for a true comparison of homogeneous alloys and dispersion alloys having the same components irradiated near their limit of applicability; a dispersion of U^{235} in a matrix of U^{238} , compared with the normal homogeneous solution of the two, would be interesting to study in this connection. The influence of particle size on matrix strength and mode of failure is yet to be completely evaluated.

Dispersion alloys as a class of dense solid fuel materials must be compared to the alternate type, homogeneous alloys. The validity of the comparison will depend upon the knowledge of the sources of instability in both types of systems. From this viewpoint a better understanding of the effect of fission-product concentration on materials and the mode of interactions between gas atoms is needed.

ACKNOWLEDGMENTS

Throughout this paper the authors refer to the studies and observations of many different investigators. Much of this work has not yet appeared in open technical publications but has been reported only in AEC literature or not reported at all. It is requested that any future reference to such work be accredited to the particular investigator associated with it and not to the authors of this paper.

This paper is by no means an exhaustive report of observations on irradiation effects in dispersion fuels. To have been so would have made the paper even more voluminous than it now is. The authors have selected the material from the viewpoint of indicating the merits and potential limitations of the dispersion fuel concept. As a result, some observations and data have been omitted because they did not lend themselves to this appraisal and critique.

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SESSION VII

Plutonium Fuel Elements

44

Fast Reactor Fuel Development at Argonne National Laboratory*

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1 INTRODUCTION

Three fissionable isotopes, U^{233} , U^{235} , and Pu^{239} , can be made available in quantities sufficient to qualify them for consideration as the fuel for fast neutron power-breeder reactors. The factors involved in comparing these potential fuels have been discussed and repeated many times and in many places.^{1-3a} (Such references should be consulted for more details than will be given here.) Suffice it to say that Pu^{239} is the favored fuel for this application because of better nuclear properties, because its use permits a tremendous increase in the world's energy supply, and because it will become increasingly available as the result of its production in various natural uranium power reactors. A system that can produce more fuel than it consumes because of the high neutron yield per fission of Pu^{239} is extremely attractive. Use of the excess neutrons to breed more fissionable Pu^{239} from the abundant and fertile but nonfissionable isotope of uranium, U^{238} , is a real boon at a time when our energy needs are expanding so rapidly.

Pertinent to our subject is the recent review by Foote⁴ wherein he considers the uses of plutonium in both fast and thermal nuclear reactors. After considering the limitations of plutonium as a metal, he develops arguments for its use in diluted form in power reactors. He also reviews its place as a fuel in Argonne National Laboratory's fast power-breeder program and mentions briefly proposed uses in programs at other installations. Also, several countries contributed recently to the first unclassified Conference on the Metal Plutonium³ held in Chicago which included sessions on developments in the use of plutonium in power reactors.

2 PLUTONIUM AS A FAST REACTOR FUEL

The unattractive properties of solid plutonium metal makes it extremely unlikely that the unalloyed metal will find use as a fuel. It melts at a relatively low temperature (640°C) and undergoes five solid state transformations on heating from room temperature to its melting point. The unusually large volume changes associated with these transformations (some are negative), the large thermal expansion coefficients of the allotropes (some also negative), along with the anisotropic behavior of some of these allotropes result in distortion of plutonium on heating and cooling. Heat-transfer considerations also preclude the use of highly concentrated solid plutonium (as well as any other fissionable fuel) in a practical fast power reactor. The high power densities require large cooling areas and thin sections not readily achieved by normal methods of fabrication. A more practical solution is to subdivide or dilute by

* This paper may also be identified as Report ANL-FGF-73.

alloying. A fertile isotope, such as U^{238} , can be used as the diluent, in which case the reactor is an "internal breeder." An inert diluent such as aluminum can also be used, in which case all the breeding is accomplished in a surrounding blanket of a fertile isotope.

The degree of dilution of plutonium necessary to make it useful as a fast power-breeder fuel results in its being the minor element so that the undesirable properties of unalloyed plutonium are no longer of concern. Instead the metallurgist is concerned about the alloying effect of plutonium on the properties of the diluent. However, the plutonium that is present is sufficient to make it necessary to use the special handling methods that have and are being developed for working safely with high intensity alpha emitters. Methods of dealing with this health hazard problem were reviewed recently at a symposium held at Harwell.⁵ However, as will be discussed later, recent developments in pyrometallurgical processing of fast reactor fuel elements necessitate remote handling since short cooling times and incomplete fission-product removal are involved. The resulting high gamma activity coupled with the alpha activity dictates the need for remote handling whether the fuel is plutonium or U^{235} .

To date fuel-element experience in fast reactors is very limited. Plutonium cylinders 5.5 in. long by 0.65 in. diameter jacketed in steel were used as the fuel in the Los Alamos Fast Reactor.⁶ This was a low-power (approximately 25 kw) mercury-cooled reactor which was intended to demonstrate that such a fast neutron reactor could be built and served principally as a source of neutrons for experiments.

The first of ANL's fast neutron power-breeder reactors, Experimental Breeder Reactor Number One (EBR-I), was designed as an experimental facility to further the understanding of the physics of such systems and to study the engineering feasibility of a NaK-cooled reactor. It was described at the 1955 Geneva Conference by Lichtenberger et al.⁷ The second of ANL's fast reactors, EBR-II, is a much larger engineering facility designed to obtain the information which will permit scaling up to a central power station of competitive size. It was also described at the Geneva Conference by Barnes et al.⁸ and more recently by Koch and co-workers.⁹

In spite of the advantages of Pu^{239} , the fuel that has been used in EBR-I and that will be used for the first loading of EBR-II is U^{235} . This can be attributed in the earlier case to availability and more recently to the relatively greater knowhow in uranium fuel-element metallurgy. However, EBR-II is designed to receive plutonium fuel at the earliest possible loading, and present plans are to fuel with plutonium the full-size power reactor that will be developed from EBR-II's findings. A promising fuel element based on plutonium is in process of development and appears to satisfy EBR-II requirements. However, it is desirable to test this fuel element in a fast neutron flux, simulating the eventual operating conditions of EBR-II. No such facility now exists. Therefore, the U^{235} fueled EBR-II will serve as the final proving grounds for the fuel element based on plutonium.

The United Kingdom's Dounreay Fast Reactor^{10,3b} and the Power Reactor Development Corporation's Enrico Fermi Fast Reactor¹¹ also will use U^{235} as the fuel to begin with but will switch to a Pu^{239} fuel when the plutonium technology has been sufficiently advanced. Several countries have shown an interest in using plutonium as a fast reactor fuel, and some are actively engaged in developments to that end.³

Of the other alloy systems that are under study as potential fuels for fast and thermal reactors, the most experience has been gained with the low plutonium-aluminum alloys.³ These alloys resemble the corresponding uranium-aluminum alloys. The phase diagram as developed by Los Alamos Scientific Laboratory,^{3c} Fig. 1, shows a eutectic at 1.7 at. % plutonium (about 13 wt. %) with a lowering of the melting point of aluminum by about 10°C. In the composition range of interest the alloys consist of $PuAl_4$, a hard, brittle compound, in a matrix of almost pure aluminum. Shuck¹² has described the manufacture of aluminum-clad aluminum-plutonium alloy fuel plates containing up to 1.25 at. % plutonium using a picture frame cover plate technique similar to that used to fabricate aluminum-uranium alloy fuel plates for MTR.¹³ Of particular importance to the fuel-element metallurgist is the fact that these plates were irradiated in MTR to essentially complete burn-up of the plutonium with no measurable dimensional or property changes. From them were isolated the first significant amounts of elements 99 and 100 (reference 14). More recently fuel elements for a complete

Fig. 1—Aluminum-plutonium phase diagram (after Los Alamos).

loading of MTR has been manufactured from this alloy in a combined effort of Los Alamos and Oak Ridge.^{3d} They will be used to make relatively large quantities of the transplutonic elements. Also, Chalk River has reported considerable reactor experience with aluminum-plutonium fuel elements in this composition range.^{3e} In addition to being stable under γ -radiation, these investigations have shown that the alloys have excellent thermal conductivity and they are readily fabricated. However, these alloys are even more prone to segregation and shrinkage cavities than the aluminum-uranium alloys.

The phase diagrams of these alloy systems have been studied by both Los Alamos^{3c} and Harwell,^{3f} where they have shown appreciable solubility of plutonium in both zirconium and, as shown in Fig. 2, in thorium. The low plutonium alloys in the composition range of reactor fuel interest are relatively soft and ductile and are fabricated with ease. ANL studies on the thorium-plutonium alloys show that they are stable to thermal cycling 200 times to 500°C. Irradiation damage studies on these alloys are in progress at ANL.

Dilution, to make it possible to use plutonium as a fast reactor fuel, can also be achieved by dispersion of particles of a plutonium compound in a matrix of another metal or by a ceramic approach. Dispersion of plutonium oxide in stainless steel and in other matrices is planned at ANL as well as other laboratories. A fast breeder reactor using a mixed oxide fuel element of UO_2 - PuO_2 has been proposed by Knolls Atomic Power Laboratory.¹⁵ The fuel has the advantage inherent in ceramic fuels of withstanding high burn-ups at high temperatures, and they report irradiation test results to substantiate this. They have also shown that the breeding ratio is still useful in this fuel in spite of the relatively large amount of oxygen.

Another fast breeder reactor concept, this one using molten plutonium, is the LAMPRE project which is in an early stage of development at Los Alamos Scientific Laboratory.^{16,3a} They propose to use as the fuel a molten plutonium-iron eutectic alloy (Fig. 3, reference 3c), containing 9.5 at. % iron and melting at 410°C, and liquid sodium as the coolant.

3 FAST REACTOR FUEL ALLOY REQUIREMENTS

The main metallurgical requirement of the fuel pin in ANL's fast power-breeder reactors is that it be dimensionally stable in the reactor. The alloys must of course have metallurgical properties which permit fabrication and handling, sometimes under unusually restricting conditions, as will be shown later. Also, for safety reasons, it is desirable that the thermal ex-

Fig. 2—Thorium-plutonium phase diagram (after Los Alamos).

Fig. 3—Plutonium-iron phase diagram (after Los Alamos).

pansion of the alloy be positive and reliable. The thermal conductivity is of great interest since the central metal temperature of the fuel is dependent upon it. In addition, the fuel-element alloys must resist attack by NaK or sodium.

Dimensional stability under irradiation is of major concern to the fuel-element metallurgist since relatively small changes can have an important bearing on the nuclear behavior of the reactor, its efficiency as a power producer, and its safe operation. To increase the reactor lifetime of a fuel before it must be reprocessed, we are aiming at a degree of dimensional stability that has not as yet been demonstrated in a working reactor. In EBR-II we have set our sights on at least 2 per cent burn-up of the total atoms before we must reprocess the fuel. Because of its importance and to clarify some of the data that are given later in this paper, it is desirable to review the methods used at ANL for most irradiation stability studies (Kittel et al.)¹⁷ and the terminology used in reporting the data.

Small specimens (approximately $\frac{1}{8}$ to $\frac{3}{16}$ in. diameter by 1 in. long) were irradiated in the high thermal flux of the MTR in lieu of a fast reactor test facility. The EBR-I and EBR-II fuel-element designs consist of fuel pins in a loose jacket so that they are free from physical restraint. Also, a thermal bond of molten NaK or sodium fills the annulus between the core and the jacket. The capsule design for irradiation studies¹⁷ simulates these conditions as shown in Fig. 4. The preferred capsule material is arc-melted crystal-bar hafnium-free zirconium because it provides the best combination of desired properties. The degree of burn-up for relatively low exposures is calculated by counting the Co^{60} gamma activity in cobalt-containing thermal flux monitors that accompany each capsule. For higher burn-ups Cs^{137} determinations are made. Changes in the mass abundance of the uranium isotopes have also been used to obtain total atom burn-ups. Since many of these studies were essentially screening tests wherein many cylindrical specimens were used to study numerous variables, conventional heat-transfer calculations were used to determine temperature, and no external heaters were used. Studies have been made which indicate that, in the vicinity of 660°C at the center of the specimen, the temperature can be calculated to about 30°C (Kittel).¹⁸ It must be recognized that these calculations are based on conditions at the beginning of the irradiation test so that the accuracy is greatly influenced by changes in conditions as the test progresses. In more recent capsule tests some variables are being studied more closely. Therefore, thermocouples embedded in the specimens are being used to supplement the calculated temperatures, and external heating is being used to achieve and control desired temperatures.

In addition to these capsule irradiation studies, full-length fuel elements are being irradiated at controlled elevated temperatures. Some of the results of these studies are included in this report.

Lengthwise growth of specimens is expressed as $\mu\text{in.}/\text{in.}$ per fission/ 10^6 total atoms. For small length changes the percentage of length change divided by the percentage of atoms burned up is approximately equal to the average instantaneous growth, G_i . However, for larger length changes the changing length of the specimen cannot be disregarded since the amount of growth at any level of burn-up is dependent upon the instantaneous length of the specimen at that time. Thus

$$G_i = \frac{1}{L} \frac{dL}{dN} = \frac{\ln L/L_0}{\text{fraction of total atoms fissioned}} = \frac{\mu\text{in.}/\text{in.}}{\text{fissions}/10^6 \text{ total atoms}}$$

where L_0 is the initial length; L is the final length; and N is the unit of atom burn-up.

Another property of importance is that the fuel be dimensionally stable to the numerous small thermal fluctuations during operation of the reactor as well as to the relatively smaller number of large thermal cycles due to startup and shutdown of the reactor. The subject of thermal cycling stability was reviewed at the 1955 Geneva Conference.¹⁹ The thermal cycling growth rate, G_t , is expressed as $\mu\text{in.}/\text{in.}$ per thermal cycle and is an average instantaneous growth analogous to the irradiation growth. Thus

$$G_t = \frac{1}{L} \frac{dL}{dN} = \frac{\ln L/L_0}{N} = \mu\text{in.}/\text{in.}/\text{thermal cycle}$$

where L_0 is the original length; L is the final length; and N is the number of thermal cycles.

Fig. 4—Assembled irradiation capsule.

4 EXPERIMENTAL BREEDER REACTOR NO. I

The EBR-I has had two complete fuel loadings, and a third loading has just been fabricated. All three loadings use U^{235} as the fissionable material. It was designed with a small critical mass of 52 kg in an undiluted form because U^{235} was not available in large amounts immediately after the war when this reactor was designed.⁷ Typical of normal operating conditions are 1.16 Mw of power with a maximum neutron flux of 1.1×10^{14} neutrons/cm²/sec, NaK coolant temperatures of 228°C in and 316°C out, and a 357°C maximum central temperature of fuel. The fuel elements are 0.384-in.-diameter rods assembled in a 20-mil-wall stainless-steel jacket with NaK as the thermal bond in the 10-mil annulus between the core and the jacket. Above and below the enriched uranium slugs and contained in the same jacket are blanket slugs of natural uranium.

4.1 First Loading

The method of fabricating the fuel elements for the first loading of EBR-I has been described by Shuck.²⁰ Each fabrication billet was made from 1 kg of unalloyed 93 per cent enriched uranium which was vacuum induction melted in a magnesia crucible and cast to 1¼ in. diameter by 6 in. long in a water-cooled copper mold. The castings were then rolled at 300°C (with one intervening beta anneal) to almost finished size and swaged to final size. Slug lengths averaging slightly less than 2 in. were made by notching and breaking. The slugs were fast beta heat-treated, to randomize the oriented wrought structure and thereby to improve dimensional stability under irradiation, after which they were annealed at 575°C. The beta treatment, which consisted in water quenching after a short time at 725°C, had been developed as the result of a study to stabilize uranium against thermal cycling.¹⁹

Studies have since shown that the beta heat-treatment does effectively reduce the tendency of 300°C rolled uranium to grow under irradiation. Paine and Kittel have reported low burn-up data at the 1955 Geneva Conference,²¹ and more recently they have reported the effects of high burn-up.²²

Length changes as a function of burn-up are plotted in Fig. 5 for 300°C rolled rod in the as-rolled and in the rolled and heat-treated conditions. Two specimens from this study are shown in Fig. 6. Note that the heat-treatment reduces the longitudinal growth but results in grain coarsening which leads to serious surface roughening under prolonged irradiation. Average growths from this study show that the heat-treatment lowered the irradiation growth, G_i , from 693 to 24 $\mu\text{in.}/\text{in.}$ per fission/ 10^6 total atoms and the thermal cycling growth, G_t , (50 to 550°C) from 395 to 35 $\mu\text{in.}/\text{in.}/\text{thermal cycle}$.

This core produced 3000 Mw-hr of heat, which amounts to an average burn-up of 0.2 at. %. Some of the central slugs received as much as 0.35 at. % burn-up, which was far greater than the 0.1 at. % burn-up originally intended for this core.²³ There was considerable concern over the fact that the wrought fuel had not been stabilized adequately for this much burn-up by the fast beta heat-treatment. The slugs had grown lengthwise to the end of the stainless jacket and had developed roughened surfaces. Also another more stable fuel alloy had been developed to the point where a full fuel loading test was justified. It was therefore deemed desirable to replace the core.

4.2 Second Loading

The second loading of EBR-I consisted of uranium-2 wt. % zirconium alloy slugs made by a centrifugal casting method developed by Shuck.²⁴ A 3-kg charge was melted in a MgO crucible and bottom poured onto the distributor of the centrifugal casting machine. The molten metal was directed through slots in the distributor into 16 copper molds that were rotating in a horizontal plane. The slugs were cast to the finished diameter and were notched and broken to the finished length. The cast slugs were used without a heat-treatment. Irradiation tests reported by Kittel et al.²⁵ proved that the cast slugs (G_i approximately 8) were definitely superior to heat-treated cast slugs (G_i approximately 40), to fabricated slugs (G_i approximately 470), and to fabricated and heat-treated slugs (G_i approximately 20).

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Fig. 5—Effect of heat-treatment on the irradiation growth of 300°C rolled uranium.

Fig. 6—Typical specimens showing the effect of heat-treatment on the irradiation growth of 300°C rolled uranium. (a) 0.26 at. % burn-up, 300°C rolled. (b) 0.55 at. % burn-up, 300°C rolled, beta quenched, and recrystallized.

This loading was partially melted during an experiment in which the reactor was being used as a critical assembly with the coolant flow stopped. The incident has been described by Zinn,²⁶ Kittel et al.,²³ and in reference 27. At the time of the meltdown the reactor had produced 1000 Mw-hr of heat, which is equivalent to 0.062 at. % burn-up in the slugs. The original machined surfaces of the unmelted slugs were undamaged, and no bumping was observed. No data were obtained on change in length of the slugs.

4.3 Third Loading

The third loading of EBR-I has just been fabricated. The fuel element was so designed that the lateral movement (or bowing) of the fuel is restrained on excursions. The U^{235} was again alloyed with 2 wt. % zirconium and was metallurgically bonded to a 0.020-in. Zircaloy jacket in an effort to restrain bowing of the fuel element. The fuel element was fabricated by direct coextrusion and cold swaging to the finished size. The rods were annealed twice at 850°C (15 min) during the swaging operation. The final heat-treatment given the rods was as follows: 15 min at 800°C followed by 1 hr at 690°C and air cooled. This heat-treatment of the 2 wt. % zirconium alloy was shown by Kittel²⁵ to be beneficial for fabricated slugs. Unpublished work by Kittel on these zirconium-clad fuel pins showed that, at a burn-up of 0.15 at. % and a center temperature of from 400 to 700°C, the average G_1 was only 8.

5 EXPERIMENTAL BREEDER REACTOR NO. II

5.1 EBR-II Reactor and Fuel Design

The EBR-II described by Koch et al.⁹ is a sodium-cooled fast neutron breeder reactor with a power output of 62.5 Mw of heat. It is a high performance reactor with a maximum power density of 1.4 Mw/liter of core volume and sodium coolant temperatures of 370°C inlet and 480°C outlet. This extremely high power density can be achieved only if the fuel alloy has a large cooling surface for its volume. This, coupled with the poor heat-transfer characteristics of the fuel alloys under consideration, means that section thicknesses must be small if excessive central metal temperatures are to be avoided.

The high thermal performance required, the high burn-ups being sought, and the simplicity demanded in the remote reprocessing scheme are the factors which influenced most the design of the EBR-II fuel element. Two general fuel designs have been considered: a "pin-type" fuel element and a "radiator-type" design. The latter is preferred from the heat-transfer point of view because of its relatively thinner sections. The "pin-type" fuel element will be used at first because it is more readily fabricated and handled under the conditions imposed by the reactor fuel reprocessing cycle.

The parts that make up the pin type fuel element for the first loading are shown in Fig. 7 (reference 9). A right circular cylinder of a fuel alloy 0.144 in. diameter by 14.22 in. long is contained in a 0.009-mil wall stainless-steel tube of 0.174 in. O.D. The resulting 0.006-in.

Fig. 7 — Pin type fuel element for EBR-II.

annulus is filled with static sodium to provide a thermal bond between the fuel pin and the jacket. A circular wire is wound helically about the external surface of the tube to provide proper spacing of the elements when clustered into subassemblies as shown in Fig. 8.

The radiator design, developed by Monson,²⁹ is included here because it illustrates the kind of fabrication problems facing the metallurgist in trying to achieve improved reactor heat-transfer conditions. As shown in Fig. 9 the fuel is the continuous portion of the hexagonal array with the coolant flowing through thin-wall tubes inserted through the cylindrical holes. A section through the radiator type fuel block, Fig. 10, shows the relatively thinner fuel sections. There are several ways of making this type of element. Powder metallurgical methods have been used to make wafers perforated with a hexagonal array of holes which can be assembled as shown in Fig. 11. Preliminary studies indicate that the radiator element can also be assembled from crimped sheets or long rods of unusual cross section as shown in Fig. 12, which includes several possible sections.

5.2 Reprocessing of EBR-II Fuel

(a) *Refining of the Alloy.* A novel feature of the EBR-II is that the fuel processing is an integral part of the reactor cycle. The metallurgical refining process and the fabrication methods that will be used involve very short cooling times and incomplete decontamination of the fuel. By reprocessing the highly radioactive fuel in remote handling facilities adjacent to the reactor, it is hoped to cut reprocessing costs and to reduce the inventory of fissionable material.

The refining method has been described by Schraidt et al.³⁰ It consists in melting and holding a 10-kg batch of spent fuel pins in an oxide crucible. Volatile and noble gas fission products are driven off, and those fission products whose oxides are more stable than uranium oxide form a dross which is readily separated on casting. The resulting ingot contains uranium, plutonium, and a group of fission products whose oxides are less stable than uranium oxide—the principal ones are zirconium, molybdenum, technetium, ruthenium, rhodium, and palladium. On subsequent recycling of the fuel these "fissium" (Fs) elements build up until they reach an equilibrium value; this is the alloy that will be used in EBR-II. Some of the variables that influence the concentration of these elements are adjustable, permitting a certain degree of control over the composition. For a given alloy and fissionable isotope content, the ratio of the amounts of these elements remains fixed among themselves. The anticipated equilibrium alloy resulting from a uranium fuel loading in EBR-I will be in the composition ranges shown in Table 1. The fission yield curve for Pu^{239} , however, is slightly

Table 1—RANGE OF FISSIUM COMPOSITION FOR U^{235} LOADING

Element	Wt. %
Zr	0.1–0.2
Mo	1.6–3.4
Tc	0.5–1.0
Ru	1.2–2.6
Rh	0.2–0.5
Pd	0.1–0.1

different than for U^{235} because of the extra mass units. Consequently this changes the relative concentrations of the fission-product elements not removed in the refining process. It is intended that an artificial equilibrium fissium alloy be used to start the reactor in order to avoid the changing alloy properties that would result if the composition changed on successive recycles.

One of the requirements of this refining process is that the jacket be readily separated from the core since the process cannot remove the elements in stainless steel. The fuel pin design with its loose fitting jacket and liquid metal bond fulfills this requirement.

Fig. 8 — Photograph of EBR-II fuel-element assembly.

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Fig. 9—Cross section of radiator type subassembly. Typical channel at right.

Fig. 10—Cross section of radiator type fuel block. Detail at right.

Fig. 11 — Radiator subassembly made from fuel wafers.

Fig. 12 — Cross section of longitudinal fuel strips.

(b) *Refabrication of the Pins.* As will be shown in the discussion of the fuel alloy studies, fuel alloy castings have more desirable properties than wrought structures especially as regards dimensional stability when irradiated at temperatures and to burn-ups of interest to EBR-II. Casting also suggests itself as a simple fabrication method where remote handling is necessary. The long thin fuel pins for EBR-II are not amenable to normal gravity casting, and the centrifugal casting machine used to make the fuel pins for the second loading of EBR-I does not lend itself to remote operation. Shuck³¹ has developed a precision injection casting technique which can be adapted to remote operation and which is capable of casting simultaneously to the final diameter of 0.144 ± 0.001 in. a large number of full length EBR-II fuel pins. Yaggee and co-workers³² have studied the various parameters of this technique using simulated EBR-II uranium-fissium alloys. This is about as simple a fabrication process as is possible since, in addition to casting, the only steps necessary to prepare finished fuel pins is to notch and break the castings to final length.

The injection casting machine, shown schematically in Fig. 13, is adapted for use in the shielded reprocessing cell. The alloy is charged into a shallow crucible, and minor alloy additions, such as replenishing the spent fuel, are made at this time. Precision bore tubes of Vycor, 96 per cent silica glass, with one end closed are used as the molds. A group of these molds is suspended above the crucible with open end down. Melting is accomplished by induction heating in vacuum. By lowering the molds to immerse their open ends in the molten bath and simultaneously pressurizing with an inert gas, the molten metal is forced into the mold cavities. To make this technique work, it is necessary to control carefully the mold preheat temperature, the amount of superheat in the melt, and the degree and timing of the applied pressure difference. Also, a refractory type coating is applied in a simple operation to the inside mold surface so as to minimize attack on the silica glass by the molten alloy. Note in Fig. 13 that all auxiliary equipment of questionable radiation resistance is shielded in a pit below the cell.

5.3 Fuel Alloy Studies for EBR-II

(a) *Reactor Requirements.* The alloys that have been developed for the EBR-II fuel elements result from a combination of reactor physics, reactor engineering, reprocessing, and

Fig. 13—Schematic injection casting furnace.

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metallurgical requirements. U^{238} is used to dilute the fissionable material. Not only does this help the heat-transfer problem, but it also results in some internal breeding. The enriched uranium fuel core that will be used at first, pending final testing of a plutonium fuel element, will consist of a total of 363 kg of 5 wt. % fissium-uranium alloy with 170 kg of U^{235} or 49 per cent enrichment of the uranium.⁹ The plutonium loading requires somewhat less fissionable material but, because of the metallurgical limitations that will be discussed next, an alloy of uranium-20 wt. % plutonium-10 wt. % fissium is now being considered with an estimated 15 to 20 wt. % U^{235} added.³³ The full-scale power-breeder reactor that will be developed from EBR-II's findings will use a lower concentration of fissionable isotope because of the much larger core size. An alloy containing less than 20 wt. % Pu^{239} and no U^{235} is contemplated.³³

(b) *Refining Requirements.* The fission-product elements not removed by the metallurgical refining process determine to a considerable degree the fuel alloy composition that will be used in EBR-II. Since an infinite number of such alloys are possible, a few reference alloys have been standardized on for test purposes. Typical reference alloys for which test data are available are shown⁹ in Table 2. The uranium-5 wt. % fissium alloy is the one that

Table 2 — TYPICAL REFERENCE FISSIUM ALLOYS

	U^{235} Fissium	Pu^{239} Fissium
Uranium	95.0	69.2
Plutonium		20.0
Zirconium	0.2	0.5
Molybdenum	2.5	2.8
Ruthenium	1.5	4.3
Rhodium	0.3	0.7
Palladium	0.5	2.5

will be used in the first U^{235} loading. For the plutonium loading, which contains about equal amounts of Pu^{239} and U^{235} , the alloy composition will be somewhere between the two compositions shown in Table 2.

(c) *Uranium-Plutonium Base Alloys.* The reasons for preferring Pu^{239} as the fuel for EBR-II and for diluting with uranium have been discussed, and mention has been made of the development of a fuel element based on plutonium that appears to satisfy EBR-II requirements. Since the concentration of the uranium diluent will exceed the concentration of plutonium by approximately five to one, the metallurgical properties can be expected to more closely resemble those of uranium than plutonium. It is desirable to examine the binary uranium-plutonium alloys since they are basic to the EBR-II fuel development. The phase diagram, Fig. 14, was developed by Ellinger and co-workers,^{3c} and several features have been confirmed at ANL. The fact that plutonium lowers the melting point as well as the transformation temperatures of uranium is pertinent to this development. The amount of lowering of the solidus by 30 wt. % plutonium is sufficient to severely limit the maximum fuel temperature in a reactor like EBR-II. Alpha uranium can dissolve up to 15 wt. % plutonium at 560°C with the solubility decreasing to about 10 or 11 wt. % at room temperature. Beta uranium can dissolve a maximum of about 18 wt. % plutonium at 600°C. Increasing the plutonium concentration beyond the solubility limit in alpha uranium introduces the zeta phase. Alloys containing even small amounts of this compound have been found in early investigations to have extremely poor metallurgical properties—the castings contain microcracks which make them so fragile they can hardly be removed from the mold without cracking, and they tend to fall apart on thermal cycling; the alloys are pyrophoric; and worst of all, contrary to the early test indications, the low-plutonium binary alloys proved to be extremely susceptible to irradiation damage. Recent work at ANL suggests that the poor properties exhibited by the binary uranium-plutonium alloys may not be inherent in them but due rather to the method of preparation of the alloys.

Fig. 14 — Uranium-plutonium phase diagram (after Los Alamos).

Fortunately the major fission-product elements not removed during the refining process, molybdenum and ruthenium, are desirable alloying elements in that they improve the irradiation stability of uranium and especially of the uranium-plutonium alloys. Molybdenum has long been known to be soluble in uranium and to lower the temperature range of stability of gamma uranium which has a body centered cubic structure. Work at ANL indicates that molybdenum acts similarly in the uranium-plutonium alloys and also suppresses formation of the undesirable zeta phase. Recently Dwight³⁴ has shown that ruthenium is soluble in uranium and has the same tendency as molybdenum to stabilize gamma uranium. Zirconium, which is fortunately a minor fission element, has been shown by Los Alamos to have deleterious effects in that it stabilizes the undesirable zeta phase.^{3c}

(d) *Irradiation Stability.* In EBR-II the degree of radiation damage that can be accommodated will determine the reactor lifetime of the fuel and therefore the frequency of reprocessing. We desire to achieve a minimum of 2 per cent burn-up of all atoms. Unlike many other types of reactors, corrosion of the fuel by the coolant is not a limitation, and the fast reactor is insensitive to fission-product poisons.

The amount of volume swelling and linear dimensional changes that can be tolerated in the EBR-II fuel-element design is dependent on factors which will be resolved only when the full size fuel assemblies are exposed to EBR-II operating conditions. One of the attractive features of the design is that the loose fit of the fuel pin in the jacket will accommodate some dimensional changes. Also, Smith and co-workers²⁸ have shown that restraint by the jacket can be expected to inhibit some of these changes if filling of the sodium annulus does occur. However, just how far other factors that affect reactor performance, such as heat transfer, can tolerate displacement or thinning of the sodium bond is not clear at this time.

Weber has estimated that a volume expansion of about 3.4 per cent must be expected for 1 per cent burn-up of all the atoms owing to lattice distortion by the newly formed fission-product elements.³⁵ Thus for the 2 per cent burn-up that is planned for EBR-II, almost one-half of the 6-mil annulus will be involved regardless of how well the fuel is stabilized against dimensional changes from other causes. It is expected that this much expansion can be tolerated with ease. The volume expansion found as the result of irradiation studies of the

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alloys of most interest appear to be not much different than the above. This is especially true of the uranium-plutonium-fissium alloys some of which show even less expansion than that which should come from formation of new fission-product elements. However, an appreciable extrapolation must be made from the test conditions for these specimens to the maximum reactor conditions.

The uranium-plutonium-fissium and related alloys that we have studied showed practically no irradiation damage effects and rate as the best uranium alloys ever tested by ANL.³⁶ Three cast uranium-20 wt. % plutonium base alloys were studied, including 5 wt. % molybdenum, 5.4 wt. % fissium, and 10.8 wt. % fissium. (Pu²³⁹ fissium composition was used for which see Table 2.) The test conditions and dimensional changes are summarized in Table 3.

Table 3—EFFECT OF IRRADIATION ON CAST URANIUM-PLUTONIUM-FISSIUM ALLOYS

Alloy, wt. %	Range of burn-up, at. %	Range of central metal temp., °C	G _i average*	V _i average†	No. of specimens
70 U-20 Pu-10.8 Fs	0.81-0.92	280-310	1.8	2.5	2
75 U-20 Pu-5.4 Fs	0.33-0.42	450-520	1.8	4.2	3
85 U-20 Pu-5 Mo	0.15-0.43	190-340	3.2	5.8	7

$$*G_i = \frac{\text{per cent length change}}{\text{at. \% burn-up}}$$

$$†V_i = \frac{\text{per cent volume change}}{\text{at. \% burn-up}}$$

The growth and volume changes were so small for the three sets of specimens as to make the differences between them meaningless. Typical of the results is the uranium-20 wt. % plutonium-10.8 wt. % fissium alloy pin shown in Fig. 15a which was irradiated at an approximate central metal temperature of 310°C to 0.9 per cent burn-up of all the atoms. The original smooth machined surfaces were preserved, and, but for slight volume increases which can be attributed to the new elements formed by fission, the dimensions were remarkably unchanged. The uranium-20 wt. % plutonium-5 wt. % molybdenum alloy pins, which also showed little effect, were not irradiated to as high a burn-up as the 10.8 wt. % fissium alloy pins. The lower fissium alloy pins were also irradiated to a lower burn-up, but their central metal temperatures were much higher, as high as 520°C.

By x-ray diffraction, dilatometric, and metallographic studies, we have shown that the 10.8 wt. % fissium alloy is essentially all body centered cubic gamma-uranium structure with an $a_0 = 3.42$ Å and no transformations to at least 500°C. The 5.4 wt. % fissium alloy shows evidence of an appreciable amount of a second phase.

In contrast to the excellent uranium-plutonium-fissium alloys, we found the binary uranium-plutonium alloys to be extremely unstable to irradiation.³⁷ Castings containing 3.7, 6.6, and 13.0 wt. % plutonium were irradiated to as high as 0.84 per cent burn-up. Figure 15b shows the badly bumped and distorted results that were typical of this group. The surface condition is indicative of an extremely coarse grain structure and made meaningless the measurements of dimensional changes.

Binary uranium-plutonium alloys containing 9.5 and 14.1 wt. % plutonium developed fiber textures on extrusion as evidenced by dilatometric studies and also by elongation when irradiated. Figure 15c shows the effect of irradiating to 0.43 per cent burn-up a uranium-14.1 wt. % plutonium extruded pin at 490°C central metal temperature. A 645°C randomizing heat-treatment resulted in excessive grain coarsening which led to the surface roughening shown in Fig. 15d.

The alloy to be used first in EBR-I, uranium-5 wt. % fissium, and some related alloys have been the subject of numerous irradiation tests by Smith.³⁸ The role of molybdenum, one of the major constituents of fissium alloys, was examined by adding various amounts of it to a uranium-fissium alloy and by including a binary uranium-molybdenum alloy. The alloys

Fig. 15 — Typical irradiation results on uranium-plutonium base alloys. (Magnification 2 $\times$.) (a) Uranium-20 wt. % plutonium-10.8 wt. % fission, cast; burn-up, 0.92 per cent; central metal temperature, 310°C. (b) Uranium-13 wt. % plutonium, cast; burn-up, 0.84 per cent; central metal temperature, 430°C. (c) Uranium-14.1 wt. % plutonium, extruded; burn-up, 0.43 per cent; central metal temperature, 490°C. (d) Uranium-14.1 wt. % plutonium, extruded and heat-treated; burn-up, 0.42 per cent; central metal temperature, 480°C.

studied are given in Table 4. Both cast and wrought specimens were included, and the effect of various heat-treatments was studied.

Results of dimensional and hardness changes are summarized in Table 5 for tests where similar conditions of irradiation permit comparison. Both the 2.5 wt. % molybdenum and the 5 wt. % fission were effective in restraining length and volume changes as shown in Fig. 16a, whereas the 3.2 wt. % fission was not as effective. However, all of these alloys had somewhat rougher surfaces as the result of irradiation than did the uranium-plutonium-fission alloys, even though they were not irradiated to as high burn-up. It can be concluded that alloying to stabilize the gamma structure of uranium is, in general, effective in improving irradiation stability.

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Table 4—COMPOSITIONS OF URANIUM-FISSIUM ALLOYS THAT WERE IRRADIATED

Composition, wt. %	No. of specimens
U-2.5 Mo	16
U-3.17 Fs	27
U-5 Fs	24
U-5 Fs-2.5 Mo	18
U-5 Fs-7.5 Mo	15

Table 5—EFFECTS OF IRRADIATION ON URANIUM-FISSIUM ALLOYS

Alloy, wt. %	Fabrication* and heat-treat	Range of burn-up, at. %	Range of central metal temp., °C	G _i aver- age†	V _i aver- age‡	Hardness, R _A		No. of speci- mens
						Before irradi- ation	After irradi- ation	
U-3.2 Fe	As cast	0.33-0.39	530-550	11.1	11.4	72	76	3
U-5 Fs	As cast	0.32-0.64	450-520	1.8	7.7	66	64	4
U-2.5 Mo	As cast	0.40-0.53	570-790	2.0	3.9	73	74	8
U-3.2 Fs	Cast, WQ	0.19-0.21	280-390	24.4	18.4	66	75	3
U-3.2 Fs	Cast, FC	0.19-0.20	270-370	3.1	17.8	66	73	3
U-5 Fs	Cast, WQ	0.19-0.21	270-380	8.1	28.9	46	73	3
U-5 Fs	Cast, FC	0.19-0.21	280-390	4.7	13.3	72	73	3
U-3.2 Fs	Wrought, WQ	0.32-0.69	230-480	53.8	27.5	67	69	4
U-3.2 Fs	Wrought, FC	0.33-0.56	320-480	1.2	8.2	67	74	3
U-5 Fs	Wrought, WQ	0.50-0.67	340-470	0.6	11.0	45	66	3
U-5 Fs	Wrought, FC	0.25-0.56	200-470	2.7	6.7	72	69	3
U-2.5 Mo	Wrought, WQ	0.42-0.54	550-760	32.7	39.5	66	70	4
U-2.5 Mo	Wrought, FC	0.42-0.56	550-770	3.4	4.1	64	71	4

*All heat-treatments: 1 hr at 850°C, and water quenched (WQ) or furnace cooled (FC).

$$†G_i = \frac{\text{per cent length change}}{\text{at. \% burn-up}}$$

$$‡V_i = \frac{\text{per cent volume change}}{\text{at. \% burn-up}}$$

From Table 5 and Figs. 16b through d, it is evident that water quenching from 850°C is not a desirable heat-treatment, whereas furnace cooling does no harm to castings and effectively disorients the wrought structures. Work at ANL³⁸ and Battelle Memorial Institute³⁹ helps to explain some of the results of these heat-treatments, but clarifying irradiation tests are still needed. As can be seen in Table 5, water quenching of the cast and the wrought uranium-5 wt. % fissium alloy from 850°C results in a relatively soft, presumably retained gamma uranium, structure, whereas neither 3.2 wt. % fissium or 2.5 wt. % molybdenum had this effect. The soft gamma structure was not retained in the uranium-5 wt. % fissium alloy by furnace cooling from 850°C. Irradiation did not appreciably change the hardness of the as cast or the furnace cooled specimens but did harden the water quenched uranium-5 wt. % fissium specimens. The BMI studies³⁹ of the heat-treating and transformation characteristics of the uranium-5 wt. % fissium composition substantially verify and expand these findings by dilatometric, metallographic, x-ray diffraction, and hardness evidence. Their results indicate a transformation at about 625°C, and they retain a single-phase gamma uranium structure by water quenching from 800°C. Subsequent heat-treatment of this metastable structure at the temperatures that were attained in the above-described irradiation tests results in substantial precipitation hardening. Overaging just below the transformation temperature softens the alloy.

Irradiation studies have also been made on full size EBR-II fuel elements of uranium-5 wt. % fissium alloy by Sowa and co-workers⁴⁰ with very encouraging results. In one test

Fig. 16—Effect of irradiation of uranium-5 wt. % fissium alloys. (Magnification 2 $\times$.) (a) Burn-up 0.32 per cent; central metal temperature, 470°C. (b) Burn-up, 0.21 per cent; central metal temperature, 295°C. (c) Burn-up, 0.19 per cent; central metal temperature, 265°C. (d) Burn-up, 0.51 per cent; central metal temperature, 249°C. (e) Burn-up, 0.66 per cent; central metal temperature, 324°C.

the upper half of the fuel pin was irradiated in MTR to at least 1.5 per cent burn-up at a maximum central metal temperature of about 425°C. This resulted in a 2.8 per cent increase in length (G_1 = approximately 2) with only slight surface roughening and a density decrease of about 3 per cent.

In another series of tests by Sowa and co-workers⁴⁰ on three full size fuel elements in CP-5, irradiations were carried to as high as 0.5 at. % burn-up and a central metal temperature of about 400°C. The fuel pins elongated less than 2 per cent (G_1 = less than 3) with some surface roughening and a density decrease of 1 to 2.6 per cent. Special attention was given in these tests to measuring the volume of fission products released from the fuel core. The ratio of the fission products in the bond to that in the fuel was 10^{-3} to 10^{-5} , and the fission gases that accumulated above the sodium were too small to detect.

(e) *Thermal Cycling Stability.* Thermal cycling tests in and out of the reactor indicate that the EBR-II fuel alloys have extremely good thermal stability. We have cycled them to reactor temperatures more than 200 times which far exceeds the number of such cycles the fuel pins will experience in the reactor.

Cast as well as extruded uranium-20 wt. % plutonium-fissium alloy pins (5.4 and 10.8 wt. % fissium) were practically unchanged as the result of 200 cycles between 25 and 500°C. In contrast, both cast and extruded binary uranium-plutonium alloy pins spall and crack badly in less than 200 similar cycles.

Full size EBR-II fuel elements containing injection cast uranium-5 wt. % fissium alloy pins have been thermal cycled by Sowa and co-workers⁴⁰ 200 times to 550°C without significant dimensional changes. Also, cast specimens and gamma heat-treated wrought specimens of this alloy have been cycled 250 times from 66 to 620°C with negligible growth or surface roughening.⁹ Hot rolled uranium-5 wt. % fissium specimens elongated 3 to 6 per cent when cycled from 150 to 750°C as reported by Saller et al.³⁹ They suggest that differences in fabrication history of this alloy may have a considerable effect on the tendency to deform on cycling.

(f) *Corrosion.* The EBR-II fuel pin must be compatible with the environment in the reprocessing cell as well as with the liquid sodium bond within the jacket. Even though the reprocessing cell contains a relatively inert atmosphere of argon, the problem of reaction of the uranium-plutonium base alloys with the working environment was not solved until the fissium elements were added. Our glove box facility in which these alloys were studied at ANL⁴¹ has a much purer helium atmosphere than the reprocessing cell will have. Yet the binary uranium-plutonium alloys containing over 15 wt. % plutonium tend to disintegrate to a powder on standing in this atmosphere. Binary alloys containing 20 to 30 wt. % plutonium disintegrate more rapidly in our helium atmosphere and are pyrophoric when exposed to air. This undesirable property has not been explained although several theories have been proposed involving various combinations of the presence of the zeta phase, microcracks in the castings, internal stresses, and hydride and oxide formation. Studies now in progress at ANL on arc-melted binary alloys may help to clarify this problem.

Fortunately, the addition of the fissium elements to make the alloys that are favored for the EBR-II fuel has solved the pyrophoricity problem. Also, these alloys have been stored for long periods in our glove box atmosphere without the slightest tendency to disintegrate.

With regard to the compatibility of the fuel alloy with the thermal bond, unalloyed uranium has such a small tendency to dissolve in or alloy with clean sodium or NaK that it is hardly measurable. Addition of plutonium and the fission-product elements to uranium does not appreciably change this picture. Numerous tests under a wide variety of conditions including long-time pile irradiations at elevated temperatures bear this out. (Practically all of ANL's irradiation tests use NaK as the thermal bond between the specimen and the container.) However, as in the case of unalloyed uranium, the sodium or NaK must be clean with respect to oxygen and probably other impurities. When present in small amounts, oxygen results in weight changes, and, when present in large amounts, spalling and cracking results.

(g) *Fabrication.* In the EBR-II reprocessing cycle, the pin fabrication technique requires very little of the fuel alloy in the way of mechanical properties. The alloy must be castable

and must possess sufficient strength and ductility to allow stripping the mold and subsequent handling operations. All the pertinent alloys, uranium-plutonium, uranium-5 wt. % fissium, uranium-20 wt. % plutonium-10 wt. % fissium, can be cast into molds. The binary uranium-plutonium alloys containing greater than 15 wt. % plutonium, however, the plutonium content is greater than 15 wt. % in the uranium-plutonium alloys, tend to crack even before they are removed from the mold. Uranium-plutonium alloys, when melted in MgO crucibles and cast, were not fabricable. Although this brittleness has been attributed to the zeta phase in this system, recent studies at ANL by Biver⁴² on arc-melted buttons show that all compositions from 5 to 50 wt. % can be hot pressed and that they have much less tendency to crack or powder on standing in the glove box helium atmosphere. The fissium alloys, both uranium-fissium and uranium-plutonium fissium, can be readily gravity cast into molds or injection cast into Vycor tubes. Saller et al.³⁹ consider the alloy to have low fluidity, and the work of Yaggee et al. on injection casting shows the alloy to have less fluidity than uranium.³² The melting range of the uranium-5 wt. % fissium is between 1002 and 1081°C as reported by Saller.³⁹ We have found that the solidus of uranium-10 wt. % fissium is 1000°C, and the solidus of uranium-20 wt. % plutonium-10 wt. % fissium is 930°C, which is about the same as the solidus of uranium-20 wt. % plutonium.

The uranium-5 wt. % fissium alloy can be hot rolled. The alloy was forged at 870°C as reported by Saller et al.³⁹ Yaggee rolled the cast material at 800°C (reference 32). Attempts to hot roll the uranium-plutonium and uranium-plutonium-fissium alloys failed even at 800°C. We have extruded the plutonium alloys (by an inverse extrusion method) at temperatures between 450 and 500°C. The billets were extruded bare with a 7 to 1 reduction at a pressure of 100,000 psi.

These alloys are somewhat harder than uranium. From 0 to 20 wt. % plutonium the hardness of the binary uranium-plutonium alloys increases from 59 R_A to 69 R_A. The hardness of the uranium-fissium and uranium-plutonium-fissium alloys in a range of 70 R_A to 75 R_A. As may be expected, the higher hardness of the fissium alloys makes machining more difficult. Carbide tipped tools and slow machining speeds are essential for any reasonable production. The presence of plutonium (to 15 wt. %), however, in uranium-plutonium alloys makes machining somewhat easier than unalloyed uranium even though the hardness is greater.

(h) *Thermal Expansion and Density.* For reactor safety reasons it is imperative that the thermal expansion of the EBR-II fuel alloy be positive and reliable on heating. The as cast uranium-plutonium-fissium and uranium-plutonium alloys behave dilatometrically about the same as cast unalloyed uranium. The thermal expansion of the cast uranium-20 wt. % plutonium-10.8 wt. % fissium and uranium-5 wt. % fissium alloys as a function of temperature are given in Fig. 17. The thermal expansion coefficients and room temperature densities for alloys pertinent to the EBR-II fuel alloy development are summarized in Table 6.

Table 6—THERMAL EXPANSION COEFFICIENTS AND DENSITIES OF CASTINGS

Alloy, wt. %	Thermal expansion		
	Temp. range, °C	Coeff., 10 ⁻⁶ /°C	Density (R.T.), g/cm ³
U-20 Pu-5.4 Fs	25-438	17.5	17.6
U-20 Pu-10.8 Fs	20-100	12.4	16.6
	20-500	15.2	
U-20 Pu-5 Mo	25-530	20	17.7
U-15 Pu	25-300	13	18.8
U-5 Fs (ref. 39)	20-100	13.7	17.95
	20-500	16	
U (ref. 9)	20-100	14.5	19.1
	20-500	18.5	

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(i) *Thermal Conductivity.* The heat-transfer performance of EBR-II must far exceed normal engineering practice. Therefore, in spite of the excellent heat-transfer characteristics of the liquid sodium coolant, the extremely poor thermal conductivity of the alloys under consideration is a matter of great concern. Addition of 10 wt. % plutonium to uranium lowers the thermal conductivity of uranium and additions of fission are expected to lower it further. Saller et al.³⁹ have shown that the thermal conductivity of uranium-5 wt. % fission at room temperature is about half that of unalloyed uranium. However, as shown in Fig. 18 and Table 7 the conductivity of the uranium-5 wt. % fission alloy increases more rapidly

Table 7 — COMPARISON OF THE THERMAL CONDUCTIVITY OF
URANIUM-5 WT. % FISSION WITH UNALLOYED URANIUM
cal/(cm²)(sec)(C)

Temp., °C	U-5 wt. % fission		Uranium ⁹
	BMI ³⁹	ANL	
20	0.026		0.066
100	0.034		0.068
200	0.044	0.040	0.069
300	0.053	0.048	0.074
400	0.062	0.056	0.081
500	0.071	0.063	0.088
600	0.080	0.071	0.096
700	0.088		0.105
800	0.097		0.115
900	0.125		0.127

with temperature than it does for uranium so that the difference is small at pile operating temperatures.

6 SUMMARY

Plutonium-239 is the favored fuel for fast neutron power-breeder reactors. However, its unattractive properties make it extremely unlikely that the unalloyed metal will find use as a fuel. Heat-transfer considerations and the limitations of normal fabrication methods suggest that the plutonium be diluted by alloying to make it usable in fast breeder reactors. The degree of dilution necessary makes plutonium the minor element, and therefore its undesirable properties no longer manifest themselves. However, the precautions necessary for safe handling of intense alpha emitters still apply.

EBR-I, a relatively small experimental reactor facility, has had two complete fuel loadings, and a third loading has been fabricated. All three loadings used U²³⁵ as the fuel. The first loading consisted of heat-treated wrought unalloyed uranium slugs, and the second consisted of centrifugally cast uranium-2 wt. % zirconium alloy slugs. For both of these loadings a column of short fuel slugs fit loosely into a stainless-steel jacket with liquid NaK as the thermal bond. An incident which resulted in partial melting of the second loading has led to a more rigid design for the third loading so as to prevent bowing of the fuel rods. It is made by coextrusion and consists of a uranium-wt. % zirconium core metallurgically bonded to a Zircaloy jacket.

EBR-II, a prototype fast power-breeder reactor, has a fuel element that is designed for high thermal performance and high burn-up. Long thin fuel pins fit loosely into a thin-walled tube with liquid sodium as the thermal bond. The simple design lends itself to a simple remote reprocessing cycle. EBR-II has been designed to receive a plutonium fuel at the earliest possible loading, and present plans are to fuel with plutonium the full size power-breeder reactor that will be developed from EBR-II's findings. A promising plutonium alloy is being

Fig. 17—Thermal expansion of uranium-5 wt. % fissium and uranium-20 wt. % plutonium-10.8 wt. % fissium alloys.

Fig. 18—Comparison of the thermal conductivity of the uranium-5 wt. % fissium with unalloyed uranium.

developed and appears to satisfy EBR-II fuel-element requirements. Because this element is still being tested, EBR-II will be fueled at first with U^{235} . The alloys that have been developed for EBR-II fuel elements result from a combination of reactor physics, reactor engineering, reprocessing, and metallurgical requirements. Diluting the fissionable material helps the heat-transfer problem, and, by using U^{238} as the diluent, some internal breeding is also achieved. The metallurgical refining process that is integral with the EBR-II does not remove certain fission-product elements (referred to as fission or Fs), and this determines to a considerable degree the fuel alloy composition. Some of these tend to stabilize the gamma phase of uranium and are therefore desirable alloying elements. The Pu^{239} alloy consists of uranium-20 wt. % plutonium-10 wt. % fission with about 20 wt. % U^{235} included because of the relatively small reactor core size; the full size power reactor will require less than 20 wt. % plutonium and no U^{235} . The non-plutonium first loading consists of a uranium-5 wt. % fission alloy with 49 per cent enrichment.

The uranium-plutonium-fission alloys that have been studied showed practically no irradiation damage effects and rate as the best uranium alloys ever studied at ANL. The uranium-5 wt. % fission alloy that will be used at first in EBR-II also behaves well under irradiation. In general the studies indicate that alloying to stabilize the gamma structure of uranium is effective in improving irradiation stability. These alloys also possess excellent thermal cycling stability; they can be remotely injection cast into long, small diameter pins; they resist attack by the liquid sodium thermal bond, and are compatible with the reprocessing cell environment; and they have reasonable thermal expansion characteristics. A limitation is that they are poor thermal conductors.

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Preparation and Sheathing of Plutonium-Aluminum Fuel Alloys for the NRX Reactor*

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ABSTRACT

Since 1952, several different types of ^{Pu-Al} plutonium-aluminum fuel rods have been fabricated for irradiation in the Chalk River NRX reactor. The first three elements each contained 350 g of ^{Pu} plutonium as cast ^{Pu-Al} plutonium-aluminum alloys, with an approximate sine-squared distribution of the plutonium along a 10-ft length. The next 23 elements were composite assemblies of a cast 20 wt. % ^{Pu-Al} plutonium-aluminum center section containing 180 g of ^{Pu} plutonium and two detachable ^{Al} aluminum-clad natural ^U uranium metal cylinders, each 3 ft long. The most recent design, in use since 1956, consists of a 10-ft-long stack of cast and machined ^{Al} aluminum-clad cylinders containing 265 g of ^{Pu} plutonium uniformly dispersed as a 3.7 wt. % ^{Pu-Al} plutonium-aluminum alloy. Ten rods of the latter type had been fabricated by October 1957.

Two alloy-preparation methods which eliminated the ^{Pu} plutonium metal production step were developed. Alloys for the first rod were made by reducing ^{PuF₃} plutonium-trifluoride with an ^{Al} aluminum excess at 900°C. A simpler technique, namely, the ^{Al} aluminum reduction of ^{PuO₂} plutonium-dioxide in the presence of cryolite, was used for all later fuel alloy preparations.

The methods of alloying, melting, casting, machining, fabrication, and testing are described, with particular emphasis on those currently in use at Chalk River.

1 INTRODUCTION

Early in 1951 a Canadian requirement arose for a plutonium-containing fuel element to enrich the NRX reactor and to supply, eventually, a source of plutonium rich in the higher isotopes for reactor-physics studies. Consequently, a program of plutonium alloy development was begun at Chalk River.

Since aluminum has a relatively low thermal-neutron absorption cross section and a well-established technology, it was chosen as the plutonium diluent. A proposed method for the fabrication of a plutonium-aluminum fuel rod was suggested by Carter et al.¹ in 1951. Plutonium metal was to be prepared on the 100-g scale by the bomb reduction of plutonium trifluoride with calcium chips. The resulting button was to be melted with aluminum and cast into an aluminum can. After casting in the alloy, an aluminum plug would be cast in one top so that a completely enclosed alloy could be removed from the glove box for sheathing.

Alloys are usually prepared, as was suggested for the above requirement, by adding the alloying constituents as metals to the solvent melt. It is often possible, however, to introduce alloying elements as chemical compounds such as oxides or halides, provided such compounds are reduced by the solvent metal, M_1 , according to the reaction:

*This paper may also be identified as Report CRL-47.

The product metal M_2 alloys with metal M_1 , which is present in excess, and the product compound M_1X may be separated from the alloy by dissolution in a flux or by volatilization. The advantages to be gained in preparing plutonium-aluminum alloys by a technique which would eliminate the expensive steps of producing and manipulating the chemically reactive plutonium metal will be apparent.

2 ALLOY PREPARATION

2.1 Aluminum Reduction of Plutonium Trifluoride

If one considers the reaction

the free-energy change at 1500°K is

$$-\Delta F_{1500^\circ\text{K}} = -15 \text{ kcal} = RT \ln K$$

where K is the thermodynamic equilibrium constant for the reaction. If, as an approximation, it is assumed that aluminum and plutonium are present as pure metals, then

$$K_{1500^\circ\text{K}} = 6.6 \times 10^{-3} = \text{partial pressure of AlF}_3 \text{ gas, } P_{\text{AlF}_3}$$

and therefore the vapor pressure of AlF_3 at 1500°K is

$$P_{\text{AlF}_3} = 6.6 \times 10^{-3} \times 0.5 \text{ atm} = 2.5 \text{ mm Hg}$$

The reaction should be shifted further to the right if excess aluminum is present, owing to the added contribution of the free energy of solution of plutonium in liquid aluminum. It might be expected, therefore, that if plutonium trifluoride and aluminum were heated in vacuum so that the volatile aluminum trifluoride was continuously removed, a fluoride-free plutonium-aluminum alloy should be formed.

Initial experiments on the 100-mg plutonium scale with an excess of aluminum reductant indicated that the reaction rate was slow at 1000°C and reasonably rapid at 1100°C. In one experiment, for example, using the vacuum furnace shown in Fig. 1, 110 mg of plutonium trifluoride was converted to a 3.4 wt. % plutonium-aluminum alloy after 2 hr at 1100°C. The plutonium yield was 98 per cent.

When the weight of plutonium trifluoride was increased to above 200 mg, a violent evolution of gas and liquid metal occurred if the furnace temperature was raised rapidly to 1100°C. It was observed that the violent reaction could be avoided by preheating the charge at 900°C for 1 to 2 hr. An explanation for the latter phenomenon was not obtained until larger scale experiments were carried out in the furnace illustrated in Fig. 2, where the reactants could be observed during the heating period.

In the latter furnace, using charges containing 30 to 60 g of plutonium, it was found that at temperatures above 1000°C the reaction proceeded with the evolution of gaseous aluminum trifluoride. Below 1000°C, however, the evolved gas was aluminum monofluoride. It was observed in addition that the rate of reduction of plutonium trifluoride was five times more rapid at 900°C than at 1125°C. Thus all subsequent production of alloys for the first fuel rod was carried out by reducing plutonium trifluoride with an aluminum excess at 900°C. In the final stages of development the plutonium yield for the conversion of nitrate solution to alloy ingot averaged 98 per cent.

Fig. 1—Detail of small vacuum furnace.

PLUTONIUM-ALUMINUM FUEL ALLOYS FOR NRX

Fig. 2—Details of quartz-tube induction furnace.

2.2 Aluminum Reduction of Plutonium Dioxide

The aluminum reduction of plutonium dioxide should proceed spontaneously since for the reaction

$$-\Delta F_{1500^\circ\text{K}} = 42 \text{ kcal}$$

If excess aluminum is used, the equilibrium should be shifted further to the right because of the energy contribution from the alloying reaction.

Small-scale experiments, in which graphite crucibles containing 2 to 3 g of aluminum ingots covered with 100 mg of plutonium dioxide were heated in vacuum, indicated that the reaction proceeded at an undesirably slow rate. The best reduction efficiency obtained was 60 per cent after heating the reactants for 3 hr at 1100°C. The unreacted plutonium dioxide was present in pockets that were separated from the alloy by a barrier layer of aluminum oxide. It appeared that long heating times would be required to reduce the plutonium dioxide completely unless the barrier aluminum oxide film could be removed either mechanically or chemically during the alloying reaction.

A suitable method for the chemical removal of the aluminum oxide film was suggested by Saller's experiments² on the preparation of uranium-aluminum alloys. When Saller added a briquetted mixture of uranium oxide and cryolite, $3\text{NaF} \cdot \text{AlF}_3$, to liquid aluminum at 1100 to 1300°C, the alloy formed rapidly with an average uranium yield of 80 per cent. The product aluminum oxide had dissolved in the liquid cryolite which floated to the surface of the melt as a slag layer.

The results of the first reductions of 60-g amounts of plutonium dioxide were encouraging, i.e., plutonium yields were >99 per cent. Thus it was decided to construct a new extension housing a laboratory of dimensions 25 by 50 ft for the express purpose of preparing plutonium fuel alloys for NRX rods by the oxide-reduction route. The glove-box line, illustrated in Fig. 3, went active in late 1953 and has been in continuous use since that time.

The first 100 alloy ingots containing a total of 6 kg of plutonium were prepared by adding a compressed mixture of plutonium dioxide and cryolite in small aluminum cans to molten aluminum at 1100 to 1200°C. Later alloys have been produced by adding a powdered plutonium dioxide-cryolite mixture to a cold graphite crucible, followed by the aluminum ingot and a covering layer of cryolite, and then heating the crucible in air for 15 min at 1200°C. Once the induction furnace is turned off, the crucible cools rapidly. Within 10 min, both the cryolite and alloy layers solidify. When the crucible is cold, it is broken by a hammer blow, and the slag-free alloy ingot is removed. The ingot may then be remelted and cast into the desired shape.

A series of chemical analyses on dissolved slags, acid-leached crucibles, and alloy samples has indicated that the plutonium yield during the routine production of 3.7 wt. % plutonium-aluminum alloy ingots containing 30 g of plutonium is a consistent 99.5 per cent.

3 EARLY FUEL-ROD DESIGNS

Alloys for the first three fuel rods were cast directly into water-cooled aluminum cans similar to the one shown in Fig. 4. After an aluminum plug had been cast on top of the alloy and then machined out to the bottom of the threads, 11 cans were screwed together to form an element 10 ft long. Since the surface of the can could be easily decontaminated and since the outer diameter was the same as that of the uranium metal used in NRX, 1.36 in., a standard three-finned aluminum sheath could be drawn over the assembly using existing equipment in an open shop. Standard end-closure techniques and end fittings could also be used. The alloy composition was varied from 0.5 wt. % plutonium in the two end cans to 20 wt. % in the center three to approximate a sine-squared distribution of the 350 g of plutonium along the length.

Once the first three rods had operated satisfactorily in the reactor, the reactor physicists decided to optimize the rod design by replacing the dilute alloys on the ends of the assembly

PLUTONIUM-ALUMINUM FUEL ALLOYS FOR NRX

Fig. 3—Glove-box line for preparation of plutonium-aluminum alloys.

Fig. 4—Aluminum casting can with trial aluminum pour.

Fig. 5—Details of end pieces for plutonium-aluminum fuel rod.

with unenriched uranium metal. Thus a composite rod was evolved which was made up of a 20 wt. % plutonium-aluminum center section, containing 180 g of plutonium, and two detachable aluminum-clad uranium metal cylinders 1.36 in. in diameter, each 3 ft long. The center section was prepared in a manner similar to that described above, i.e., by casting the alloy in threaded cans, screwing three together, and drawing a sheath over the assembly. Twenty-three elements, or about 4 kg of plutonium, were prepared for irradiation as composite assemblies.

The irradiation experience with the composite fuel rods was not so favorable as with the full-length alloy rods. Although the first three rods were irradiated without difficulty to plutonium burn-ups of 55 to 60 per cent in the center, i.e., 1.5 per cent of the total atoms, many of the composite rods showed mechanical deformation after only a few months of service. In July 1955 one of the elements failed, damaging the reactor. The failure was attributed to inadequate cooling following entry of water into the finned sheath and a buildup of steam pressure sufficiently high to lift the sheath out of contact with the casting can.³ Subsequently the alloy temperature rose, and eventually the molten alloy penetrated the casting can, the inner and outer sheaths, and the reactor vessel wall.

4 PRESENT FUEL-ROD DESIGN

As a result of the accident just referred to, the following changes were made in the fuel-element design:

1. The aluminum-aluminum interface between the casting can and the finned sheath was removed; the machined alloy slugs are now loaded directly into the sheath.
2. The diameter of the fuel slug was increased to 1.360 in., the same as NRX uranium metal rods.
3. A limit of 600,000 Btu/sq ft/hr was placed on the heat flux at the sheath-coolant interface, which imposes a limit of 0.92 g per centimeter of fuel length, about 3.75 wt. %, on the plutonium concentration of the alloy.

The fuel element now in use consists of a stack of 12 plutonium-aluminum alloy cylinders, 9.022 ± 0.005 in. long and 1.360 ± 0.002 in. in diameter, plus two aluminum end pieces encased in a finned aluminum sheath 0.080 in. thick. The end pieces are drilled deeper than the threading to provide a reservoir for helium gas, and the outer end fittings are vented as shown in Fig. 5. A complete element is shown in Fig. 6.

Fabrication of such a rod involved the development of new techniques of casting, machining, assembly, and testing, since bare alloys rather than enclosed ones were to be handled. The methods that have been developed are described below.

5 PRESENT FABRICATION TECHNIQUE

5.1 Preparation of Alloy Slugs

(a) *Preparation of Alloy.* The alloy is prepared by the method already mentioned in part, i.e., plutonium received as nitric acid solution is precipitated as oxalate, the precipitate is dried and calcined at 650°C to form oxide, and the oxide is reduced with aluminum in the presence of cryolite and sufficient excess aluminum to produce an alloy of the required composition. The precipitation and calcination steps are carried out in batches containing up to 200 g of plutonium. A separate reduction is done for each alloy slug required. To produce enough 3.7 per cent alloy for one slug, 28 g of plutonium as oxide and 758 g of high-purity aluminum are used. The reduction billets weigh about 780 g and contain approximately 27.8 g of plutonium. The remaining 200 mg is lost to the slag and crucible.

(b) *Melting and Casting.* The reduction billets are induction-melted in graphite crucibles in air. No flux cover is used.

The molten alloy is heated to 850°C, stirred thoroughly, and poured into a heavy-walled (4 in. O.D. by 1.43 in. I.D. by 14 in. deep) graphite mold tilted about 30 deg from the vertical. The use of tilted molds avoids blow holes due to gases entrapped by splashing metal during the early stages of pouring.

A sample is poured into a small graphite mold immediately before the casting is poured. This sampling method yields a representative sample and minimizes analytical inaccuracies caused by segregation when samples are cut from the solid castings.

The castings are 12 in. long and 1.41 in. in diameter, with about 2.5 in. of pipe. They weigh 765 g and contain approximately 27.2 g of plutonium. Loss as oxide during melting is, therefore, about 2 per cent. Longitudinal segregation is responsible for a maximum variation of 5 per cent in the plutonium concentration from the top to the bottom of the castings. Some inverse segregation of plutonium at the surface of the castings has also been noted. The reasons for the latter type of segregation and methods of preventing it are now being studied.

(c) *Finishing.* The cast slugs are machined to the diameter of 1.360 ± 0.002 in. The resulting surface is free of visible porosity. The piped ends are then cut off, and the slugs are finished to the length of 9.022 ± 0.005 in. using a slitting saw set up in the chuck of the lathe.

Fig. 6—Completed fuel rod.

Fig. 7—Plutonium-aluminum alloys being loaded into an aluminum sheath.

Initially, carbon tetrachloride was used as a coolant in the machining operations. Recently, however, satisfactory machining techniques have been developed using a jet of compressed air as coolant and a lubricating coating of graphite on the slitting saw.

The finished slugs weigh 595.0 ± 1.0 g and contain approximately 21.7 g of plutonium. About 3.5 g of plutonium is contained in the piped end cap cut from the casting, and the remaining 2 g is in the machine cuttings. The finished slugs are cleaned with carbon tetrachloride, weighed, and removed from the glove-box line into sealed polythene envelopes.

Each slug is subjected to radiographic examination before use, and any showing porosity or internal piping are remelted.

The piped ends are later remelted. Lathe cuttings and melting drosses, however, are chemically processed to recover their plutonium content.

(d) *Plutonium Recovery.* The over-all plutonium recovery, from nitrate solution to finished slug, has averaged about 77 per cent. Approximately 13 per cent is contained in the end cap and is recovered by remelting. Hence the plutonium recovery without chemical processing is 90 per cent. Approximately 7 per cent contained in lathe cuttings and 2 per cent in melting drosses are recovered by chemical processing. The remaining 1 per cent, representing dusting losses and losses to crucible and slag during reduction, is not economically recoverable.

5.2 Assembly of Fuel Elements

(a) *Preparation of Sheaths.* Finned aluminum NRX fuel-element sheaths 1.410 in. in inner diameter with walls 0.080 in. thick are used. The sheaths are received from the manufacturer with one end drawn down for easy gripping in the draw-bench carriage. For use with plutonium alloys, this end is further drawn down, flattened, and sealed by welding. The integrity of the sheath and end weld is checked by a helium leak test before use.

(b) *Loading of Sheaths.* The finished slugs, in polythene envelopes, and the inner end pieces are placed in a fume hood having filtered exhaust. The open end of the sheath is introduced into the fume hood through a hole cut in one end, with the sheath supported on a long bench as shown in Fig. 7.

The bottom end piece is first placed in the sheath. The polythene envelopes are then cut open, and the 12 alloy slugs are inserted into the sheath, followed by the top end piece.

During these operations, continuous air samples are taken. To date, no evidence of contamination has been discovered. Contamination of the tools used in loading is also very slight, indicating almost complete absence of loose particles on the surface of the alloy slugs.

The inside of the open end of the sheath is decontaminated, and a one-hole rubber stopper containing a length of copper tubing connected to a vacuum valve is inserted.

(c) *Vacuum Baking.* The assembly is removed from the fume hood to an oven, and the vacuum valve is connected to a roughing pump with filtered exhaust. It is then evacuated, heated to 160°C, held at this temperature for 4 hr, and allowed to cool to room temperature under vacuum. This operation is carried out to remove adsorbed water from the inner surfaces of the element.

Air samples taken during the operation have failed to show any contamination, and none has been found on the exhaust filter of the vacuum pump.

(d) *Drawing.* The assembly is removed from the oven and returned to the fume hood, where the vacuum connection is removed and a felt plug is inserted. The plug consists of three disks of $\frac{3}{8}$ -in.-thick felt, slightly larger than the inner diameter of the sheath and held together by a $\frac{1}{2}$ -in. bolt and nut. It acts as a wiper as the sheath elongates during drawing and prevents escape of contamination.

The assembly is then taken to a draw bench in an open shop and pulled through a die which draws the sheath down into close contact with the slugs. During drawing, it is necessary to exert pressure on the stack of slugs to prevent gaps from forming between them as they pass through the die. An effort was made to use a hydraulic jack running on a track mounted behind the die for this purpose. The jack was attached to the trailing end of the sheath so as to follow

during drawing. However, it was found that, with both ends of the sheath held rigidly and with pressure applied to the slugs, even very slight misalignment of the fins with the die apertures, or slight curvature of the fins, caused serious damage to the sheath. In three cases out of eight, damage was sufficient to necessitate desheathing and reassembly of the element.

Although this difficulty could probably have been overcome by modification of the equipment, it proved simpler to have pressure exerted by a strong man against a stout stick, e.g., a broom handle, inserted into the end of the sheath and bearing against the felt plug mentioned above. This method, although primitive, has been successful. During drawing, the sheath elongates about 18 in., and the wall thickness remains essentially unchanged.

Continuous air samples are taken during the operation, but neither these nor swipes taken on the equipment used have revealed any contamination.

(e) *Finishing and Testing.* After drawing, the element is again placed in the fume hood, and the ends of the sheath are cut off, leaving about $\frac{1}{2}$ in. of metal protruding beyond each end piece. The insides of the ends are decontaminated, and the element is removed to the regular machine shop.

The element is placed in a lathe, the ends of the sheath are faced off, leaving $\frac{3}{16}$ in. protruding beyond each end piece, and this metal is spun down over the end pieces. The outer end fittings are then screwed into place and welded (see Fig. 5). The integrity of the welds is checked by taping a polythene sleeve securely over the element, covering both welds, pressurizing the sleeve with helium to about $\frac{1}{2}$ lb above atmospheric pressure, and evacuating through the vents shown in Fig. 5 and a mass-spectrometer leak detector. The vents are then sealed by welding.

The element is subjected to a further leak test before being accepted for irradiation in the reactor. This test is carried out by suspending the element in a 4-in.-diameter Pyrex column, which is then filled with ethylene glycol and evacuated. Any leaks present are indicated by bubbles rising through the liquid.

6 FUEL-ROD REQUIREMENTS

A firm requirement exists for 24 fuel rods containing 6 kg of plutonium for the NRX reactor. Thus far, 10 rods of the newest design have been fabricated, eight of which are now being irradiated. The remaining 14 will be fabricated during the next 6 months.

It is anticipated that 3 kg of fresh plutonium will be added to the NRX reactor each year as plutonium-aluminum alloys. During the next few years, therefore, a significant quantity of highly irradiated plutonium will be generated. As an interesting by-product, an appreciable number of elements should become available for detailed postirradiation studies.

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Plutonium-Aluminum Fuel-element Development*

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ABSTRACT

Techniques and facilities for handling ^{Pu}plutonium at several laboratories in the U. S. are described. Hazards involved in the handling of fissionable and highly toxic material are discussed, and the procedures used to guarantee the safety of laboratory personnel are described.

The tentative ~~aluminum-plutonium~~ ^{Pu}phase diagram prepared by Los Alamos for compositions ranging from 50 to 100 at. % ~~aluminum~~ ^{Pu}is presented. This system is similar to the ~~aluminum-uranium~~ ^{Pu}system; the alloys, however, have a greater tendency to segregate upon casting. A eutectic is formed at 1.7 at. % ~~plutonium~~ ^{Pu}, and no solid solubility of ~~plutonium~~ ^{Pu} in ~~aluminum~~ ^{Pu} is observed.

A brief description of the Plutonium Recycle Program at Hanford and their experience and future plans with the use of ~~aluminum-plutonium~~ ^{Pu}alloys as reactor fuel materials are reported.

~~Aluminum-plutonium~~ ^{Pu}fuel-element experience at the Chalk River Project in Canada, as well as the fabrication of the "napkin" rings by Los Alamos and Argonne, and the fabrication of ~~Materials-Testing-Reactor~~ ^{MTR} type fuel assemblies containing ~~aluminum-plutonium~~ ^{Pu}alloys by Los Alamos and the Oak Ridge ~~National Laboratory~~ ^{ORNL} are also discussed.

From the limited amount of irradiation experience that has been gained with this fuel material, there has been no indication of dimensional instability, and there have been no indications of unsatisfactory performance caused by reactor irradiation.

Even though the health hazard associated with ^{Pu}plutonium makes its handling more difficult, safe and economically feasible solutions to fuel-element fabrication problems do exist. Further developments on the utilization of ~~plutonium~~ ^{Pu} as a reactor fuel material will increase the world supply of fissionable material and contribute to the peaceful application of nuclear energy throughout the world.

1 INTRODUCTION

Plutonium is a by-product of almost all nuclear power reactors owing to the transformation of the fertile isotope of uranium, U^{238} , to plutonium by neutron absorption. Some of the plutonium is fissioned, *in situ*, to add its energy to that of the U^{235} ; however, even in the most efficient reactor, much of the plutonium that is generated is discharged unburned in the spent fuel elements. As more and more power reactors come into operation, increasing amounts of plutonium will become available, and the incentive for its use as a nuclear reactor fuel will become greater. The high average yield of approximately 3 neutrons/ Pu^{239} fission makes the use of plutonium particularly attractive as a fuel for power breeder reactors. Breeding, as a reactor fuel cycle, would extend the world's supply of fissionable material.

The ability to use plutonium as a reactor fuel material will have a profound effect upon the entire power reactor economy. Developments in the field of plutonium fuel-element technology

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will have direct application to all enriched reactors and especially to fast reactors in which there is a special incentive to use plutonium as a fuel.

To date there has been only limited experience with plutonium or its alloys as a reactor fuel material, and the alloys have not been in the composition range that is of immediate interest to power reactor designers. In general, engineering heat-transfer requirements in power reactors preclude the use of fuel elements with high plutonium concentrations; therefore dilute alloys of plutonium are presently of prime interest. However, a low-melting alloy of high plutonium concentration to serve as the fuel in a homogeneous power reactor is now being studied at Los Alamos.

The two plutonium systems that have received the most attention for use as reactor fuel elements are dilute plutonium alloys with aluminum and with uranium. Recently the thorium-plutonium system has been considered as a reactor fuel material. In addition to these metal fuel systems, a mixed-oxide fuel element consisting of UO_2 and PuO_2 is being developed at Knolls Atomic Power Laboratory (KAPL) for a fast breeder cycle.^{1,2} Most of the studies on plutonium fuel elements in the U. S. are being conducted at Los Alamos Scientific Laboratory (LASL), Argonne National Laboratory (ANL), and Hanford Atomic Products Operation. A considerable amount of work on aluminum-plutonium alloys as a reactor fuel material has been performed at the Chalk River Project in Canada. Much of the work performed in both countries has been very similar and, in some cases, has been a joint effort.

This paper is a résumé of the completed work or work that is planned in the near future on the application of aluminum-plutonium alloys as reactor fuel materials in the U. S. It will be restricted to a discussion of alloy compositions up to 20 at. % plutonium.

2 HANDLING OF PLUTONIUM

A discussion of plutonium-containing fuel elements would be incomplete without a brief description of the precautions that must be observed and the equipment that is used in handling the metal and its alloys. Plutonium is a fissionable material, and it is a long-lived alpha emitter; hence its handling involves problems of criticality and health hazards.

All fissionable materials have a certain critical mass owing to neutron multiplication. The critical mass of plutonium is smaller than that of other fissionable materials, and extra care must be taken to prevent the accumulation of an excessive amount in any one place. The exact amount in any given instance, however, depends upon the particular conditions, and each situation must be individually analyzed. The small amounts of material involved in research and development work usually do not create a criticality problem, except in the storage of the metal. The fabrication of plutonium alloy fuel elements for reactor loadings, however, would require that the possibility of accumulating a critical mass in any fabrication procedure be under constant consideration.

The hazard of primary concern in the handling of plutonium is the health hazard because it is relatively independent of the quantities of plutonium involved. The health hazard is the consequence of the fact that plutonium is a long-lived alpha emitter with a half life of 24,300 years. The alpha particles have an energy of 5.15 mev and a range of 3.68 cm in air. Their average range in body tissue is about 45 μ ; consequently, they cause severe body damage to a localized area immediately surrounding the point of plutonium deposition. Every precaution must be taken to prevent the entry of plutonium into the body.

When plutonium is taken into the body, it is primarily deposited in bones and excreted very slowly. The current maximum permissible body burden of plutonium fixed in bone matter has been set at 0.04 μc or about 0.5 μg . At Hanford a person is not permitted to work with plutonium or a biologically similar isotope when his body burden is judged to exceed one-fifth the maximum permissible limit. The body burden is checked periodically by a determination of the plutonium content in the urine, based on an average urinary excretion rate of 0.01 per cent/day. To guard against inhalation of plutonium, continuous air samples are taken in all potentially contaminated areas and are counted daily. The maximum permissible concentration of plutonium in the atmosphere has been set at 2×10^{-12} mc/cm³.

Plutonium is normally thought of as being only an alpha emitter; however, it is usually a mixture of isotopes, and there is always some associated low-energy gamma and X radiation. Handling times must therefore be kept to a minimum in order to prevent excessive hand exposures. These radiations are determined by the previous history of the metal and up to now have not created a serious problem. In the future, however, when it becomes necessary to work with long-exposure plutonium from power reactors, the activity of the material may require shielding and remote manipulations.

In general, all plutonium-handling equipment is housed in sealed glove boxes that are constantly maintained at a slightly negative pressure so that any leakage would be into the box and not into the laboratory. Exhaust from these hoods is thoroughly filtered, and the plutonium concentration in the exhaust air is maintained at less than 2×10^{-12} mc/cm³. Operations are normally performed through long gauntlet gloves that are sealed to the box. Plutonium and plutonium-containing alloys and materials are always protected during handling outside the hooded enclosures.

Plutonium metal oxidizes rapidly in air, and the rate is accelerated in the presence of moisture. Plutonium metal in finely divided form is pyrophoric and creates a serious contamination potential when ignition and burning occur. Also some plutonium compounds and many of its alloys are more pyrophoric than the pure metal. Fortunately the aluminum-plutonium alloys are not pyrophoric, and, in the composition range of less than 25 at. % plutonium, they have very good corrosion resistance in air for extended periods of time. The rate of oxidation increases with increasing plutonium content, but it is not excessive in any instance, and no indication of pyrophoricity has been observed in alloys containing as much as 50 at. % plutonium.

2.1 Plutonium Facilities at Hanford

Plutonium-handling practices at the different laboratories may differ in detail, but they are all based on similar principles, and all are directed toward the safety of the operating personnel. At Hanford most pieces of equipment are located in individual rooms, and, when more than one major item of equipment is located in a single room, each is isolated from the other by a contamination barrier or compartment. Through past experience compartmentation has been found very advantageous in eliminating the spread of contamination and the amount of cleanup effort required in the event of a serious contamination incident.

Glove boxes for handling plutonium have three general types of atmosphere control: The first type of glove-box-atmosphere control is a dynamic system in which room air flows into the box through filters. The box, of course, is always maintained at a slightly negative pressure so that any leakage will not be into the laboratory. Air locks as well as techniques involving diathermally sealed vinyl bags are used to transfer materials in and out of the boxes. This type of hood atmosphere control is commonly used for operations in which the formation of surface oxides is not important and there is no danger of fires. Such operations may include weighing, billet preparation, room-temperature physical-property testing, and room-temperature mechanical working. The tendency at Hanford, however, has been to eliminate this type of hood atmosphere control and its associated operating limitations altogether and use static inert-atmosphere types of enclosures exclusively.

The second type employs controlled static atmospheres of either helium or argon. The hood construction is essentially the same as that of the dynamic-air atmosphere hoods; however, extreme care is taken to obtain an enclosure that is as free of leaks as possible. The control system is different in that there is no continuous flow of gas through the hood and the pressure is controlled at slightly less than atmospheric. After the outside door of an air lock has been opened to the room, the air lock is thoroughly flushed with the inert gas before the inner door is opened. The purity of the hood atmosphere is maintained by flushing; no gas-purification systems, with the exception of drying units, have been used to date. Inert-atmosphere hoods are required in operations where it is necessary to reduce the amount of surface oxide where pyrophoric materials are handled or where testing or mechanical working is performed at elevated temperatures.

The third type of atmosphere control box is a vacuum tank type of container that can be evacuated to exclude the air. The evacuated container is backfilled with a purified inert atmosphere to slightly less than atmospheric pressure for operation. The glove ports are covered with plates during evacuation to prevent the gloves from being sucked in, and unused glove ports are protected to prevent the inleakage of air and water vapor. This type of container is used where operations that require extreme atmosphere purity are performed or where quality control is an important consideration. An atmosphere of higher purity can be achieved and maintained by evacuating and backfilling than one obtained simply by flushing. Welding of reactive materials and fuel-element end closures are good examples where this type of enclosure is required. Operations in which plutonium is heated to high temperatures, such as melting and casting, are conducted in the best vacuums attainable. Additional plutonium fuel-element fabrication equipment is being installed for the fabrication of the aluminum-plutonium fuel elements for the Plutonium Recycle Program Reactor (PRPR) which will be described below. This equipment will be hooded where necessary, and runouts will be provided to permit handling 10-ft-long fuel-element sections. Figures 1 to 9 are photographs of typical hooded facilities at Hanford.

A plutonium fuel-element-fabrication pilot plant is being designed for construction and will be used in support of the over-all plutonium fuel-element program and the Plutonium Recycle Program. This facility will contain full-scale fuel-element-fabrication equipment enclosed in inert-atmosphere and vacuum type inert-atmosphere containers. The design of the facility and the equipment therein will be as versatile as possible to cope with the pilot-plant fabrication of any type of plutonium-containing fuel element that may be conceived. Such a facility will play an important role in the advancement of plutonium fuel-element technology.

2.2 Plutonium Facilities at Los Alamos

LASL, having been in operation since 1943, has far more experience with plutonium than any other laboratory in the U. S. The original work with plutonium in the U. S. was conducted at Los Alamos, and the scientists there have pioneered the field of plutonium technology in this country.³ The first work with plutonium was performed at Los Alamos during the war years when very little was known about the hazards involved in handling the material. Fortunately no known injuries to personnel resulted, and a great deal has been learned about safe handling procedures since that time.

Plutonium-handling procedures used at Los Alamos differ slightly from those used at Hanford and ANL. Los Alamos has found that complete gastightness of the glove boxes is not essential for adequate health protection. Most of the glove-box operations are performed in air atmospheres, and, in fact, very few operations are performed in glove boxes with inert atmospheres. Inert atmospheres are used in certain operations where there is a potential fire hazard, such as finely divided metal or plutonium hydride; however, the main purpose of the inert atmosphere is not to prevent corrosion of the material but to maintain the oxygen content concentration below the point at which it will support combustion.

2.3 Plutonium Facilities at Argonne

The plutonium laboratory at Argonne is a research facility and has been used to good advantage for this purpose since operations³ began in 1954. All the glove boxes are housed in one laboratory room and, in general, are interconnected into a single closed system so that a specimen once introduced into the system can be taken anywhere within the boxes without removal into the laboratory. Great care was taken in the design and construction of the Argonne glove boxes to ensure complete gastightness, even to the sensitive mass spectrometer test. A purified inert helium atmosphere is used in all the glove boxes and is continuously recirculated and purified to guarantee the best possible atmospheric purity. Potentially contaminated auxiliary equipment such as vacuum systems are housed within contamination barriers to eliminate the possible spread of contamination during maintenance operations. The physical size of the glove boxes is kept as small as possible to permit easy access to all its parts and also to keep the size of the gas-purification system to a minimum.

PLUTONIUM-ALUMINUM FUEL-ELEMENT DEVELOPMENT

Fig. 1—Vacuum melting furnace (15 kva).

Fig. 2—Rolling mill (4 in.) and hood.

Fig. 3—Metallography hood line.

Fig. 4—Balance, 20,000-lb testing machine, and 10-in. lathe hoods.

PLUTONIUM-ALUMINUM FUEL-ELEMENT DEVELOPMENT

Fig. 5—Vacuum melting furnace (15 kva) and hood line.

Fig. 6—Tensile machine (440,000 lb) and removable hood.

Fig. 8—Vacuum induction melting furnace (30 kw).

Fig. 7—Air tracer lathe (20 in.).

PLUTONIUM-ALUMINUM FUEL-ELEMENT DEVELOPMENT

Fig. 9—Vacuum welding box.

Argonne is constructing a plutonium fuel-element fabrication facility that will be used for the fabrication of the fuel elements for the Experimental Breeder Reactor (EBR).⁴

3 PLUTONIUM-FUELED REACTORS

3.1 Present and Future Reactors

The first reactor to operate with metallic plutonium fuel elements in the U. S. was the Clementine fast reactor at LASL. This reactor,⁵ which went critical in November 1946, was a fast reactor and operated at a power of 25 kw. The fuel elements were 6-in.-long rods of pure plutonium cased in mild steel and spaced with clad rods of natural uranium. Clementine operated at full power in March 1949 until a ruptured uranium spacer contaminated the mercury coolant in March 1950. After repairs it operated until December 1952, when a fuel element ruptured; it was dismantled in 1953. Since that time no reactors have actually operated with complete loadings of plutonium alloy fuel elements.

A low-melting high-plutonium alloy is being developed as the fuel for a homogeneous power reactor at Los Alamos.⁶ The alloy is a eutectic composition of plutonium-9.5 at. % iron and melts at 410°C; it will be used in the Los Alamos Molten Plutonium Reactor Experiment. The molten fuel will be contained in a tantalum container. The thermal power output of the reactor will be 1 Mw.

ANL is working on a U²³⁸-plutonium alloy that will be used as the fuel material in EBR-II, which is scheduled for start-up in 1958. This will be a fast heterogeneous reactor with outputs of 62.5 Mw (heat) and 15 Mw (electrical).

The Atomic Power Development Associates, Inc., are actively investigating and working on the application of plutonium as a fast breeder reactor fuel material. It is apparent that, even though the fields of plutonium-fueled reactors and plutonium fuel-element technology are in infancy, more and more interest is being generated in the use of plutonium as a reactor fuel, and it is inevitable that these programs will be accelerated.

3.2 Plutonium Recycle Program at Hanford

A Plutonium Recycle Program has been initiated at Hanford to demonstrate that power-producing reactors can be designed to operate with natural or depleted uranium fuel, which generates its own plutonium enrichment.⁷ After initial enrichment with Pu²³⁹ or U²³⁵, the reactor can produce sufficient plutonium that, upon reprocessing, can be used as a source of enrichment for the second cycle. Repeated cycles of this type can be continued indefinitely without further additions of enrichment to the system. This differs from those systems that use U²³⁵ enrichment from an expensive isotope-separation plant and dispose of the plutonium generated in some other fashion.

The broad objective of this program is the development of safe, economical methods of using plutonium fuels in power reactors. A necessary part of the program means the demonstration of the plutonium recycle concept through the design, construction, and operation of an experimental reactor and its associated plutonium fabrication and separation facilities.

The PRPR will be a vertical pressure tube type that is heavy water cooled and moderated with a thermal power rating of 70 Mw generated in 85 tubes. The reactor core and shielding are shown in Fig. 10. Initially the reactor will be fueled with uranium fuel elements and plutonium-containing fuel elements as the spike enrichment. It should be kept in mind that the reactor is an experimental tool and that, to evaluate the recycle concept most effectively, many different fuel-element types and loading combinations will be tried before the optimum combination will be achieved. The initial loading will consist of UO₂ in the form of a nested tubular fuel element as shown in Fig. 11, and the plutonium spike enrichment will be provided in the form of aluminum-plutonium alloy rods, 1/2 in. in diameter by about 9 ft long, canned in Zircaloy, and assembled into 19-rod clusters, as shown in Fig. 12. The aluminum-plutonium alloy was chosen as the fuel material for the initial operation of the PRPR because of the similarity of the aluminum-uranium and aluminum-plutonium systems. Irradiation data on the alumi-

Fig. 10—Reactor core and shielding.

Cross Section of Fuel Element in Process Tube

Fig. 11 — UO₂ nested tubular fuel element.

Fig. 12—Plutonium-aluminum 19-rod-cluster fuel element.

num-uranium system are expected to be directly applicable to the aluminum-plutonium system. Also it is felt that the aluminum-plutonium fuel material could be most easily fabricated with the present equipment.

4 ALUMINUM-PLUTONIUM ALLOY SYSTEM

A tentative aluminum-plutonium phase diagram⁸ as shown in Fig. 13 was worked out by LASL and reported in 1950. On the basis of the incomplete data reported in LA-1000, the following tentative suggestions are made concerning features of the equilibrium diagram of the aluminum-plutonium system:

1. Essentially zero solid solubility of plutonium in aluminum at all temperatures.
2. A eutectic composition of 98.3 at. % aluminum. The eutectic temperature is 647°C, and the two phases involved are pure aluminum and an intermediate phase.
3. An intermediate phase of complex crystal structure in the composition range PuAl_4 .
4. A second intermediate phase of complex crystal structure corresponding to PuAl_3 , which may react peritectically to form the intermediate phase in the range of PuAl_4 .
5. A third intermediate phase corresponding to the formula PuAl_2 , which may react peritectically to form PuAl_3 . The structure of PuAl_2 has been established as cubic of the Cu_2Mg type and is isomorphous with UAl_2 , with a value for a_0 of 7.820 Å.
6. A fourth intermediate phase that exists in the region of PuAl . It appears to have a crystal structure distorted from cubic, possibly tetragonal, with an axial ratio of 0.98.

There is a similarity between the aluminum-plutonium binary system and the aluminum-uranium system, at least on the aluminum-rich side of the diagram. Aluminum-plutonium intermetallic compounds, PuAl_2 , PuAl_3 , and PuAl_4 , have been prepared at the Chalk River Project in Canada, and the crystal structures were determined as a first step in the quantitative determination of the aluminum-plutonium binary system.⁹ PuAl_2 is reported to be face-centered cubic and isomorphous with that of UAl_2 . The crystal structure of PuAl_3 proved to be more complex than the simple cubic UAl_3 .

The work that has been done on fuel elements using these alloys is generally concerned with two phase structures between aluminum and PuAl_4 compound and mostly around the eutectic composition. Since the solid solubility of plutonium in aluminum is essentially nil, the plutonium will be tied up as the compound PuAl_4 which will be dispersed in a matrix of primary crystals of pure aluminum or in the eutectic mixture. This is an ideal dispersion type fuel material in which the fissile phase, PuAl_4 , is dispersed in a continuous matrix of nonfissile material (in this case aluminum, which predominates volumetrically and exists as a continuous matrix surrounding the fissile phase). The aluminum acts as the structural material in the fuel element because the PuAl_4 is extremely hard and brittle and of little value structurally. Also aluminum has a very low thermal-neutron absorption cross section. The object of a dispersion type fuel material is to concentrate the damage in the dispersed phase and in a highly localized region surrounding the dispersed fissile particle. Hence this type of fuel material provides a region free of fission products around the damage zone, and the reactor stability of some of these dispersion type fuels has been proved satisfactory.

Alloys containing up to about the eutectic composition of plutonium are easily cast, but great care must be taken to avoid segregation and shrinkage cavities. Even though the phase diagram is very similar to the aluminum-uranium system, the tendency to segregate is much greater for the aluminum-plutonium alloys, as found by recent work at Los Alamos. Alloys containing up to the eutectic composition can be cold rolled as much as 96 per cent without serious cracking and without need for intermediate annealing. However, as greater amounts of plutonium are introduced, the tendency for edge cracking becomes quite prevalent. Alloys in this composition range machine well, even better than pure aluminum.

The rule of mixtures should apply for determining the thermal conductivity of the two-phase aluminum-plutonium alloys containing from 80 to 100 at. % aluminum, since the solid solubility of plutonium in aluminum is essentially nil and the conductivity of PuAl_4 is very low

PLUTONIUM-ALUMINUM FUEL-ELEMENT DEVELOPMENT

Fig. 13—Tentative phase diagram of the plutonium-aluminum system (LA-1000).

compared to that of aluminum. In effect, PuAl_4 can be considered as voids in a matrix of aluminum whose conductivity is about equivalent to pure aluminum.

5 PREPARATION OF ALUMINUM-PLUTONIUM ALLOYS

The small-scale preparation of aluminum-plutonium alloys by the reduction of plutonium oxide or plutonium trifluoride in aluminum has been reported by Runnalls¹⁰ at the Chalk River Project in Canada. Aluminum-plutonium alloys were prepared by reducing PuO_2 and PuF_3 with liquid aluminum at 1100°C in a vacuum. The PuO_2 reaction is retarded by the formation of an Al_2O_3 barrier, whereas in the PuF_3 reaction the product aluminum fluorides sublime from the reduction zone and the reduction rate of PuF_3 is, therefore, more rapid. A fuel rod containing 337 g of plutonium was prepared for the Canadian National Research Experimental Reactor (NRX) by reducing PuF_3 with liquid aluminum in a vacuum.¹¹ The process was developed to the state where the over-all plutonium yield from the starting $\text{Pu}(\text{NO}_3)_4$ solution to the finished alloy was 95 per cent.

The technique of using cryolite to dissolve the product aluminum oxide and thus accelerate the rate of the reduction reaction was first used by Saller¹² in the preparation of uranium-aluminum alloys and was later adopted by Runnalls for the production of an experimental NRX fuel rod. Work has been done at Hanford to study the reduction of plutonium oxide by aluminum using the cryolite technique and to evaluate this process as a means of preparing aluminum-plutonium fuel material for the PRPR.¹³

Lyon reported that the reduction of plutonium oxide with aluminum using a cryolite flux should find application in the preparation of aluminum-plutonium spike fuel material for the PRPR. Losses encountered in the batch-reduction process are low (~ 0.2 per cent), and over-all costs should compare quite favorably with the alternative method which requires plutonium metal. Preparation of a master alloy, followed by dilution with aluminum or aluminum-silicon during remelting and casting of the fuel element, is the recommended procedure. The process has been successfully demonstrated on a semicontinuous basis wherein additions of aluminum and oxide and withdrawals of alloy product and waste cryolite were made with the reaction crucible held continuously at 1050 to 1080°C . A semicontinuous cell wherein the by-product aluminum oxide is reduced electrolytically has been investigated and appears to be a means of circumventing the disposal or recovery of spent cryolite and crucibles.

A more common method of forming the alloy is the addition of metallic plutonium to aluminum and melting and casting in vacuum or inert atmosphere. This procedure has been used at Los Alamos, Argonne, and at Hanford in the preparation of aluminum-plutonium fuel materials.

Recently at Hanford aluminum-plutonium alloy fuel materials have been prepared by making metallic plutonium additions to a bath of molten aluminum contained in an open type pot furnace. The plutonium is protected from oxidation by being submerged in the molten aluminum, and any oxide on the surface of the plutonium is reduced by the aluminum. This method has proved very successful and eliminates the need for a vacuum type furnace.

The effects of gravity segregation of the dense PuAl_4 phase have been minimized by such techniques as casting into water-cooled copper molds and by careful adjustment of pouring rates and temperatures. Twelve-inch long sections of $\frac{1}{2}$ -in.-diameter rods (1.8, 10, and 15 wt. % plutonium in aluminum) have been cast into graphite molds at Hanford with a minimum of segregation and shrinkage cavities. The segregation problem becomes more acute as the plutonium concentration of the alloy is increased, and carefully controlled directional solidification is necessary to eliminate piping and other shrinkage cavities.

6 ALUMINUM-PLUTONIUM FUEL-ELEMENT EXPERIENCE

6.1 Work at Hanford

The work on aluminum-plutonium fuel elements at Hanford has been and will be in support of the Plutonium Recycle Program. As mentioned above the spike enrichment required for

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PRPR operation will be in the form of 19-rod clusters of aluminum-plutonium alloy fuel rods about $\frac{1}{2}$ in. in diameter and 8 ft long canned in Zircaloy cans. There will not be any bond between the can and the fuel material, whose nominal composition is aluminum-1.65 wt. % plutonium. The differential coefficients of thermal expansion of Zircaloy and aluminum will be relied upon to provide physical contact and hence a heat-transfer path under operating conditions. Techniques and methods of producing the spike enrichment of aluminum-plutonium fuel elements for the initial operation of the PRPR are being developed. These efforts include thermal cycling experiments, billet casting techniques, canning and welding methods, fuel-element testing techniques, and cluster engineering. A reactor loading for the PRPR consists of about 25 19-rod clusters of aluminum-plutonium. Fuel-element-fabrication techniques that appear promising from the standpoint of simplicity and reduced fuel-element costs are being investigated. These investigations include pressure and vacuum-injection casting directly into the cans, swaging, roll cladding, and cryolite reduction techniques, etc. Another important activity is the in-pile testing and evaluation of aluminum-plutonium fuel materials and fuel elements in cold and high-temperature water.

(a) *PCTR Test Assemblies.* About 64 ft of aluminum-plutonium alloy fuel elements were fabricated and used for Physical Constants Test Reactor (PCTR) lattice physics tests in conjunction with the Plutonium Recycle Program.¹⁴ The tests conducted with these fuel elements are an important step in obtaining needed information concerning the economic feasibility of plutonium recycle and other problems related to the PRPR, such as lattice and fuel-element parameters.

The fuel material was an alloy of aluminum-1.8 wt. % plutonium about $\frac{1}{2}$ in. in diameter and of various lengths. Some of the bare fuel rods are shown in Fig. 14. Eighteen outer buffer assembly rods were 34 in. long and canned in aluminum jackets with a 0.030-in. wall thickness.

Fig. 14—Plutonium-aluminum fuel rods ($\frac{1}{2}$ in. diameter).

Six end buffer assembly rods were 8.25 in. long and canned in aluminum. Three 16.25-in.-long test assembly rods were canned in aluminum, and three were canned in Zircaloy. The test assembly rods were made in two sections to allow for the insertion and removal of the flux monitoring disks for counting purposes.

The aluminum-plutonium alloy fuel rods were formed by casting from a master alloy into a graphite mold and then were machined to size. Master aluminum-plutonium alloys of 15 wt. % plutonium were prepared to eliminate the necessity of handling small quantities of plutonium when the dilute or 1.8 wt. % plutonium alloys were prepared. The master alloy castings were also made in graphite molds. The fuel rods were vacuum cast 12 in. long and eight at a

time; however, a considerable amount of difficulty was caused by the formation of internal shrinkage voids. A tapered mold and the experimental determination of the proper pour and mold temperatures reduced the formation of these internal voids to a minimum. The mean plutonium composition of the rods was 1.794 wt. % plutonium with an average maximum and minimum of 1.818 at the bottom of the castings and 1.789 at the tops of the castings. Analysis of variance applied to the analytical results indicated that there was a 2 per cent variation from the mean composition, which was within the physics specifications. No significant variations in composition across the diameter of the fuel rods were found. The problem of vertical segregation due to the settling of the more dense PuAl_4 phase may become more serious when larger castings are made.

All the rod castings were radiographed prior to machining to determine whether or not there were any internal shrinkage voids. Some voids were present, but these were reduced to a minimum by these improved casting techniques. Machining properties of the alloy were similar to those of 2S aluminum, and rods were easily machined to the proper diameter and length. The fuel material was then inserted into the tubes, and the final closure was made by welding end caps in place. To prevent radioactive weld inclusions, the lip of the can opening was protected during assembly by a brass bushing that fitted in the end of the can. The final welds were made in front of a high-velocity open-front hood.

A specimen of one of the aluminum-plutonium fuel rods with a freshly machined surface and untouched by gloves in the lathe hood was easily cleaned with alcohol in an open-front hood so that no smearable contamination could be detected on any surface of the sample. This simple experiment indicates favorable possibilities for future handling of this plutonium-bearing alloy.

Sound end closures were necessary to decrease the possibility of alpha-contamination spread and the inleakage of heavy water in the test reactor. Each closure was, therefore, visually inspected and carefully examined in a bubble tester.

(b) *Irradiation Specimens.* Aluminum-plutonium alloy fuel elements are presently being considered as the spike enrichment for use in the initial operation of the PRPR. The aluminum-plutonium alloy is being planned for initial reactor operation because it can be quite easily fabricated; at the present time it appears to hold the most promise of satisfactory reactor performance. Additional experience in irradiating aluminum-plutonium alloys is needed, along with proof of their radiation stability. Actually there has been a very limited amount of plutonium fuel-element experience, especially to the burn-ups anticipated in the PRPR (50 to 60 per cent burn-up of the plutonium atoms), and the performance of any particular type of fuel element can ultimately be determined only by actual reactor exposure.

One $\frac{1}{2}$ -in.-diameter 2-in.-long aluminum-plutonium capsule canned in a 0.030-in.-thick Zircaloy jacket has been irradiated in the MTR to 20 per cent burn-up of the plutonium atoms, and a similar capsule of aluminum-plutonium-silicon alloy has been successfully irradiated to a similar burn-up. One of the zirconium capsules is shown in Fig. 15. Two other capsules are being irradiated to 50 to 60 per cent burn-up of the plutonium atoms. This experiment is the first in a series of irradiation experiments to be conducted.

Because of the lack of proper sized tubing, the capsule jacketing components were machined from a solid rod of reactor-grade Zircaloy-2. The base closure on the tubes was conducted in a vacuum type welding chamber that had been evacuated to a pressure of 25 to 50 μ and backfilled with purified helium. These welds were then leak checked with a helium leak detector to ensure the integrity of the cans before any plutonium-containing fuel materials were inserted.

The techniques used in casting the MTR irradiation specimens were essentially the same as the techniques used for the PCTR test pieces. A master alloy of 15 wt. % plutonium was diluted to cast cores with nominal compositions of aluminum-1.64 wt. % plutonium and aluminum-12 wt. % silicon-1.61 wt. % plutonium in graphite molds. It was desired to obtain irradiation experience on the latter alloy because it has been reported that silicon additions enhance the corrosion resistance of this material.

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Fig. 15—Irradiated Zircaloy capsule containing plutonium-aluminum ($\frac{1}{2}$ in. diameter, $2\frac{1}{2}$ in. long).

Fig. 16—Aluminum-1.65 wt. % plutonium alloy capsule after 20 per cent burn-up of the plutonium atoms ($\frac{1}{2}$ in. diameter, 2 in. long).

Difficulties were encountered with the usual casting defects such as pipes, blow holes, and cold shuts. Cold shuts were eliminated by heating the mold prior to pouring; the piping problem was minimized by promoting directional solidification. Vacuum outgassing of the mold prior to casting reduced the number of blow holes. Vertical segregation was reduced to a minimum by careful control of mold temperatures and was held to a 2 per cent variation from the mean composition along the length of the rod.

All castings were subjected to radiographic examination and then machined to final dimensions in a hooded lathe. Assembly of the capsules was similar to the assembly of the PCTR pieces, and the same preventative measures were taken to eliminate radioactive welds and contaminated external surfaces. There was no bond, either mechanical or metallurgical, between the fuel material and its jacket; in fact there was a 0.003-in. gap (at room temperature) to allow for differential thermal expansion and accommodate the growth of the fuel material. There will be intimate surface-to-surface contact between the fuel material and its jacket at operating temperatures to provide a heat-transfer path.

A welding station was built in an open-front hood, and the sample to be welded was purged with an inert atmosphere and supported in a rotating copper chill block. The fusion weld closure was produced by the d-c inert gas shielded arc process. Each capsule was subjected to a bubble test prior to autoclaving for 100 hr in 100 psi steam. No autoclave failures were detected.

Two of the capsules have completed their irradiation in the MTR and are being examined in the Hanford radiometallurgy facility. One of the uncanned specimens is shown in Fig. 16; however, complete examination results are not available at this time. The water-coolant temperature in the MTR is 45°C , and the irradiation data for these two capsules are given in Table 1. The large differences between the average and maximum values listed in the table for these 2-in.-long specimens are caused by the steep flux gradient in the reactor. A preliminary metallographic examination has been made of the aluminum-1.64 wt. % plutonium

Table 1—IRRADIATION DATA

	Capsule 5	Capsule 11
Composition, wt. %	Al-12 Si-1.61 Pu	Al-1.64 Pu
Thermal neutron flux, nv		
Average	1.39×10^{14}	1.02×10^{14}
Maximum	1.69×10^{14}	1.14×10^{14}
Fissionable material (Pu), g/in.	0.140	0.145
Calculated Values		
Core surface temp., °C		
Average	164	136
Maximum	190	145
Central core temp., °C		
Average	182	149
Maximum	212	160
Heat output, watts/in.		
Average	1165	872
Maximum	1416	975
Heat flux, Btu/hr/sq ft		
Average	324,000	242,000
Maximum	393,000	270,000
Specific power generation, kw/cu in.		
Average	5.90	4.42
Maximum	7.18	4.94
Specific power generation, kw/ft		
Average	14.0	10.5
Maximum	17.0	11.7
Fractional burnout (Pu atoms), %		
Average	15.4	19.1
Maximum	18.7	21.3

capsule, and no changes in the microstructure were detected. Rockwell H hardness values obtained for the aluminum-1.64 wt. % plutonium specimen before and after irradiation were 50 and 94, respectively. An examination of the decanned capsule cores does not indicate any dimensional changes or instability due to reactor irradiation to these levels of burn-up.

6.2 Work at Chalk River

The Canadians at the Chalk River Project have had a considerable amount of experience with aluminum-plutonium fuel elements.¹⁵ Aluminum-plutonium fuel rods have been used in the NRX reactor not only for reactor enrichment but also to provide plutonium richer in its higher isotopes. Fuel rods have been prepared by reducing PuO_2 and PuF_3 with aluminum and more recently by the reduction of PuO_2 with aluminum and cryolite to form aluminum-plutonium alloys of up to 20 wt. % Pu. The plutonium alloys were then cast directly into 1.0-in.-I.D. 1.36-in.-O.D. aluminum cans which were then sealed by pouring a cap of pure aluminum on top of the plutonium alloy. Eleven canned sections, when screwed together, form an assembly of proper fuel-rod dimensions, and this assembly is sheathed in a finned aluminum tube with welded end closures. The plutonium content was varied along the length of the fuel rods in a sine² fashion from a maximum concentration of 20 wt. % plutonium at the center to about 0.5 wt. % plutonium at the ends.

Several fuel rods of this type have been fabricated and irradiated in the NRX.¹⁶ One rod was successfully exposed to an average burn-up in the fuel rod of about 28 per cent of the

plutonium atoms (about 0.37 per cent of total atoms) and was removed from the reactor because it was no longer providing enrichment. Other fuel rods were exposed to slightly lesser amounts of irradiation with no deleterious effects occurring. Some irradiation difficulties were experienced but were not attributed to irradiation instability or unsatisfactory reactor performance of the aluminum-plutonium alloy fuel material.

6.3 Aluminum-Plutonium Alloy Irradiation Specimens Manufactured by Los Alamos and Argonne

Aluminum-10 wt. % plutonium and aluminum-5 wt. % plutonium alloy specimens were fabricated and irradiated in the MTR jointly by ANL and LASL. The fabrication techniques and the successful irradiation of these specimens which were used to obtain the first significant amounts of elements 99 and 100¹⁷ are pertinent to this discussion on aluminum-plutonium alloys as reactor fuel materials. The irradiation specimens have been called "napkin rings" because they were in the form of split cylinders $1\frac{1}{4}$ in. O.D. and 2 in. long with a total wall thickness of 60 mils. The specimens were fabricated by casting, rolling, and roll cladding the cores with 2S aluminum by the picture-frame technique. Forty-four such specimens were made containing 5 wt. % plutonium cores, and 47 of the specimens had 10 wt. % plutonium cores.

The castings were made by vacuum melting in 6-g melts into magnesium oxide crucibles forming buttons approximately $\frac{3}{4}$ in. in diameter and $\frac{3}{8}$ in. thick. The buttons were flattened to $\frac{1}{4}$ in. thickness and rolled at room temperature in a bullion mill to a thickness of 0.180 in. They were rolled to 0.085 in. thickness after vacuum annealing at 450°C. The plates were badly warped after rolling and had to be straightened. The cores were blanked in a die and assembled in a picture-frame sandwich that was sealed around its periphery by welding. They were then outgassed at 600°C and evacuated before the final closures were made. These composite sandwiches were bonded by rolling at 600°C and tested for blistering by exposure in a furnace at 600°C for 30 min. They were then trimmed to size, rolled into cylinders, and form annealed prior to irradiation.

No detailed irradiation performance data are available to the writer; however, it is known that no significant irradiation damage to the napkin rings was observed, even though essentially 100 per cent of the plutonium atoms were burned up in the experiment.

6.4 MTR Type Plates

Six full-sized MTR plate type fuel elements were fabricated using an aluminum-10 wt. % plutonium alloy instead of enriched uranium to obtain small quantities of the higher plutonium isotopes.¹⁸ The plutonium alloy cores were prepared at Los Alamos by melting, casting, rolling, and blanking.¹⁹ After the billets were assembled in the aluminum sandwich and sealed off, they were sent to Oak Ridge National Laboratory for rolling into fuel plates and assembly in the same manner as the standard MTR fuel elements.

The procedures used were essentially the same as those employed in the fabrication of the napkin rings, except that the geometries involved were different. The final fuel assembly consists of 19 fuel plates clad with aluminum, with a nominal 0.115-in. water gap between them, brazed into a pair of aluminum side or spacer plates.²⁰ Seventeen of the fuel-bearing plates are 0.050 in. thick, and the two outer plates are 0.065 in. thick to give added cladding thickness and structural integrity to the fuel component. The over-all assembly width is 2.996 in., and the assemblies are 24 in. long.

The aluminum-10 wt. % plutonium alloy is poured into a water-cooled copper mold, and, with careful control of pouring rate and temperature, an ingot having little or no segregation or shrinkage is obtained. The ingots are rolled to about 20 mils thicker than the final size at 550°C in a mill with rolls heated to 250°C. They are then cold rolled to final size and straightened and punched in a press. After thorough cleaning the billets are assembled and sealed in a picture-frame sandwich by welding. The assemblies are outgassed at 540°C in a furnace, and the final seal of the evacuated assembly is made by crimping off the vacuum tube. This sealing procedure eliminates any trapped gases that may cause blistering upon rolling. The

composite fuel assembly is hot rolled at 590°C in six separate passes to achieve a sound metallurgical bond between the cladding and core material. The fuel plates were then flux annealed to prevent the formation of blisters upon subsequent processing or reactor service before cold rolling to final thickness. They are then annealed at 590°C, inspected, and assembled into the final fuel-element assembly. The first group of aluminum-plutonium MTR type fuel elements was rejected for excessive dimensions and blistering. The fuel-element constitution and fabrication were reviewed, and a new aluminum-plutonium ratio and revised rolling technique have been suggested.²¹

Data on the irradiation performance of these fuel elements are not available to the writer at this time; however, a great deal of satisfactory irradiation performance has been experienced with this type of fuel element which contained an aluminum-U²³⁵ alloy core, and, as pointed out previously, the irradiation performance of aluminum-plutonium alloys should be similar.

7 CONCLUSIONS

A résumé of the published information on alloys of low plutonium and aluminum has been presented. The quantity of work that has been expended on an evaluation of these and other plutonium alloys for power reactor application is not consistent with the potentialities of plutonium as a reactor fuel material. Research and development efforts concerned with investigating the applicability of and furthering the use of plutonium as a power reactor fuel material are expanding at a rapid rate. Even though the health hazard associated with plutonium makes its handling more difficult, safe and economically feasible solutions to the handling and fuel-element fabrication problems do exist. The successful demonstration of plutonium as a power reactor fuel material will extend the world supply of fissionable material and make a major contribution to the peacetime application of nuclear energy throughout the world.

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