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PROGRESS RELATING TO CIVILIAN APPLICATIONS
DURING FEBRUARY, 1961

by

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REPORTS RELATING TO CIVILIAN APPLICATIONS
ISSUED DURING FEBRUARY, 1961

- BMI-1495 "Radiation-Induced Nitration of Hydrocarbons", by Mary J. Oestmann,
E. Jack Kahler, Garson A. Lutz, and John F. Kircher.
- BMI-1496 "Progress Relating to Civilian Applications During January, 1961", by
Russell W. Dayton and Clyde R. Tipton, Jr.

REACTOR MATERIALS AND COMPONENTS (AEC-DRD)

R. F. Dickerson

The general objective of the research tasks reported in this section is to provide basic structural material and component support to the over-all Atomic Energy Commission reactor development program. These studies are concerned with the effect of ultrahigh pressures and high temperatures on the structure of materials, the effect of irradiation on the mechanical properties of Type 347 stainless steel and Zircaloy-2, the development of high-strength niobium-base alloys for use in the EBR, the friction and wear of sliding surfaces in sodium environments, the determination of oxygen in sodium at concentrations below 10 ppm, and the development of a thermal-neutron flux-sensing device.

High-Pressure High-Temperature Solid-State Studies

W. B. Wilson and C. M. Schwartz

OBJECTIVE To determine if ultrahigh pressure can be utilized to produce new materials.

PROGRAM APPROACH The effects of pressure on reactions of uranium oxide with other oxides are currently under investigation. Emphasis, at present, is being placed on the study of reactions between U_3O_8 and Al_2O_3 .

PROGRESS REPORTED PREVIOUSLY The development and calibration of an apparatus capable of pressures above 150,000 atm and temperatures above 2000 C have been previously reported in BMI-1328. The apparatus has been employed to study the effects of pressure on the uranium-oxygen system.

The U_3O_8 - Al_2O_3 reaction is being studied. Two new compounds ("X" and "Y") are produced in this system under the combined influence of high temperature and pressure. The "Y" phase is a high-temperature product and little or no detailed study of this material has been undertaken to date. Recent work has been directed toward obtaining single crystals of the "X" phase to confirm earlier indexing of the powder patterns.

WORK THIS PERIOD Structural studies of two high-pressure phases have been undertaken. Single crystals of a reaction product between U_3O_8 and Al_2O_3 have been obtained for study. During the search for these crystals, a single crystal of gamma U_3O_8 , the high-pressure form of U_3O_8 , was obtained. This crystal has been mounted and oriented for structural analysis. Results will be discussed when available.

PLANS FOR FUTURE WORK Single-crystal studies of the two high-pressure phases will be continued.

Irradiation-Surveillance Program on Type 347 Stainless Steel

W. E. Murr, R. Lieberman, F. R. Shober, and R. F. Dickerson

OBJECTIVE To determine the effects of fast-neutron irradiation (neutrons having energies greater than 1 Mev) on the mechanical properties of AISI Type 347 stainless steel.

PROGRAM APPROACH Subsize tensile, cyclic-strain fatigue, and impact specimens of Type 347 stainless steels are being irradiated in core positions of the ETR. Evaluation of irradiation-induced changes will be based on results of mechanical tests made after exposures of about 0.5 to about 3.0×10^{22} nvt (fast). The information thus obtained will be used to predict safe operating life for loops in reactors constructed of this material.

PROGRESS REPORTED PREVIOUSLY The total accumulated fast-flux exposure for capsules currently operating in or removed from the ETR through Cycle 33 (December 14, 1960) was previously reported in BMI-1489. Test results from Charpy and subsize Izod specimens irradiated to exposures of about 5.7×10^{21} nvt and tested at room temperature and -300 F are reported in BMI-1448 (Rev.). A definite embrittlement was noted in the specimens, particularly in those tested at liquid-nitrogen temperatures.

WORK THIS PERIOD The four-hole filler piece containing ten stainless steel surveillance capsules was transferred intact from the G-13 to the I-13 position of the ETR at the end of Cycle 33. The I-13 position is located in the southwest corner of a 6 x 6 facility previously occupied by a Pratt & Whitney loop. At the present time, there are no plans to relocate the capsules from this position.

Cycle 34 was completed on February 14, 1961, after an accumulation of 3499 megawatt-days. The additional fast-flux exposure to specimens in the I-13 position during Cycle 34 will be reported after analysis of exposed dosimeter wires. The ETR is now operating in Cycle 35, which is scheduled to end on about March 6, 1961.

PLANS FOR FUTURE WORK Work will continue in an attempt to evaluate the use of iron wire for determining fast flux as a possible substitute for the nickel wire presently employed as dosimeters in the ETR. In nickel-wire dosimetry, Co^{58} which is produced through the reaction $\text{Ni}^{58} (n, p) \text{Co}^{58}$ is depleted by the reaction $\text{Co}^{58} (n, \gamma) \text{Co}^{59}$. A current experiment which uses cadmium-covered nickel wire to shield thermal neutrons will give information on the amount of Co^{58} depletion from the above reaction.

It was planned to discharge Capsule BMI-24-2, which contains six subsize tensile and six cyclic-strain fatigue specimens irradiated to exposures of about 7.1 to 7.6 x 10^{21} nvt, at the end of Cycle 33. This plan has since been abandoned. It is now planned to discharge a capsule containing tensile and fatigue specimens at an exposure of about 5.7×10^{21} nvt, which corresponds to the exposure level of the Charpy and Izod specimens previously tested. The remaining capsules will be discharged and specimens tested at exposures ranging from 1.0 to 3.0×10^{22} nvt.

Development of High-Strength Niobium-Base Alloys

J. A. De Mastry, F. R. Shober, and R. F. Dickerson

OBJECTIVE To develop high-strength niobium-base alloys which will be compatible with sodium and uranium-plutonium fuel for cladding applications at 800 to 1000 C in the EBR II.

PROGRAM APPROACH Additions of 2.37 w/o chromium, 3.34 w/o zirconium and 5.21 w/o vanadium were made to niobium. The effects of these additions on the hot and cold fabricability, the tensile and creep strength at 650, 800, and 1000 C, and the recrystallization temperature are being determined.

PROGRESS REPORTED PREVIOUSLY Ingots weighing 4 to 5 lb of each composition were consumably arc melted, forged to 0.50-in. -thick slabs at 540 C, and then rolled at room temperature to 0.030-in. -thick sheet.

The results and evaluation of tensile testing were reported in BMI-1469. Room-temperature hardness measurements of all three alloys after a 1-hr anneal at 1038 C indicated that stress relief had occurred. Higher annealing temperatures, >1038 C, did not reduce these hardnesses appreciably.

WORK THIS PERIOD The stresses to produce deformation rates of 0.001, 0.01, and 0.1 per cent per hr at 650, 800, and 1000 C are shown in Table A-1. On a weight percentage basis chromium is the most effective strengthener of the alloying additions being studied. All three alloys have creep strengths superior to that of unalloyed niobium.

Specimens of all three alloys being studied which were given a 1-hr anneal at 1038, 1149, and 1260 C were examined metallographically for evidence of recrystallization. There was no evidence of recrystallization in specimens heat treated at 1038 or 1149 C, while all three alloys appeared to be recrystallized after annealing at 1260 C. All three alloys were given a 1-hr anneal at 1200 C and are being prepared for metallographic examination.

TABLE A-1. STRESSES TO PRODUCE DEFORMATION RATES OF 0.001, 0.01, AND 0.1 PER CENT PER HR AT 650, 800, AND 1000 C IN THE BINARY NIOBIUM ALLOYS

Test Temperature, C	Alloy Addition (Balance Niobium), w/o	Stress to Produce Creep Rates Shown, psi		
		0.001 Per Cent Per Hr	0.01 Per Cent Per Hr	0.1 Per Cent Per Hr
650	2.37 Cr	47,800	53,000	58,000
	3.34 Zr	41,500	41,800	42,000
	5.21 V	52,800	59,000	63,800
800	2.37 Cr	33,600	37,000	40,500
	3.34 Zr	32,000	--	--
	5.21 V	40,000	43,000	46,000
1000	2.37 Cr	11,400	17,500	23,500
	3.34 Zr	9,000	14,700	20,400
	5.21 V	15,500	20,300	25,200

PLANS FOR FUTURE WORK Creep testing at 650 and 1000 C is completed, while testing is continuing at 800 C. All three alloys which were given a 1-hr anneal at 1200 C will be examined metallographically for extent of recrystallization.

Investigation of the Creep Properties of Zircaloy-2
During Irradiation at Elevated Temperatures

F. R. Shober, P. B. Shumaker, and A. P. Young

OBJECTIVE To compare the creep properties of Zircaloy-2 at 650 F in a fast flux of 1×10^{14} nv with those at 650 F in the absence of a fast flux and to study strain aging of Zircaloy-2 to elucidate the extent to which it may influence creep strength at 650 F.

PROGRAM APPROACH In-reactor and out-of-reactor creep experiments are planned in which total deformations of sheet specimens in 1000-hr creep tests will be compared. Total deformation will also be indicated during the test by a differential transformer, the output of which will be recorded. The effects of stress under these creep conditions will be investigated by incorporating three different widths in the gage section of the test specimens. The reactor portion of these tests is to be conducted at the WTR and the out-of-reactor part at Battelle. Evidences of strain aging are being investigated by means of short-time tensile tests and deformation studies performed at room and elevated temperatures.

PROGRESS REPORTED PREVIOUSLY An instrumented capsule, as described in BMI-1430, has been designed. The MgO which filled the annulus between the capsule wall and the cast aluminum blocks has been replaced by 15 equally spaced vertical copper tubes. These changes have been made to increase the thermal conductivity in this section. The capsule has been designed to combine gamma heating with electrical heating to maintain the designated specimen test temperature in a reactor position having a gamma-heating rate of approximately 14 w per g of aluminum.

Tensile tests made at room temperature and at 400, 450, 550, and 650 F as part of the strain-aging studies have shown a yield point after straining and aging at all test temperatures except room temperature and 400 F. These and other data pertaining to the strain-aging studies are reported in BMI-1448 (Rev.) and BMI-1445. A comparison of the deformation characteristics of Zircaloy-2 at room temperature and 650 F has been made using electron microscopy of thinned sections of previously deformed tensile samples.

WORK THIS PERIOD Preparations for the first in-pile experiment at the WTR were continued. Data received from the WTR early in February indicated that the core facility tentatively selected for the first in-pile-creep experiment of this program has a fast-neutron (energy level greater than 1 Mev) flux peak of approximately 1.5×10^{14} nv and a gamma flux peak which will generate approximately 9 w per g in aluminum. Since these levels are suitable for this irradiation, effort was directed toward inserting the first capsule for Cycle 11, which was scheduled to start about February 23.

Assembly of the capsule proceeded on schedule, but final high-pressure leak checking showed that one of the convolutions of the bellows loading assembly had failed. (Three previous leak checks of this unit during various stages of capsule assembly indicated no leaks.) The unit could not be repaired; replacement is now in progress.

Additional samples of thin-sheet Zircaloy-2 were tested at room temperature and 650 F to study deformation mechanisms. Sections were thinned for electron-microscopy transmission studies in an attempt to relate changes in mechanisms with test temperature. Striations previously noted in the initial specimens after deformation at room temperature were less apparent in this second set of samples. It was thought formerly that these striations were in some way related to the slip mechanism in Zircaloy-2. The second set does not substantiate the original findings.

The influence of strain aging on the mechanical properties of Zircaloy-2 at elevated temperatures was reviewed and possible mechanisms postulated. Research was planned which will attempt to define whether the strain-aging phenomenon is related to grain boundary or the matrix of polycrystalline Zircaloy-2.

PLANS FOR FUTURE WORK Assembly of the irradiation capsule after the bellows replacement is planned for completion about March 15, 1961. If no additional difficulties are encountered, installation of instrumentation and insertion of the capsule will be made shortly thereafter. A series of short-time tensile tests is planned to aid in a study of the yield point in Zircaloy-2. The effect of grain size and strain rate at two temperatures to study the role of grain boundaries in the yield-point phenomenon will be investigated. Various holding times of 5, 30, and 60 min at stresses within the proportional limit of Zircaloy-2 will be studied to investigate the effect of elastic deformation on the yield point. It is also planned to conduct several creep tests in an attempt to determine an activation energy for creep at temperatures above and below the temperature in which a yield point is observed. These are primarily studies of the effect already observed which may lead to an identification and understanding of the mechanism causing this observed effect.

Friction and Wear of Sliding Surfaces in Sodium Environments

W. A. Glaeser and J. W. Kissel

OBJECTIVE To develop general principles applicable to selection of materials and design of mechanical parts involving sliding surfaces in high-temperature molten sodium.

PROGRAM APPROACH The friction and wear behavior of various materials resistant to corrosion in liquid sodium is being studied by measuring the stick-slip friction characteristics of a ball sliding on a flat in liquid sodium and under a carefully controlled environment. Interpretation of stick-slip traces is supplemented by analysis of surface films formed during exposure to sliding in sodium.

PROGRESS REPORTED PREVIOUSLY The friction and wear behavior of molybdenum, tungsten, Inconel X, Stellite 3, tungsten carbide, and titanium carbide has been investigated, and in each case, except for the two carbides, improved operation resulted when sodium was present between the rubbing surfaces. In the case of molybdenum sliding against itself, the improved behavior has been definitely correlated with the presence of a Na_2MoO_4 film. It was subsequently shown that formation of this film is thermodynamically feasible under any of the variety of temperature-environment conditions which might prevail during friction experiments. Thermodynamic analyses, when applied to the components involved in the various friction tests, indicated a favorable tendency toward formation for Na_2WO_4 and Na_2CrO_4 , but a generally unfavorable tendency toward formation for Na_2CoO_3 and for Na_2C_2 . These analyses suggest that the reason sodium does not appear to influence friction of the carbide cermet is that there is no chemical reaction between the sodium and the cermet.

Mathematical analysis of the stick-slip friction traces, obtained during friction experiments, revealed that viscous action is occurring during sliding in liquid sodium. These methods were shown to provide a means of detecting changes in the viscous properties of the rubbing surfaces.

WORK THIS PERIOD Modifications to the slow-speed stick-slip apparatus were completed. These permit remote variation of the specimen loading and magnetic release of the upper specimen arm to provide a reproducible driving force for initiation of "slip" motion between the rubbing specimens. These devices will facilitate the detection and measurement of changes in the viscous effects which are present between specimens.

The design of equipment for carrying out simple friction and wear experiments between specimens rotated at medium speed and in high-purity flowing sodium was established. Construction of this device and of the associated sodium-purification loop is under way.

PLANS FOR FUTURE WORK Experimentation involving the stick-slip fraction apparatus as well as the studies of the composition and properties of surface films on particular specimen combinations are being temporarily suspended so that full effort may be directed toward early completion of the high-purity flowing-sodium experiments. The objectives of this program are to produce evidence supporting the contention that: (1) surface films can be formed in high-purity sodium systems, and (2) these films can be maintained in such systems. Realization of these objectives will establish the validity of applying results obtained via the stick-slip laboratory apparatus to actual large-scale sodium systems.

Development of Miniature Heating Elements for a Power-Balancing-Type Thermal-Neutron Flux Sensor

J. G. Buck, P. M. Steinback, D. R. Grieser,
and W. H. Goldthwaite

OBJECTIVE To develop miniature heating elements suitable for use in a power-balancing-type thermal-neutron flux sensor.

PROGRAM APPROACH Two distinct approaches are being used toward the development of a miniature heater. One is based on the fabrication of a film-conductance element and the other on a buried, sheathed-wire heater. The ultimate element is to be about 1/8 in. in diameter and 1/2 in. long, have a nominal resistance of approximately 100 ohms, and be capable of thermal cycling and sustained operation at a maximum temperature of 1500 F in a reactor-core radiation environment. The element must also contain a specific quantity of uranium in the range of 1 to 10 mg and a thermocouple junction.

PROGRESS REPORTED PREVIOUSLY Imbedded-Wire Element. A preliminary design was made based on commercial materials. Essential components were ordered and fabrication procedures outlined.

Film-Conductance Element. Preliminary studies of carbon and palladium films were made. Initial attempts to produce rugged electrical end contacts for use at 1500 F proved unsatisfactory.

WORK THIS PERIOD Imbedded-Wire Element. A discharge welding technique has been developed for making precisely spaced differential thermocouple junctions from 40-gage Chromel and Alumel wire. Differential thermocouple units have been fabricated by inserting the joined wire into 30-mil-OD alumina insulators, inserting this into 58-mil-OD stainless tubes, vacuum welding, and pressure bonding in helium at 10,000 psi and 2200 F for 3 hr. These compacted units will serve as a spine upon which to fabricate imbedded-wire elements. The 13-mil-OD sheathed Chromel P "heater" wire for these elements has not been received as yet.

Recent information leaves some doubt as to the reliability of using the Chromel P thermocouple alloys for a long-life heater wire at 1500 F. Consequently, some larger, but otherwise identical, sheathed wire is being run at the present time to determine whether a problem exists. Several other Chromel alloys having promise of longer high-temperature life are being experimentally examined as possible alternates in the event of failure of the Chromel P alloy.

Film-Conductance Element. The effort this period has been concentrated on the development of high-temperature end contacts. Two approaches have been studied. One involves the use of a titanium-nickel eutectic alloy and the other a molybdenum-manganese metallizing process.

In the titanium-nickel method, the alumina substrates are coated pyrolytically with carbon, the ends are coated with a thin nickel layer, titanium caps are forced over the nickel-coated ends of the ceramic rods, and then they are fired in very dry helium at 1832 F for 15 min. Firm bonding of the titanium caps is obtained by the formation of a titanium-nickel eutectic alloy at the bond interface and the penetration of titanium through the porous carbon layer to the alumina substrate. Wetting of the carbon film by the eutectic alloy should provide good electrical contact. Although four satisfactory elements have been produced by this technique, further work is indicated in order to avoid the erratic changes in film conductance which occur during the end-contact fabrication process.

Titanium caps have been bonded successfully to alumina substrates by metallizing the ends of the ceramic with molybdenum-manganese, nickel plating, pressing on the end caps, and helium firing at 1832 F, as with the titanium-nickel technique. Units of this type will be coated with palladium resinate to form conductive-film heaters.

PLANS FOR FUTURE WORK Imbedded-Wire Element. The pressure-bonded differential thermocouple units will be evaluated at elevated temperatures to determine stability. Evaluation of several Chromel alloys will be continued to determine their relative suitability as heater wires for extended life at 1500 F.

An investigation into the plausibility of making a satisfactory element with a bare heater wire will be made, since only the Chromel P alloy is immediately available as a miniature sheathed wire.

Film-Conductance Element. Both pyrolytic carbon and palladium-film elements will be fabricated with suitable end contacts, encapsulated in stainless steel enclosures, and evaluated at temperatures up to 1500 F.

Determination of Oxygen in Sodium at Concentrations Below 10 PPM

E. H. Hall, J. McCallum, and D. R. Grieser

OBJECTIVE To demonstrate the feasibility of a method for the determination of oxygen in sodium at concentrations below 10 ppm with a sensitivity of ± 1 ppm.

PROGRAM APPROACH Two approaches are presently being investigated - one is the application of a mass spectrometer, the other the technique of coulometry. The mass spectrometric method is described in BMI-1398 and the coulometric method in BMI-1469. Feasibility of these techniques for the detection of small quantities of sodium oxide in sodium is being sought.

PROGRESS REPORTED PREVIOUSLY Mass Spectrometry. Results from the HgO calibration runs indicated adequate instrument sensitivity; however, higher oven temperatures than previously obtainable would be required for Na₂O analyses.

Coulometry. Coulometric runs were obtained in sodium without breakdown of the anode film. Lack of duplication of results in replicate tests, however, left doubt as to the ability of this technique to detect oxygen.

WORK THIS PERIOD Mass Spectrometry. A new oven has been built for the purpose of attaining higher temperatures for the decomposition of residual Na₂O in the mass spectrometer. Some modifications of the original design were necessary to reduce heat losses. In the most recent check, the oven was heated to 800 C by radiation from a tungsten helix. A final modification has now been made, and check on heating by electron bombardment of the oven is being made at present.

Coulometry. Coulometric runs in sodium have been made this period in which samples of sodium were taken from the coulometric cell both before and after running. It was believed that a reduction of impurity content indicated by mercury amalgamation analyses would confirm the gettering capability of the coulometric technique, and would give an independent check of the gettering behavior derived from coulometric measurements. Analysis of the coulometric data from this run did suggest that gettering had occurred. The amalgamation data, however, were totally ambiguous, and therefore feasibility was not confirmed.

Analysis of sodium from the cell for elemental content other than sodium by arc spectrometry showed a calcium content of 200 ppm. The presence of this amount of highly active impurity might well explain the erratic behavior that has been noted in all of the coulometric experiments to date. Not only would the calcium reduce any sodium oxide present in the sodium but it would also destroy the aluminum oxide film on the probe. The integrity of this film is essential to the operation of the coulometer.

PLANS FOR FUTURE WORK Mass Spectrometry. After completion of the checkout on the new oven a sample of sodium plus a known amount of HgO will be placed in the oven. The added HgO will provide a known Na₂O concentration at a higher level than that available from the loop. The temperature required to decompose the residual Na₂O from this mixture will then be determined. Subsequently, additional sodium samples containing much less oxygen will be studied.

Coulometry. The results from all of the coulometric runs to date will be reviewed in the light of the recent sodium analysis in an effort to evaluate the potential of the coulometric technique for the measurement of low oxygen impurity levels in sodium.

STUDIES OF FUELS (AEC-DRD)

R. F. Dickerson

The development of new and the improvement of existing fuel materials require continued research effort. The research reported in this section is supported by the AEC Division of Reactor Development for the purpose of contributing to the technology of both existing and new fuel materials.

The work denoted to new materials is concerned with the development of niobium-base-uranium alloys for high-temperature applications, the study of plutonium-containing alloys and compounds as possible intermediate-temperature fuels of "spike" fuels for power reactors, and the development of uranium-containing thorium compounds for use in thermal breeder reactors.

As a contribution to the technology of existing fuel materials, one program under way has as its objective the establishment of an understanding of the important causes of fission-product release from refractory fuels while in another the irradiation behavior and phase stability of metastable beta-phase uranium alloys are being studied.

Development of Niobium-Uranium Alloys

J. A. DeMastry, D. P. Moak, A. A. Bauer, and R. F. Dickerson

OBJECTIVE To determine the fabrication characteristics, physical and mechanical properties, corrosion behavior, and irradiation stability of high-strength niobium-uranium alloys.

PROGRAM APPROACH The high-temperature strength characteristics of niobium-uranium alloys indicate that they may possess high-temperature irradiation stability. Niobium alloys containing additions of 10, 20, 30, and 50 w/o uranium are being studied to determine those properties of interest for potential application of the alloys as fuel materials. The properties of interest are fabricability, tensile strength, creep strength, physical properties, corrosion resistance in various selected media, and irradiation stability.

PROGRESS REPORTED PREVIOUSLY The initial phase of this investigation was reported in a topical report, BMI-1400. The results of physical-property studies were reported in BMI-1434 and BMI-1448. Planning and construction of capsules for irradiation tests have been completed and were reported in BMI-1464.

Difficulties in the fabrication of alloys containing 30 w/o or more uranium have been encountered. A program to prepare niobium-uranium alloy ingots with structures amenable to fabrication was conducted. Alloys containing 10, 20, 30, and 50 w/o uranium and a test ingot of unalloyed niobium were prepared by skull melting utilizing the consumable-electrode procedure.

WORK THIS PERIOD Slabs 2 by 2 by 1/2 in. of the skull-melted ingots of niobium-10 and -20 w/o uranium alloys were successfully reduced 85 per cent by rolling in air at 1000 F. The niobium-30 w/o uranium alloy showed edge cracking during rolling at 1000 F; however, after the rolling temperature was increased to 1850 F this alloy was reduced 80 per cent with no further difficulty. Fabrication of an alloy containing 50 per cent uranium was not successful at 1000 or 1850 F.

Creep and tensile specimens are being machined from the fabricated material described above. Chemical analyses of all skull-cast materials are in progress.

PLANS FOR FUTURE WORK The fabricability of the niobium-50 w/o uranium alloy will be investigated by rolling small slabs (2 by 1 by 1/2 in.) at 2000 to 2400 F. These slabs will be protected from oxidation during rolling by being enclosed in a molybdenum pack.

As soon as the specimens being machined are available, creep tests will be initiated. It is tentatively planned to establish the stresses necessary to produce creep rates of 0.1 and 0.001 per cent per hr at 1600 and 2000 F.

Irradiation studies of fuel pins will begin as soon as suitable reactor space is available.

Development of Uranium-Containing Thorium Compounds

M. S. Farkas, A. A. Bauer, and R. F. Dickerson

OBJECTIVE To investigate thorium and thorium-uranium compounds with the aim of developing high-temperature fuels for thermal breeder reactors and of determining those properties which will indicate the suitability of such compounds for various reactor applications.

PROGRAM APPROACH High-melting compounds having a high thorium (uranium) density and a low thermal-neutron cross section, namely, Th_2Al , ThBe_{13} , ThB_4 , ThC , ThC_2 , ThN , ThS , Th_3Si_2 , and ThSi and these same compounds with a 10 a/o addition of uranium, are being evaluated from the standpoint of preparation, corrosion resistance, and mechanical and physical properties.

PROGRESS REPORTED PREVIOUSLY Satisfactory cylindrical arc castings of Th_2Al , ThC , ThC_2 , Th_3Si_2 , and ThSi and these compounds with a 10 a/o uranium addition were obtained. Arc-melted buttons of the beryllides and borides were made; however, satisfactory arc-cast cylinders were not obtained. Density measurements showed that the castings produced were within 2 per cent of theoretical density. Dry-air and CO_2 oxidation tests at 1100 F showed that the borides and beryllides were particularly resistant to attack. Corrosion tests in 350 C Santowax indicated that the aluminides, beryllides, and dicarbides were the best performers in this medium. Water-corrosion tests at 90 C showed that the borides and beryllides were superior, though the aluminides and silicides had negligible weight losses, while the carbides reacted very rapidly. Oxidation and corrosion data were reported in BMI-1480, BMI-1489, and BMI-1496.

WORK THIS PERIOD Testing of the thorium and thorium-uranium compounds in 1200 F NaK is continuing.

Air-oxidation tests of the thorium-uranium monocarbides and dicarbides with additions of low-cross-section carbides were performed at 1100 F. The results, shown in Table B-1, indicate that very little, if any, improvement in oxidation resistance can be brought about by small additions of low-cross-section carbides. However, the addition of 5 mole per cent SiC to ThC-10 w/o UC does improve its oxidation resistance by a factor of two.

TABLE B-1. OXIDATION OF THORIUM-URANIUM CARBIDES AT 1100 F IN AIR

Nominal Compound Composition, mole per cent	Weight Gain in 1100 F Air, mg/(cm ²)(hr)
(Th ₉ U)C	6.4
ThC-10 UC-5 NbC	6.7
ThC-10 UC-5 SiC	3.2
ThC-10 UC-2.5 Mo ₂ C	8.7
ThC-10 UC-5 ZrC	4.3
(Th ₉ U)C ₂	3.5
ThC ₂ -10 UC ₂ -5 NbC	4.7
ThC ₂ -10 UC ₂ -5 SiC	3.7 ^(a)
ThC ₂ -10 UC ₂ -2.5 Mo ₂ C	3.4
ThC ₂ -10 UC ₂ -5 ZrC	3.7

(a) Average of two tests.

PLANS FOR FUTURE WORK Studies planned include determinations of thermal expansivity, thermal conductivity, and strength characteristics.

A Study of Plutonium-Containing Fuel Alloys

V. W. Storhok, A. A. Bauer, and R. F. Dickerson

OBJECTIVE To investigate those plutonium alloys which may have potential application as fuels for reactors operating at relatively high temperatures or as fuels for possible use as "spike" elements in power reactors.

PROGRAM APPROACH Plutonium-containing alloy systems have been selected for study on the basis of the behavior of similar uranium-alloy systems. The compositions selected are based on the niobium, thorium, uranium-molybdenum, and uranium-niobium alloy systems with plutonium. These systems are being studied at the plutonium-lean end. Initial evaluation is based on metallographic studies and hardness measurements. Those alloys exhibiting desirable phase distribution and evidence of strength on the basis of hardness measurements will be subjected to more detailed property studies.

PROGRESS REPORTED PREVIOUSLY As a result of unfavorable microstructures exhibited by binary niobium-plutonium alloys, it was decided that niobium-base alloys could be made useful only by tying up the plutonium as a compound or as a high-melting alloy phase (BMI-1469). A niobium-25.6 w/o plutonium-6.1 w/o silicon alloy (theoretically niobium-30 volume per cent PuSi_2) was found to consist of two phases (BMI-1489). Cast structures of niobium-10 w/o plutonium-10 and -30 w/o zirconium alloys were found to be three-phase. Two of the three phases were present at the grain boundaries (BMI-1496). A ternary thorium-10 w/o plutonium-10 w/o zirconium alloy was harder and more resistant to room-temperature oxidation than binary thorium-plutonium alloys containing 5 to 30 w/o plutonium (BMI-1489).

WORK THIS PERIOD On the basis of hardness tests, it appears that 90 per cent cold reduced thorium-5 and -10 w/o plutonium alloys completely recrystallize within 1 min at 700 C. The thorium-5 w/o plutonium alloy decreased from an as-rolled hardness of 117 DPH to 67 DPH after 1 min at 700 C. A thorium-10 w/o plutonium alloy similarly treated decreased in hardness from 135 to 73 DPH. No further changes in hardness accompanied longer annealing times.

X-ray diffraction studies tentatively show a niobium-25.6 w/o plutonium-6.1 w/o silicon alloy to consist of free niobium and Nb_5Si_3 . Further analysis is necessary to confirm this. These X-ray data generally agree with metallographic observations and hardness measurements, which showed a two-phase microstructure. One phase was very hard, as might be expected of a compound, while the matrix phase (niobium) was softer.

PLANS FOR FUTURE WORK Recrystallization studies of thorium-base alloys cold reduced 80 and 90 per cent will continue. Hardness tests and metallography will be employed to determine the degree of recrystallization. Thorium-base alloys will be examined to determine the effect of heat treatment on microstructure and hardness.

Depending on the results of X-ray diffraction analysis, niobium-10 w/o plutonium-10 and -30 w/o zirconium alloys will be heat treated in an effort to spheroidize what appears to be a plutonium-rich grain-boundary phase. Additional niobium-plutonium-silicon alloys will be prepared and investigated in an effort to more completely understand the phase relationships in the niobium-rich corner of the system and to provide a basis for selecting alloys for detailed study.

Compatibility of PuO_2

S. J. Paprocki, D. L. Keller, and W. M. Pardue

OBJECTIVE To study the compatibility of PuO_2 with various metallic and ceramic materials.

PROGRAM APPROACH Heat treatments of powder mixtures and abutted surfaces of PuO_2 with the material in question are being conducted. The appearance of new phases will be followed by X-ray diffraction measurements, metallographic examination, and changes in the physical appearance of the compacts.

PROGRESS REPORTED PREVIOUSLY A preliminary screening procedure using calculations of standard free energies to indicate metal-PuO₂ reactions is summarized in BMI-1455. The as-received PuO₂ particles average 9.4 μ in diameter. Ten volume per cent of an extraneous phase was tentatively identified as Pu₂O₃. An oxidation of the loose powder at 600 to 800 C eliminates this phase and increases the average particle diameter to 13.1 μ . Sintering in dry hydrogen or argon for 1-1/2 hr at 1700 C causes a chemical reduction or thermal decomposition to a lower oxide with melting of the pellets. Liquid-immersion density determinations and selective chemical dissolution tests indicate that the melted material is not PuO₂, but a lower oxide or the metal hydride. Sintering for 1-1/2 hr at 1600 C increases the density of PuO₂ from 60 to approximately 90 per cent of theoretical. On the basis of preliminary runs, MgO appears to be the most suitable container material for PuO₂ at 1700 C.

WORK THIS PERIOD X-ray diffraction techniques showed the material previously melted in dry hydrogen at 1700 C has a hexagonal structure with lattice constants in the ratio of $c/a = 1.55$. This is in excellent agreement with the 1.551 ratio reported for Pu₂O₃.

Results of recent experiments have been most helpful in understanding the behavior of PuO₂ at high temperatures in both hydrogen and argon atmospheres. A series of PuO₂ pellets compacted from as-received powder (powder containing 10 to 15 volume per cent Pu₂O₃) and sintered in hydrogen for 1.5 hr at 1600 C were quite sound after heat treating with no signs of melting. Identical PuO₂ pellets sintered in argon for 3.5 hr at 1700 C became quite dense (95 per cent of theoretical) and also showed no signs of melting.

These results should be compared with results of previous experiments in which PuO₂ pellets that were sintered in hydrogen at 1700 C completely melted, and those pellets sintered in argon at the same temperature, although structurally erect, showed definite signs of partial melting.

In a hydrogen atmosphere at a temperature of 1727 C, it has been calculated, from available thermodynamic data, that a moisture content of approximately 1 per cent (+42 F dewpoint) would be required to prevent the continuous reduction of PuO₂ in a flowing atmosphere. At significantly lower moisture contents, it is predicted that the PuO₂ would be reduced to Pu₂O₃ (but not to metal) which would in turn melt at the temperature involved. This is essentially what did occur in the initial hydrogen-sintering experiments, and the melted material, which has a hexagonal structure, must certainly be Pu₂O₃. At a lower temperature, 1527 C, in hydrogen a moisture content of less than 0.09 per cent (-5 F dewpoint) would be expected to promote reduction of PuO₂. However, at the lower temperatures, visual observation of the reaction rate would be significantly slower because of the lower temperatures, the formation of a solid rather than liquid reaction product, and the weak driving force resulting from the same difference in the equilibrium water content and that maintained in the influent hydrogen atmosphere.

With regard to the apparently conflicting results obtained in argon, the explanation must lie with the performance of the 10 to 15 volume per cent of Pu₂O₃ contained in the presintered pellets. Since the flowing argon gas used in these experiments contains a small quantity of moisture and oxygen, it becomes a question, at the higher temperatures, of whether the Pu₂O₃ will melt before it is oxidized to PuO₂. In initial experiments where melting did occur, the specimens were heated quite rapidly to 1700 C in

argon which had been passed through a drying train. However, in more recent experiments, the pellets were held overnight at 1000 C in argon which was not dried prior to use, providing ample time for the Pu_2O_3 to be oxidized to PuO_2 . Therefore, no melting was observed on subsequent heating to 1700 C, well above the apparent melting point of Pu_2O_3 .

In view of all evidence, it is concluded that melting is caused by the prior existence of Pu_2O_3 in argon or the reduction of PuO_2 to Pu_2O_3 in dry hydrogen sintering atmospheres.

Compatibility determinations were performed for PuO_2 pellets which were completely encased in cold-pressed metal powders. The metals used were Types 304, 316, 318, and 347 stainless steels as well as Inconel. Heat treatments were 2 hr at either 1900 or 2000 F in hydrogen. The compacts appeared sound visually, no reaction zones were noted in as-polished metallographic specimens, and X-ray diffraction examination of the PuO_2 after sintering detected only the face-centered-cubic structure in all cases.

PLANS FOR FUTURE WORK The compatibility of PuO_2 with several refractory metals such as tungsten and molybdenum and with MgO and Al_2O_3 will be examined.

Fission-Product Release from Refractory Fuels

J. B. Melehan, S. D. Beck, and F. A. Rough

OBJECTIVE To establish an understanding of the important causes of fission-product release during irradiation of refractory fuels, starting with uranium dioxide, and to obtain engineering information which will aid in the design of fuel elements utilizing these fuels.

PROGRAM APPROACH The principal effort is devoted to the study of the continuous release of fission products during irradiation. This work is supported by studies concerned with characterization of the materials and postirradiation diffusion measurements.

PROGRESS REPORTED PREVIOUSLY A UO_2 irradiation program recently conducted has yielded information on fission-gas release rates at temperatures up to 1800 F. It was possible to relate the microstructural characteristics of sintered and fused single-crystal UO_2 to gas-release behavior in terms of a surface-induced release caused by passage of fission recoils. Thus, in these tests, gas release was independent of temperature through the surfaces up to 1800 F but was noticeably affected by changes in specimen-surface area.

WORK THIS PERIOD Theoretical analysis of the several release mechanisms was continued with applications to sintered and dense releasing bodies of several different geometries. A relation given below has been developed to describe in-pile steady-state release rate from a dense body of plate geometry by simultaneous operation of the diffusion and recoil mechanisms:

$$\frac{R+Q}{B} = \frac{\nu}{4} + \frac{\sinh \sqrt{\mu}}{2\sqrt{\mu} \cosh \sqrt{\mu}} + \frac{1}{2\nu\mu} \frac{(1 - \cosh (1-\nu)\sqrt{\mu})}{\cosh \sqrt{\mu}},$$

where

R = diffusion release rate per unit volume

Q = recoil release rate per unit volume

B = production rate of the released species per unit volume

$$\nu = \frac{\epsilon}{a}$$

ϵ = recoil range

a = half-thickness of plate

$$\mu = \frac{\lambda a^2}{D}$$

λ = radioactive decay constant

D = diffusion coefficient.

In preparation for future fission-gas-release experiments, modifications were begun on the beam-tube furnace to extend its capability to above 3000 F. The effort will consist of developing a satisfactory electrical insulation for the furnace induction coil and evaluation of changes in furnace geometry for improved thermal and electrical efficiency and material stability.

PLANS FOR FUTURE WORK Studies to improve the high-temperature reliability of the beam-tube furnace will continue.

Irradiation Study of Metastable Beta-Phase Uranium Alloys

M. S. Farkas, D. B. Hamilton, A. A. Bauer, and R. F. Dickerson

OBJECTIVE To study the irradiation behavior and phase stability during irradiation of metastable beta-phase uranium alloys.

PROGRAM APPROACH Uranium alloys with additions of 0.3 w/o chromium and 0.3 w/o chromium-0.3 w/o molybdenum to retain the metastable beta phase have been developed by Nuclear Metals, Inc. Eighteen specimens of these alloys, prepared from uranium of 10 per cent enrichment, in a variety of conditions of heat treatment, are to be irradiated in two temperature-controlled capsules. The specimen compositions and heat-treatment conditions were reported in BMI-1489.

Capsule design is based on maintaining a specimen center-line temperature of 850 F with a specimen effective flux of about 10^{13} nv. The specimens in the first capsule are to be irradiated in the BRR to a burnup in the range of 0.01 to 0.05 a/o over a 2 to 3-day period. These specimens are to be examined after irradiation primarily to determine if the beta phase has been retained during irradiation. The specimens in the second capsule are to be irradiated under similar conditions as the first capsule to a burnup of about 0.3 a/o to investigate irradiation stability of the alloys.

PROGRESS REPORTED PREVIOUSLY A capsule-design study was initiated to provide irradiation systems appropriate for the combination of specimen temperature and fission heat-generation rate desired. A nuclear mock-up experiment involving a capsule similar to that envisioned for the actual experiments was conducted at the BRR and indicated that a peak specimen effective flux of approximately 0.75×10^{13} nv was achievable.

WORK THIS PERIOD Capsule design was completed, and fabrication of various components was begun. The design involves a double-wall system in which nine 0.25-in.-diameter (by approximately 0.6 in. long) specimens are aligned within the inner containment shell along the capsule axis. The heat-transfer medium between the specimens and the inner shell will be NaK, and narrow fins (machined into the outer wall of the inner shell) will provide thermal contact between the inner and outer shells. Thermocouples will be positioned adjacent to the specimens to monitor temperatures, and auxiliary heaters will be incorporated into the system for temperature-control purposes.

One somewhat unusual feature of the capsule is the provision for the irradiation of a natural-uranium specimen (the others will be enriched to 10 per cent) at the bottom of the stack. This pin will produce a relatively small amount of fission heat. Therefore, to maintain the center line of this pin at approximately the same temperature as for the enriched specimens, it is necessary to reduce the heat-dissipation characteristics of the system in its immediate locale. This will be done by locating a hollow metal spacer just above the natural-uranium pin to retard heat flow in the axial direction and by eliminating the radial fins opposite this specimen to present a low-conductance annulus of helium.

The first (low burnup) capsule will be irradiated at the BRR. However, because suitable space is not available at the BRR for the second (high burnup) capsule, it will be necessary to conduct this irradiation at another testing reactor. During February, the appropriate space-negotiation steps were initiated cooperatively by Battelle and Nuclear Metals, Inc.

PLANS FOR FUTURE WORK X-ray diffractometer tracings will be obtained on all uranium specimens prior to encapsulation. These will be used to determine the relative amounts of alpha and beta uranium present; charts will be compared to similar postirradiation diffractometer data to determine the extent of transformation which occurred during irradiation.

Barring unforeseen delays, the low-burnup capsule will be irradiated at the BRR during the week of March 22. The high-burnup capsule will be readied for shipment to the assigned reactor facility by about April 1.

GENERAL FUEL-ELEMENT DEVELOPMENT (AEC-DRD)

S. J. Paprocki

The studies reported in this section are being performed for the AEC Division of Reactor Development.

Techniques have been developed for the fabrication of cermet fuels containing 80 volume per cent of UO_2 and 20 volume per cent of the metals chromium, molybdenum, niobium, and stainless steel. In comparison to bulk UO_2 , these materials possess much improved thermal-shock resistance, thermal conductivity, and rupture strength. On the basis of these measured improved properties, an irradiation program has been formulated to correlate these results with the irradiation behavior of bulk UO_2 .

The cermet fabrication studies have been extended to include UN and UC fuels. Although the thermal conductivity of these materials is superior to UO_2 , an additional benefit is obtained in the cermet structure because the metal phase in the cermet can be metallurgically bonded to the cladding, eliminating the cladding-to-core void. In addition, there is a significant improvement in structural strength and thermal-shock resistance.

The techniques of hot pressing and gas-pressure bonding are increasing in importance as methods for bonding of nuclear fuel and structural components, and a study is being conducted to obtain a better understanding of the kinetics and mechanism of these bonding processes.

In some reactor applications, tubular fuel elements offer distinct advantages over flat-plate fuel systems; however, established techniques for the fabrication of tubular fuel elements are restrictive and of relatively high cost. A study is being conducted to evaluate new techniques for fabrication of tubular elements with emphasis on simplicity and low cost.

Irradiation of Cermet Fuels

S. J. Paprocki, G. W. Cunningham, D. E. Lozier, and E. O. Fromm

OBJECTIVE To investigate the irradiation stability of UO_2 refractory metal (chromium, molybdenum, and niobium) cermet fuels.

PROGRAM APPROACH Two capsules containing clad (with 35 mils of Type 430 stainless steel or niobium) cylindrical specimens of UO_2 -refractory metal fuels are being prepared for high-temperature high-heat-flux irradiations at the Materials Testing Reactor. Three refractory-metal matrices, chromium, molybdenum, and niobium, are involved; each is combined with 80 volume per cent UO_2 enriched to 20 per cent. Each capsule will contain six specimens, two each of the three materials indicated above, and will be equipped with thermocouples for specimen-temperature monitoring. The two capsules will be irradiated in similar thermal-neutron

fluxes but for different periods of time to achieve two levels of specimen burnup (approximately 2 per cent of the total uranium atoms present during three normal MTR cycles in the one case and approximately 5 a/o during eight normal cycles in the other).

PROGRESS REPORTED PREVIOUSLY The capsule design for these irradiations was selected on the basis of containment of the specimens in a thermocoupled double-wall stainless steel system. The heat-transfer characteristics were chosen to satisfy thermal parameters such as specimen center-line temperatures in the neighborhood of 0.7 of the melting point of the refractory-metal matrix (about 2650 F for the molybdenum- UO_2 and niobium- UO_2 and about 2350 F for the chromium- UO_2) and a specimen-surface heat flux of approximately 1×10^6 Btu/(ft²)(hr). A specimen surface-cladding interface temperature of 1700 F is desired. The three materials have significantly different thermal conductivities, and, consequently, specimen diameters are varied to obtain the desired combinations of thermal conditions; the diameters selected are approximately as follows:

Molybdenum- UO_2 0.40 in.

Chromium- UO_2 0.30 in.

Niobium- UO_2 0.25 in.

Specimens containing a cermet of 80 volume per cent UO_2 -molybdenum have been clad with Type 430 stainless steel by gas-pressure bonding for 3 hr at 2300 F under a helium gas pressure of 10,000 psi. The UO_2 used in these cermets was depleted minus 100 plus 200-mesh spherical particles. The UO_2 tube used in the irradiation specimens will have the same particle size and shape but will be enriched to 20 per cent uranium-235. A 1/8-in.-long void space will be incorporated at each end of the irradiation-specimen core within the cladding for the collection of fission gases and reduction of internal pressure.

Metallographic examination showed a continuous bond between the core and cladding after bonding; however, a reaction was evident between the molybdenum in the core and the Type 430 stainless steel cladding. Thermally cycling a specimen between 1850 and 200 F for 55 times had no harmful effects on the cladding, core, or interface; however, a 168-hr heat treatment caused cracking at the innermost edge of the reaction zone. Additional specimens were, therefore, made by lining the stainless steel cladding with 0.005-in. molybdenum sheet.

WORK THIS PERIOD The capsule design was completed and fabrication of capsule components begun. Tentative arrangements were completed for appropriate irradiation space at the MTR.

The dummy specimens containing the molybdenum barrier foil were gas-pressure bonded under 10,000-psi helium for 3 hr at 2300 F. This barrier prevented any reaction between the core and cladding. A specimen remained intact with no apparent defects after thermally cycling 25 times between 200 and 1850 F and heat treating for 1 week at 1800 F. It was decided from this experiment that a barrier layer of molybdenum would be employed in the irradiation specimens having the molybdenum metal phase as a part of the 0.035-in.-thick cladding.

Cermet specimens containing 80 volume per cent UO_2 in a chromium metal phase have been prepared. An external contamination, possibly from the autoclave atmosphere, produced an etching effect on the cladding surface and microcracks at the grain boundaries of the stainless steel cladding material. Metallographic examination showed a satisfactory dense core and good bonding between the core and cladding; therefore, all additional specimens will be surface protected by wrapping with stainless steel foil during pressure bonding.

PLANS FOR FUTURE WORK Fabrication of the components will be continued. According to present plans, the two capsules will be ready for irradiation before June.

The 20 per cent enriched UO_2 fuel has been received, and a portion of it will be coated with niobium to the extent of 20 volume per cent by vapor deposition. The niobium-coated UO_2 will then be used as the core of the niobium- UO_2 irradiation specimen.

Disks will be machined for green pressing the cores to the three different diameters. Dummy specimens will then be pressed and pressure bonded to check the specimen dimensions after pressure bonding.

Fabrication of Cermet Fuel Elements

S. J. Paprocki, D. L. Keller, G. W. Cunningham, and D. E. Kizer

OBJECTIVE To develop fabrication techniques for producing UN cermets containing a minimum fuel loading of 60 volume per cent to densities of 90 per cent of theoretical or greater as well as to conduct a cursory evaluation of fabrication techniques for producing UC cermets.

PROGRAM APPROACH Specimens are being fabricated by the gas-pressure-bonding technique. Cermet evaluations are being made on the basis of microstructure and density. In addition, metal-ceramic compatibility results are being obtained from fabricated cermets.

PROGRESS REPORTED PREVIOUSLY Densities of 60 to 80 volume per cent UN-molybdenum, -niobium, -chromium, and -Type 347 stainless steel have been reported after gas-pressure bonding for 3 hr at 2200 to 2400 F under a helium gas pressure of 10,000 psi. Values ranged from 73 to 99 per cent of theoretical. A reaction between UN-niobium at 2300 and 2400 F has been reported as well as the formation of a grain-boundary precipitate in the stainless steel in the Type 347 stainless steel-UN cermets.

WORK THIS PERIOD Etching of the Type 304 stainless steel cladding used on the UN-Type 347 stainless steel cermets gas-pressure bonded at 2300 F revealed a reaction layer at the cladding interface. Heat treating the UN-Type 347 stainless steel cermet at 2000 F for 1 hr followed by cooling to black heat in approximately 2 min failed to remove the grain-boundary precipitate in the stainless steel. This precipitate has not been definitely identified as a UN reaction product, but because of the

necessity of limiting the number of materials for future work, no further studies will be conducted on UN-stainless steel cermet dispersions at this time.

Previous gas-pressure-bonded cermets were bonded with four cermet cores assembled in a compartmentalized tube. To determine if the compartmentalized tubes affected the pressure-bonded density of the cermets, three additional tubes were assembled containing 80 volume per cent UN dispersed in molybdenum, chromium, and Type 347 stainless steel. After evacuating and sealing, the three assemblies were gas-pressure bonded for 3 hr at 2400 F under a helium gas pressure of 10,000 psi. The cermets were ground out of their containers using a silicon carbide wheel and cutting-oil lubricant. No difficulty was encountered during machining. Measured densities were 90.4, 85.0, and 95.1 per cent of theoretical, respectively, for the molybdenum, chromium, and Type 347 stainless steel cermets. The molybdenum and stainless steel results are in agreement with densities previously reported. The chromium cermet density is lower than expected and may be a result of a can leak during the bonding run.

PLANS FOR FUTURE WORK Cermets of 80 volume per cent UN dispersed in molybdenum and chromium are being prepared for densification. These specimens will be used for thermal-conductivity measurements. In addition, microscopic examinations of green-pressed UC and UN gas-pressure bonded at 2600 F in contact with green-pressed cores of molybdenum, niobium, rhenium, and tungsten will be undertaken to assess compatibility and determine the feasibility of preparing UN and UC cermets with these metals.

Factors Affecting Pressure Bonding

D. C. Carmichael, G. W. Cunningham, and J. W. Spretnak

OBJECTIVE To determine the mechanism of solid-phase bonding of metal components under the application of heat and pressure.

PROGRAM APPROACH Hot pressing or gas-pressure bonding under various conditions of temperature, pressure, and time are being used to prepare specimens for study. The specimens are of different designs and preparations and are composed of two components of the same metal. Evaluation of the bonds is based chiefly on metallographic examination, using special techniques. Observations are made of the extent of contact between mating surfaces and of the behavior of grain boundaries, dislocations, and interfacial voids which affect the elimination of the interface during bonding.

PROGRESS REPORTED PREVIOUSLY The mechanism for the self-bonding of copper has been established and the effects of pressure, temperature, grain growth, impurities, and surface roughness have been investigated. In order to produce a metallurgically sound bond, i. e., no discontinuities or changes in the structure in the bond region, the first requirement is the application of sufficient pressure to place the surfaces in intimate contact. For copper, it was found that the pressure required could be related directly to Meyer hot-hardness values.

Grain growth across the bond interface and thus elimination of the interface has been found to be dependent upon the presence or absence of microvoids in the bond region. Microvoids can be created during bonding by insufficient flow of metal or by condensation of excess vacancies at impurity nuclei. Decreasing the number and size of microvoids to a level permitting grain growth depends upon the availability of vacancy sinks in the metal. In copper, the most effective sinks were found to be grain boundaries.

WORK THIS PERIOD The pressure-bonding mechanism is now being studied in more detail and in metals other than copper. Investigations are directed initially toward examining the mechanism and pressure hot-hardness relationships for obtaining intimate contact during pressure bonding. Various types of metals of different crystal structures, stacking-fault energies, dislocation behavior, and melting points will be studied. Modification of the present hot-pressing equipment for operation at higher temperatures was not successful. Components for a new furnace and shielding were ordered, and the new heating unit is presently being constructed. Suitable materials for specimens are being obtained; some have already been received. Basic background information which will be required for planning experiments and interpreting results is being surveyed and studied.

PLANS FOR FUTURE WORK The new heating unit for the hot-pressing equipment will be completed and operated next month, and additional materials for specimens will be obtained. During the coming months, suitable specimens will be prepared for investigation of some aspects of the mechanism of pressure bonding of metals other than copper.

Development of Low-Cost Tubular Fuel Elements

S. J. Paprocki, R. J. Carlson, and E. G. Smith, Jr.

OBJECTIVE To develop techniques for fabricating low-cost tubular fuel elements of consistent quality.

PROGRAM APPROACH Several approaches are under current investigation. One of these involves the assembly of concentric core and cladding components followed by densification, bonding, and sizing by techniques such as explosive forming or pressure bonding. Various ways to locate the core powder mixtures are being considered, including tamp packing into the annulus between two concentric cladding tubes and the use of binders to form the core mixture into sheet which can then be formed into a tubular shape.

In another approach, multiple-cored fuel plates are fabricated in a conventional manner with each core running the length of the plate. Subsequent to rolling, two such plates are lined up core-for-core and joined together by a technique such as seam welding in such a manner that the areas between the cores can be expanded or opened up to form tubular shapes, the cores from each plate making up half of the circumference of the tubular cross section. Hydraulic, pneumatic, or mechanical methods may be used to open up the tubular sections.

PROGRESS PREVIOUSLY REPORTED Experiments using a plastic binder such as Acryloid showed that a relatively large amount was required to obtain the desired working characteristics in a stainless steel- UO_2 powder mixture (20 w/o with minus 325-mesh stainless steel powder and 10 w/o using minus 100-mesh material). Recent experiments described below indicate that essentially no binder residue remains after sintering at 1600 and 2300 F for 1 hr in hydrogen.

Early attempts to explosively compact specimens with plastic-binder-fabricated cores using inadequate backup jiggling resulted in rupture of the specimens. A special two-piece backup die has been constructed for future explosive-forming studies.

An expanded multiple-tube assembly was prepared using spot welding as a means of joining the two fuel plates in the desired areas. Expansion of the individual tubular fuel sections was accomplished by mechanical means. In addition, several plates were seam welded to achieve a more continuous joining operation than could be achieved by spot welding.

WORK THIS PERIOD Metallographic examination of sintered powder-binder mixtures showed that little if any binder residue remains after heat treatment. This was not in agreement with previously reported results. In addition, there is some question as to the validity of the method used to calculate binder residue. As a result, binder-residue calculations have been repeated, this time using a slightly different approach. Previous methods neglected the binder lost through evaporation during the mixing, weighing, and rolling of the powder mixture and reflected only that weight lost during sintering. This amount was found to be appreciable, amounting to 37 per cent of the original binder weight. Upon sintering the powder-binder sheet in hydrogen at 1600 and 2300 F, each for 1 hr, a negligible amount of binder residue was indicated within the accuracy of the calculations.

Several tubular specimens containing binder-powder mixtures in the annulus formed by concentric stainless steel tubes have been explosively compacted and sized. They had been previously heat treated in hydrogen for 1 hr at 1600 F to facilitate binder removal. The explosive charge consisted of one and two strands of Prima Cord placed down the center of the tubes. A special backup die was constructed to contain the specimen during impact.

Two strands of Prima Cord were found necessary to densify the core as evidenced by "ring" tests and the appearance of the tube-annulus thickness after impact. The rough and wrinkled appearance of the tube surfaces after compacting indicated that areas of porosity or low density were present in the core before compacting. Metallographic sections were taken from specimens to compare the condition of the core and core-cladding bond as compacted with that after heat treatment.

Fabrication experiments on spot welds were completed. Both hot and cold rolling were employed to break up the weld cast structure along with several reduction schedules. No evidence of weld failure was observed in any of the specimens. Metallographic samples are now being prepared.

FUTURE WORK Major emphasis in the component-assembly approach to producing tubular elements will be placed on achieving a more uniform green density in the fuel loading prior to densification. Variations in both loose-powder and plastic-binder incorporation techniques will be investigated for this purpose. In addition, there will be some effort to extrude the plastic core mixtures directly onto the OD of the inner tube. Other fabrication processes such as hydrostatic pressing, swaging, and pressure bonding are also to be considered.

Some effort will be made to employ liquid explosives to form the tubular elements. Use of a liquid explosive for compacting geometries of this shape might reduce the cost of the process by eliminating the elaborate jigging dies and evacuation systems required with conventional explosives.

GAS-PRESSURE BONDING OF CERAMIC, CERMET, AND DISPERSION FUEL ELEMENTS (AEC-FUEL CYCLE)

S. J. Paprocki, S. W. Porembka, D. L. Keller,
E. S. Hodge, and C. B. Boyer

OBJECTIVE To refine and develop the gas-pressure-bonding process as a method for fabricating low-cost ceramic, cermet, and dispersion fuel elements.

BACKGROUND Since both fuel densification and cladding are accomplished in a single pressure-bonding operation, the technique appears promising as a method for producing quality fuel elements at a reduced cost. The work is being carried out in support of the AEC Fuel-Cycle Development Program.

PROGRAM APPROACH Major emphasis has been placed on the uranium dioxide ceramic fuel system as clad with Type 304 stainless steel. Past investigations have involved studies of initial oxide compacting techniques, characteristics of pressure-bonded oxides, and various basic fuel-element geometries.

PROGRESS REPORTED PREVIOUSLY The evaluation of various types of uranium dioxide powders has been established through studies of their initial compacting and pressure-bonding characteristics. Mixtures of ceramic-grade and fused oxides have been found to demonstrate optimum properties for successful pressure bonding at those conditions which also produce acceptable Type 304 stainless steel bonding. More recently, the definition of preliminary process specifications for several basic fuel geometries was suspended in favor of producing fuel rods for irradiation in the VBWR.

WORK THIS PERIOD Based on the materials specifications defined previously, the required uranium dioxide and stainless steel tubing have been ordered by the Atomic Products Division of the General Electric Company. Tubing tolerances established in this order have served as the basis for the design of UO_2 and stainless steel powder compacting dies.

PLANS FOR FUTURE WORK Compacting dies will be fabricated and the preparation of several small-scale tubes of the VBWR design will be initiated. These tests will define the basic deformation behavior required prior to pressure bonding full-scale assemblies.

DEVELOPMENT OF URANIUM CARBIDE (AEC-FUEL CYCLE)

F. A. Rough and W. Chubb

Uranium carbides and their alloys are being developed for the AEC as a part of the Fuel-Cycle Development Program. The objective of this program is to lower the cost of power produced from nuclear energy by lowering the costs of manufacturing, using, and reprocessing reactor fuels. Foremost among the various ways in which these costs can be reduced are: (1) lowering the cost of fabricating the fuel, (2) increasing the temperature at which the reactor coolant and fuel operate, (3) increasing the life of the fuel in the reactor, and (4) decreasing the cost of reprocessing the fuel. Uranium carbides seem capable of producing dramatic savings in connection with the second and third of these items, and the costs of fabricating and reprocessing of fuel elements using uranium carbides will probably be quite similar to the costs of fabricating and reprocessing fuel elements containing uranium oxide or uranium metal.

To assist in the accomplishment of the aforementioned objective, an integrated program of research on the preparation and properties of bulk uranium carbides is in progress at Battelle. This program includes: (1) studies of the production and properties of hot-pressed uranium carbide powders to determine if these materials differ in any important and useful way from cast uranium carbide, (2) development of skull-melting and casting techniques to provide a method for commercial production of cast uranium carbides in large quantities and sizes, (3) determination of the mechanical, physical, and chemical properties of uranium carbides at room and elevated temperatures, (4) measurement of the rates of diffusion of uranium and carbon in uranium carbides to provide a basic understanding of the behavior of these materials under a variety of different conditions at elevated temperatures, and (5) irradiations designed to produce basic information on the nature of radiation-damage processes in the structure and upon the integrity of uranium carbides. These studies have now been in progress for over a year and a half. During this time the emphasis in the research effort has been in the first four areas mentioned above. During the next year, emphasis will be shifted gradually toward property studies and toward analysis of the nature of radiation-damage processes in uranium carbides.

Alternate Fabrication Methods for UC

S. J. Paprocki, D. L. Keller, and J. M. Fackelmann

OBJECTIVE To develop economical methods for fabricating dense, pure, uranium carbide components by powder-metallurgy techniques and to measure the high-temperature properties of such bodies.

PROGRAM APPROACH Powder that has been obtained by crushing arc-melted buttons, or commercial forms of uranium carbide, is being compacted at room temperature, sealed in niobium capsules, and isostatically hot pressed. Sealing has been done under high vacuum with an electron-beam welder, and helium has been the pressure medium. The principal variables being studied are particle size and type of powder, pressing conditions, and their effects on density and compositional control. In addition, some work is being done on the effect of Mo_2C additions on densification and hot strength.

PROGRESS REPORTED PREVIOUSLY Isostatic hot pressing of compacts prepared from coarse mesh fractions of crushed uranium carbide ingots has resulted in high densities, about 95 per cent of theoretical, with microstructures consisting of UC and a small amount of U_2C_3 . Where large amounts of UO_2 were present, densities up to 99 per cent of theoretical were observed in conjunction with greater quantities of U_2C_3 . Hot-pressing temperature has been varied from 1300 to 1480 C in obtaining these results.

WORK THIS PERIOD A series of capsules containing cores of uranium carbide and UC-10 w/o Mo_2C alloys has been hot pressed at 1480 C. The latter alloy was prepared by two methods. In the first, chemically pure Mo_2C obtained from Shieldalloy Corporation was mixed with uranium carbide powder obtained from arc-melted buttons in a V-mixer for 2 hr. The other alloying method made use of a master-alloy button arc melted from pure uranium, graphite, and molybdenum metals. The button was crushed and compacted in a manner similar to that used for unalloyed UC. Density measurements before and after sintering, as well as particle-size data, are tabulated in Table F-1. Since the theoretical density of UC-10 w/o Mo_2C is 13.0 g per cm^3 , the densities of 12.8 g per cm^3 for the master alloy and 13.0 g per cm^3 for the powder mixture appear very good.

TABLE F-1. DENSITY MEASUREMENTS OF CORES ISOSTATICALLY HOT PRESSED 3 HR AT 1480 C AND 10,000 PSI

Type Power	Particle Size, mesh	Nominal Composition, w/o			Density, g per cm^3	
		Carbon	Molybdenum	Uranium	Green	Hot-Pressed ^(a)
Vitro shot	-80	4.78	.0	Balance	10.3	12.5
		4.78	0	Balance	10.2	12.5
Crushed arc-melted buttons	-80	4.85	0	Balance	10.4	12.8
		4.85	0	Balance	10.4	12.7
Crushed arc-melted prealloyed buttons	-100	4.91	9.41	Balance	9.5	12.8
Commercial Mo_2C powder plus crushed arc-melted buttons	-100 (UC), -230 (Mo_2C)	4.91	9.41	Balance	9.6	13.0

(a) Measured by liquid-buoyancy methods.

Results on the unalloyed uranium carbide substantiate results reported in BMI-1496 for the cores prepared from Vitro shot. They were more porous than those prepared from crushed buttons. This difference may be due to the slight differences in composition of the starting materials. The density value of 12.8 g per cm^3 is about 94 per cent of the theoretical UC value of 13.63 g per cm^3 . The true void volume will probably be less than 6 per cent when the quantity of U_2O_3 is measured.

PLANS FOR FUTURE WORK Hot-hardness measurements will be made on both pure UC and alloyed cores at a later date. When this information becomes available, it will be reported in another section. No further studies are planned under this program.

Melting and Casting Techniques for Uranium-Carbon Alloys

B. C. Boesser, E. L. Foster, and R. F. Dickerson

OBJECTIVE To develop techniques amenable to large-scale production of high-quality cast shapes of uranium carbide.

PROGRAM APPROACH Skull-type arc-melting procedures are being applied to the melting and casting of uranium carbide. The effects of process variables such as the quality of the charge material, furnace atmosphere, arc current and voltage, and the grade of graphite used for the electrode tip are being investigated in the interest of producing high-purity castings with good compositional control. Evaluations of composition and homogeneity are based on chemical analysis. Casting soundness is determined by radiography.

PROGRESS REPORTED PREVIOUSLY Casting research covering the first 1-1/2 years of this program is summarized in BMI-1370 and BMI-1488. Research in the several months since the issuance of BMI-1488 has dealt with the effect of vacuum-outgassed commercial-grade graphite (used both as a charge addition and as an electrode tip) upon the control of the composition of the product. It was found that five castings produced using outgassed graphite varied less than ± 0.1 w/o carbon while castings produced from the same grade of graphite that had not been outgassed varied by ± 0.3 w/o carbon.

WORK THIS PERIOD Seven replicate melts were made under identical melting conditions using vacuum-outgassed AGOT nuclear-grade graphite both as the alloy additions and as the electrode tips. Analyses of the castings showed 4.8, 5.4, 5.3, 4.9, 5.3, 5.2, and 4.7 w/o carbon, thus indicating a spread of ± 0.3 w/o carbon. This type of spread was experienced previously when using commercial graphite which was not outgassed. Splashing of the melt during the dissolution of the graphite in these charges was not excessive; however, a large amount of electrode-tip erosion was noticed. In some cases, 50 per cent of the AGOT graphite tips were lost during melting. These large and variable AGOT graphite tip losses caused the above-mentioned fluctuations in the carbon content of these castings.

A series of seven melts using vacuum-degassed TSF-grade graphite, both as the alloy additions and as electrode tips, has been completed, and analyses of castings are in progress.

PLANS FOR FUTURE WORK The evaluation of the effects of using various grades of outgassed graphites, both as alloy additions and as electrodes, and of using different feed materials, such as commercially supplied UC, upon casting purity and upon compositional control will be completed. A series of melts is being considered to determine the effect of a helium or possibly an argon atmosphere on compositional control, casting purity, castability, and the yield of molten carbide.

Mechanical and Physical Properties of Uranium Monocarbide

B. C. Boesser, R. W. Endebrock, E. L. Foster, and R. F. Dickerson

OBJECTIVE To obtain measurements of mechanical and physical properties such as strength, hardness, thermal conductivity, and resistivity at room and elevated temperatures and to determine the effect of alloy additions and heat treatment on the properties of uranium carbides.

PROGRAM APPROACH Specimens of uranium monocarbide are being prepared for measurements of certain mechanical and physical properties. Equipment is being modified to permit property measurements at 1000 to 1600 C. Test environments will be limited to either vacuum or helium. In the interest of improving the properties of UC, research concerned with alloying, coating, and heat treating is also being performed.

PROGRESS REPORTED PREVIOUSLY Mechanical- and physical-property data obtained during the last 1-1/2 years are presented in two interim progress reports, BMI-1370 and BMI-1488. The strength and hardness of uranium carbides in the as-cast condition is relatively insensitive to composition in the range of 4.8 to 9.0 w/o carbon. When heat treated to produce U_2C_3 , the 7.0 w/o carbon alloy has a hardness of about 1100 KHN as compared to about 700 KHN for UC and 500 KHN for UC_2 . Moisture adversely affects the strength and integrity of uranium carbides. Alloying with Mo_2C , NbC, VC, ZrC, and TiC results in improved strength, hardness, and corrosion resistance. A promising protective coating for UC appears to be a copper-20 w/o silicon alloy applied by dipping at 2450 F. Various heat treatments have been given to specimens with carbon compositions of 4.8, 7.0, and 9.0 w/o. Results of these heat treatments were described in BMI-1469.

A UC-20 w/o vanadium alloy exhibiting phases identified by X-ray diffraction as UC, uranium, and vanadium has been prepared. Various ternary alloys of UC with combinations of NbC, VC, molybdenum, niobium, and vanadium have been prepared for evaluations in terms of electrical resistivity, corrosion resistance, and metallographic structure. Heat treatments of as-cast uranium-7.0 w/o carbon alloy specimens to determine the transformation rate to the U_2C_3 structure indicated that treatments of less than 15 min are required for transformation in the 1400 to 1700 C temperature range. Hot-hardness measurements from 1000 to 1500 C have been obtained for uranium-5.0 w/o carbon and uranium-9.0 w/o carbon alloys.

WORK THIS PERIOD Several uranium-4.8 w/o carbon alloy specimens 3-1/2 in. in diameter by 2 in. thick were cast for high-temperature thermal-conductivity measurements. After these specimens are examined for soundness, the best will be selected and machined into a 1-in.-thick disk

An as-cast uranium-5.9 w/o carbon alloy showed a structure of UC with UC_2 needles, with a heavy concentration of UC_2 at the grain boundaries, while metallography of a 6.2 w/o carbon alloy revealed an intimate two-phase mixture of UC and UC_2 indicative of a eutectic. A section of a 6.5 w/o carbon alloy exhibited UC_2 with UC needles with heavy regions of UC at the grain boundaries. This would indicate a minimum in the liquidus curve at around 6.2 w/o carbon, and raises the question as to whether this minimum is associated with a two-phase region, i.e., a eutectic, or a one-phase region, which would require it to be identified simply as a "minimum". To resolve this

question, a sample of a uranium-6.5 w/o carbon alloy was heated for 20 min at 2050 C and showed evidence of being heated in a two-phase region. On the other hand, the metallographic appearance of specimens of a uranium-6.5 w/o carbon alloy heated for 5 min at 2100 C, and for 2 min at 2300 C could be interpreted as having entered a single-phase region, as did a 6.2 w/o carbon alloy specimen heated 5 min at 2200 C.

PLANS FOR FUTURE WORK Hot-hardness measurements of uranium 4.8, 7.0, and 9.0 w/o carbon alloys will be continued. High-temperature thermal-conductivity, thermal-expansion and electrical-resistivity determinations on uranium alloys are to be conducted.

Studies of Diffusion in Uranium Monocarbide

W. Chubb, R. W. Getz, and F. A. Rough

OBJECTIVE To obtain the rates of interdiffusion of carbon and uranium and the rates of self-diffusion of uranium and carbon in uranium monocarbide.

PROGRAM APPROACH Rates of interdiffusion are determined by measuring the rate of growth of the uranium carbide layers between graphite and liquid uranium saturated with carbon. Details of the procedure are given in BMI-1370. Rates of self-diffusion of uranium in uranium monocarbide are determined by measuring the gamma activity of samples ground from a diffusion couple consisting of a foil of enriched uranium sandwiched between two rods of depleted uranium monocarbide. Details of the procedure are given in BMI-1488. Rates of self-diffusion of carbon in uranium monocarbide are being determined by measuring the beta activity of carbon-14 in diffusion couples prepared from two rods of uranium monocarbide, one of which contains carbon-14. Details of the procedure are given in BMI-1473, BMI-1480, and BMI-1489.

PROGRESS REPORTED PREVIOUSLY Determination of the rate of interdiffusion of carbon and uranium has been completed; the results were reported in BMI-1370. Determination of the rate of self-diffusion of uranium in uranium monocarbide has been completed; the results were reported last month in BMI-1496. Details of a technique for determining the rate of self-diffusion of carbon in uranium monocarbide have been described previously. The initial couple in this latter study was assembled for annealing.

WORK THIS PERIOD Metallographic examination of a couple annealed for 15 min at 1600 C indicated that the interface between the two lengths of uranium monocarbide was free of contamination and that there was limited grain growth across the interface.

The beta activity of the carbon-14 was measured by counting the activity of the face exposed by grinding away the couple perpendicular to its axis with 600-grit silicon carbide powder. The diffusion zone was approximately 0.0098 in. wide and a preliminary calculation of the diffusion coefficient gave 5×10^{-8} cm² per sec for the self-diffusion of carbon in uranium monocarbide at 1600 C.

The activity of the carbon-14 was 10,000 cpm above the activity of the uranium background. Another uranium monocarbide casting has been made; the activity of this

casting was about 50,000 cpm above the activity of the background. Carbon has been ordered for preparing an additional casting.

PLANS FOR FUTURE WORK The second couple in the study of the rate of self-diffusion of carbon in uranium monocarbide will be annealed for 15 min at 1800 C and analyzed. Additional couples are to be prepared.

Effects of Radiation on UC

D. G. Freas, A. E. Austin, J. E. Gates,
C. M. Schwartz, and F. A. Rough

OBJECTIVE To study and understand the important mechanism of damage occurring in uranium monocarbide as a result of irradiation and temperature.

PROGRAM APPROACH Specimens of uranium monocarbide (UC), uranium sesquicarbide (U_2C_3), and uranium dicarbide (UC_2) are being irradiated in the Battelle Research Reactor at surface temperatures ranging from 500 F or less to 1600 F and burnups from 0.01 a/o to 0.7 a/o of the uranium. The specimens are contained in six NaK-filled capsules. Evaluation of the irradiated specimens is based on dimensional stability, microstructural stability, and effects on the electrical resistivity and lattice parameters.

PROGRESS REPORTED PREVIOUSLY Specimens of hyperstoichiometric UC, composed of natural uranium, were irradiated in Capsules 1 and 2 to burnups of 0.01 and 0.03 a/o of the uranium at surface temperatures below 500 F. The changes in dimensional properties of these specimens were found to be small, and only slight decreases in density were measured. The electrical resistivity increased by almost a factor of three after irradiation to both 0.01 and 0.03 a/o burnup of the uranium. Since the resistivity values did not show a hyperbolic-type increase with increasing burnup, it was thought that saturation of displaced interstitial atoms and vacancies in the lattice was attained during irradiation. X-ray diffraction studies of the crystal lattice of specimens from both burnup levels also indicated that saturation of displaced interstitial atoms and vacancies had occurred. A metallographic examination of a specimen from both levels of burnup failed to reveal any structural changes. The electron-microscopy examination of a specimen with 0.01 a/o burnup of the uranium showed no detectable changes as compared to an unirradiated control specimen.

Capsule 4, which contained four uranium-5 w/o carbon specimens, two of which had been heat treated to relieve casting stresses, and two heat-treated specimens of uranium-6.7 w/o carbon, was discharged from the reactor after detection of fission products in the reactor coolant. The specimens included in this capsule were all composed of 10 per cent enriched uranium. It was estimated that these specimens had experienced a uranium burnup of approximately 0.1 a/o at the time of their discharge.

Because of a lower than anticipated neutron flux, mixtures of inert gases were incorporated into the outer annuli of the capsules to help produce temperatures nearer to the originally designed 1400 to 1600 F range.

WORK THIS PERIOD Capsule 3 was discharged from the reactor after the specimens attained a burnup of 0.15 a/o of the uranium at temperatures below 300 F. This capsule contained four uranium-5 w/o carbon specimens, two of which had been heat treated to relieve casting stresses, and two heat-treated specimens of uranium-6.7 w/o carbon.

The irradiation of the remaining two capsules is continuing in the BRR. The specimens in these capsules are all composed of 10 per cent enriched uranium with carbon contents of 5.0, 6.7, and 8.5 w/o. Difficulties have been encountered with the control of specimen temperatures by the incorporation of mixtures of inert gases into capsule annuli. Recent experiments have produced widely varying temperatures with small changes in gas composition.

PLANS FOR FUTURE WORK With the completion of the irradiation of the remaining two capsules, the specimens will be examined. Studies of the dimensional stability, microstructural stability, electrical resistivity, and lattice parameters will be undertaken to duplicate the study of the UC specimens of natural uranium irradiated earlier in the program. The postirradiation examination of the specimens from the second two capsules of this program is scheduled for the near future.

GROWTH OF UO_2 SINGLE CRYSTALS (AEC-DR)

J. D. Jackson, C. A. Alexander, H. L. Goering,
and F. A. Rough

OBJECTIVE To prepare large single crystals of UO_2 .

BACKGROUND While a great deal of research has been done and is being done on UO_2 , the fundamental physical behavior of stoichiometric and high-purity UO_2 remains to be determined. The present program is being supported by the AEC Division of Research with the aim of securing a limited quantity of high-purity single crystals of UO_2 suitable for such fundamental property determinations.

PROGRAM APPROACH Various high-temperature sources are being evaluated to melt UO_2 (melting point about 2760 C) and to control its solidification to form large single crystals.

PROGRESS PREVIOUSLY REPORTED The following fusion methods have been investigated:

- (1) Electron-beam melting
- (2) Resistance heating
- (3) Arc melting
- (4) Plasma-jet impingement
- (5) Induction heating
- (6) Radiation heating from resistance element.

Most of the experimental program has employed the last three methods. The resistance furnace using a tungsten heating element appears to give the greatest promise for success, and the present objective is to improve the furnace to reach and maintain a temperature of 2800 C.

WORK THIS PERIOD During January, work continued using the high-temperature tungsten-resistance furnace to grow single crystals of UO_2 from the melt.

An X-ray analysis was performed on the UO_2 used in the run reported last month in BMI-1496. This run was made in vacuum to an indicated temperature of 2880 C, and the charge appeared to have melted. Analysis indicated that only stoichiometric UO_2 was present. If any impurities were present, they were at concentrations below the limit of detectability by X-ray techniques. This would seem to indicate that tungsten is compatible with molten UO_2 , and that dissociation of UO_2 does not occur, at least up to the melting point.

Microscopic examination of the porous "clinker" indicated that it was composed of very small crystals as would be encountered when a melt was quenched. The X-ray

examination of this material indicated that here, too, only UO_2 was present. Extrapolation of the vapor-pressure curve of UO_2 to 2880 C indicated that the vapor pressure would be in the millimeters-of-mercury range and would be considerably greater than the system pressure, which was maintained at less than 200 μ during this run. Any liquid UO_2 would boil under these conditions, and the appearance of this porous clinker has been interpreted as that of a quenched boiling liquid.

From the above results, it would appear that a sufficiently high temperature can be reached with the furnace to melt UO_2 if the furnace is run in vacuum. To circumvent the problem of boiling under reduced system pressures, a tungsten lid was fabricated for the crucible. Calculations indicated that about 135 g of mass would be necessary to prevent the vapor from lifting the lid.

A run utilizing this lid was not successful in that the resistance element shorted at a relatively low temperature (2450 C). The exact cause of this failure is not known, although the crucible may have touched the resistance element through some misalignment caused by differential expansion in the system.

In another run the system pressure was maintained slightly higher than the estimated vapor pressure of the UO_2 to prevent boiling while still gaining the advantage of low conductivity in the rarified gas. The run was made at a pressure of argon of 45 mm of mercury. From a plot of temperature versus power input, it became apparent that 2650 C was the maximum temperature that could be reached under these conditions without dangerously overloading the heating element. This temperature was maintained for 1 hr and then the furnace was cooled.

Subsequent examination of the crucible indicated that many crystals had grown from the vapor, a number of them to dimensions greater than 2 mm. Microscopic examination indicated that the crystal habit was tetrahedral and that growth had occurred on the (111) planes.

From the past month's effort, it has been established that the tungsten-resistance furnace is capable of obtaining and maintaining a temperature sufficiently high to melt UO_2 . It is now possible to establish during the course of a run the temperature at which the power-versus-temperature curve becomes asymptotic. The temperature at which this occurs appears to depend on the gas present and on the specific heating element.

PLANS FOR FUTURE WORK During the coming month it is planned to continue work with the resistance furnace in growing UO_2 crystals from the melt. In addition, vapor growth will be more fully investigated, in those runs in which it is obvious that the melting point cannot be reached with the specific element employed.

RADIOISOTOPE AND RADIATION APPLICATIONS (AEC-OID)

D. N. Sunderman

Three research programs are under way at Battelle as part of the program of the Office of Isotopes Development. The first is concerned with the development of technology necessary for the application of intrinsic radioactive tracers to industrial process control. In the intrinsic-tracer concept a radioactive tracer is added directly to a process stream in the same physical and chemical form as the element or compound whose concentration is to be controlled. As physical or chemical separation steps are performed upon this material the radioactivity level of the stream continues to be a measure of the concentration of the single species tagged with radiotracer. Since measurement of radioactivity is less strongly influenced by the chemical and physical composition of the stream, systems of simpler design may be used to monitor and control the industrial process.

The second program is a study of the influence of structural factors on graft polymerization by ionizing radiation. Graft polymerization has been demonstrated capable of modifying substantially the physical properties of polymeric materials, and broad interest is being given this process industrially. However, it is necessary to learn more concerning the influence of molecular structure upon the ability to form graft copolymers before the full capabilities of this process can be achieved. In this study a series of substituted methacrylate polymers is subjected to the ionizing radiation from cobalt-60, and the product is analyzed by electron paramagnetic resonance, chemical, mass-spectrometry, gas-chromatographic, and infrared techniques. Information is being obtained on rate of free-radical formation and decay as well as on the mechanism of the reaction induced.

The third program is directed toward the development and evaluation of safety performance standards for sealed radiation sources. There are presently no detailed formal standards to insure the safe performance of sealed radiation sources. The ever-increasing usage of these sources industrially has indicated a need for such standards both to provide for public safety and to encourage further application of these devices. Such safety performance standards should be sufficiently rigorous to assure that a source conforming to them would not constitute an unusual hazard under either normal or abnormal conditions of use. Establishment of definite criteria should also assist in creating an atmosphere that will encourage increased industrial utilization of such sources.

Use of Intrinsic Radioactive Tracers for Process Control

J. L. McFarling, P. Gluck, J. F. Kircher, and D. N. Sunderman

OBJECTIVE To develop the technology essential to the application of intrinsic radio-tracers to the control of certain industrial chemical process operations.

PROGRAM APPROACH Several potential intrinsic radiotracer control applications are being evaluated according to previously established criteria. The particular application chosen for intensive study is the use of intrinsic radiotracers to control precipitation-filtration purification operations.

An important phase of the program is the demonstration of intrinsic radiotracer control applications with a laboratory-scale model of the process system being studied.

In conjunction with the experimental program, an evaluation is being made of the possible hazards to consumers from use of intrinsic radiotracers for process control.

PROGRESS REPORTED PREVIOUSLY The removal of impurity iron from a nickel-refinery stream was the first intensively studied process. The use of iron-59 tracer as an aid in efficiently removing iron from a mixed cobalt-nickel solution has been demonstrated using the process model. It was shown that using radioactive iron could improve the accuracy and shorten the response time of the control system. It was also shown that there were no significant radioactivity contamination hazards in the proposed application.

Last month's report (BMI-1496) contained early results of experiments using manganese-54 to facilitate removal of impurity manganese from process water.

In the hazards-evaluation study, it was concluded that there would be negligible contamination of drinking water and food from using steel products containing the maximum allowable level of radioisotopes.

WORK THIS PERIOD Five experiments were completed in which different initial concentrations of manganese and different pH levels were used. The results of these experiments are summarized below:

- (1) In general, good agreement was obtained between the manganese concentration calculated from the activity measurement and the concentration determined by chemical analysis of the filtrate.
- (2) The activity measurements of the filtrate taken during the run were usually higher than those taken later on the same filtrate samples. This was presumably due to the deposition of a small amount of manganese tracer on the walls of the counting cells.
- (3) At manganese concentrations below 0.05 ppm, the radioactivity measurement gave a greater precision than the chemical analysis as well as being many times faster.

Table H-1 shows the results from the first dynamic experiment, in which process conditions were varied during the experiment. The filtrate activity reading was obtained from a strip-chart recorder. In this case the initial concentration of manganese in the feed solution was 2.79 ppm and the manganese-54 activity in the feed was $21,200 \pm 500$ cpm. The last two columns of the table show good agreement between the calculated manganese concentration and the chemical analysis. The generally higher values in the fifth column of the table show the effect of manganese deposition on the walls of the counting cell.

The study of hazards to consumers using steel products containing radiotracer residues has shifted to the consideration of nonbiological radiation effects on sensitive materials. An example is the use of such steel to make containers for storage of photographic or X-ray film.

TABLE H-1. EXPERIMENTAL DATA FROM STUDY OF MANGANESE REMOVAL USING MANGANESE-54

Sample	Elapsed Time Since Start of Run, min	Apparent Filtrate Activity During Run, cpm $\pm \sigma$	Filtrate Activity From Later Recount, cpm $\pm \sigma$	Apparent Manganese Concentration in Filtrate, ppm		
				Calculated From Activity During Run	By Chemical Analysis of Filtrate	Calculated From Activity Recount
1	145	1520 $\pm$ 62	1245 $\pm$ 12	0.20 $\pm$ 0.012	0.19 $\pm$ 0.01	0.164 $\pm$ 0.006
2	190	1275 $\pm$ 61	1060 $\pm$ 11	0.168 $\pm$ 0.013	0.146 $\pm$ 0.01	0.139 $\pm$ 0.005
3	205	690 $\pm$ 53	400 $\pm$ 8	0.091 $\pm$ 0.007	0.056 $\pm$ 0.005	0.053 $\pm$ 0.003
4	235	210 $\pm$ 46	160 $\pm$ 7	0.028 $\pm$ 0.006	0.018 $\pm$ 0.005	0.021 $\pm$ 0.002
5	290	1350 $\pm$ 62	1135 $\pm$ 10	0.177 $\pm$ 0.013	0.172 $\pm$ 0.005	0.150 $\pm$ 0.005
6	325	640 $\pm$ 52	455 $\pm$ 8	0.084 $\pm$ 0.008	0.065 $\pm$ 0.007	0.060 $\pm$ 0.003
7	340	1850 $\pm$ 65	1660 $\pm$ 10	0.243 $\pm$ 0.016	0.223 $\pm$ 0.005	0.219 $\pm$ 0.007
8	355	5400 $\pm$ 82	5200 $\pm$ 18	0.710 $\pm$ 0.028	0.735 $\pm$ 0.01	0.683 $\pm$ 0.02
9	385	--	4125 $\pm$ 20	--	0.562 $\pm$ 0.005	0.543 $\pm$ 0.015
10	420	240 $\pm$ 46	150 $\pm$ 7	0.032 $\pm$ 0.007	0.01 $\pm$ 0.005	0.020 $\pm$ 0.002

PLANS FOR FUTURE WORK One or two more dynamic experiments in the manganese-removal study are planned to define more closely the problem of activity buildup on the counting-cell walls. After these runs are completed, work will begin on a new application of intrinsic radiotracer control of impurity removal.

Graft-Polymerization Studies

F. A. Sliemers, E. Gülbaran, W. B. Gager,
J. F. Kircher, and R. I. Leininger

OBJECTIVE To determine the influence of structural and compositional factors on the behavior of polymers subjected to gamma irradiation and to correlate the radiation-induced changes which occur with the ability of the polymer to form graft copolymers.

PROGRAM APPROACH It is anticipated that a mechanism of radiation attack on the various polymer systems can be established. Polymers are irradiated in vacuo to various total doses. Free-radical site concentrations are determined both as a function of dose and as a function of time, using electron paramagnetic resonance (EPR) measurements. Vapor-phase chromatography and mass spectrometry are used to determine quantitatively the volatile fragments of the irradiation. Grafting techniques are employed to correlate free-radical site concentrations and grafted copolymer.

PROGRESS REPORTED PREVIOUSLY A number of polyalkylmethacrylates have been examined extensively. The data suggest that: (1) free-radical formation is accomplished by means of hydrogen scission or complete or partial ester scission, (2) the size and configuration of the hydrocarbon tail of the ester group influence the efficiency of site formation, (3) site formation is accompanied, in some cases, by a scission on the polymer backbone, and (4) the amount of graft

copolymer is influenced by polymer structure as well as by the concentration of available free-radical sites. More recently, the work has been extended to other polymer systems.

WORK THIS PERIOD The study of the effect of molecular weight on site formation has been completed using PMMA. The data, presented in Table H-2, indicate that the efficiency of site formation decreases with increasing polymer molecular weight. The efficiency of site formation is expressed as free radicals per monomer unit per unit dose.

TABLE H-2. EFFECT OF POLYMER MOLECULAR WEIGHT ON SITE FORMATION IN POLYMETHYLMETHACRYLATE

Dose, rads	Sites per Monomer Unit $\times 10^3$ (a)				
	$M_w=30,900^{(b)}$	$M_w=225,000$	$M_w=267,000^{(c)}$	$M_w=295,000$	$M_w=436,000$
3×10^5	0.33	--	--	--	0.18
5×10^5	--	0.34	--	0.39	0.42
6×10^5	0.54	--	0.25	--	0.73
1×10^6	0.92	--	0.81	--	0.84
					0.73
3×10^6	3.07	2.35	2.00	1.61	0.70
5.5×10^6	--	3.38	--	2.84	0.54
1×10^7	5.80	--	3.64	--	1.27
1.4×10^7	--	2.90	--	2.70	--
					1.00
3×10^7	5.45	3.36	3.54	2.34	0.77

(a) By EPR measurements.

(b) $M_n = 4,400$ (boiling-point-elevation method).

(c) $M_n = 11,400$ (boiling-point-elevation method).

During the month, the investigation of the influence of total dose on site formation for polymethylacrylate (PMA) was continued. The new data, Table H-3, support the previous hypothesis that molecular mobility is of considerable importance in the production of long-lived free radicals in cross-linking polymers. In the irradiation of PMA, measurable numbers of free-radical sites are formed considerably more rapidly in preirradiation cross-linked material than in previously unirradiated material. The preirradiated polymer would, of course, have a considerably greater molecular weight and a correspondingly reduced mobility. The rigid network appears to provide adequate free-radical "shielding" and, consequently, sites produced in these surroundings are long lived. It should be noted that the effect of molecular weight on site formation in cross-linking polymers is apparently the reverse of that found for degrading polymers.

Site measurements versus dose have been made for polyvinyl acetate. The polymer was prepared by irradiation of the monomer in bulk. It has the structure

The results of the site measurements, listed in Table H-4, show that the

efficiency of free-radical formation is quite low. Again, as in the case of the PMA, we are dealing with a cross-linking material, and, probably, polymer mobility has not been reduced to the point where large numbers of stable sites can be produced.

The volatile products from the irradiation of polycyclohexylmethacrylate have been measured quantitatively by means of mass spectrometry and vapor-phase chromatography. The data from this study are now being analyzed.

PLANS FOR FUTURE WORK During March, the anticipated program of work will include: (1) analysis of the volatile-fragment data obtained for polycyclohexylmethacrylate, (2) initiation of an investigation of site formation in polyacrylic acid and polyisopropenyl acetate (the α -methyl derivative of polyvinyl acetate), and (3) volatile-product analysis of polyacrylic acid. It is also hoped that the study of site formation in the four isomeric butylmethacrylates can be continued.

Development and Evaluation of Safety Performance Standards for Sealed Radiation Sources

C. W. Townley, R. B. Price, J. M. Fackelmann, C. L. Selander,
R. A. Ewing, and D. N. Sunderman

OBJECTIVE To develop and evaluate safety performance criteria for sealed radiation sources.

PROGRAM APPROACH During Phase I of this program, sealed radiation sources and their applications are being surveyed to accumulate information on current source design, fabrication techniques, composition, and applications. Upon evaluation of these data, safety performance criteria and a classification scheme will be established, and appropriate test procedures selected and developed to measure performance against these standards.

PROGRESS REPORTED PREVIOUSLY Questionnaires were sent to all organizations in North America known or believed to manufacture sealed sources, requesting information on source design, fabrication techniques, composition, testing procedures used, and applications. A similar questionnaire was also sent to manufacturers of devices containing sealed sources.

Preliminary studies were initiated on the development of performance criteria and of possible test procedures for their measurement. A survey was begun of standard test procedures from other industries which might be applicable to the testing of sealed sources.

TABLE H-3. SITE FORMATION IN POLYMETHYLACRYLATE

Dose, rads	Sites per Monomer Unit $\times 10^4$ (a)	
	No Preirradiation Treatment	Preirradiated to 2.3×10^7 Rads
2×10^5	N.M.(b)	--
5×10^5	0.96	--
6×10^5	--	N.M.(b)
1×10^6	N.M.(b)	4.82
3.4×10^6	0.84	--
5×10^6	1.63	2.78
1×10^7	2.26	2.93
2×10^7	--	3.42
2.4×10^7	2.47	--
4.1×10^7	3.83	--
1.4×10^8	1.87	--

(a) By EPR measurements.

(b) Not measurable.

TABLE H-4. SITE FORMATION IN POLYVINYL ACETATE

Dose, rads	Sites per Monomer Unit $\times 10^4$ (a)
5×10^5	0.25
1×10^6	1.66
3.5×10^6	0.83
6×10^6	0.47
1×10^7	0.78
3×10^7	3.29

(a) By EPR measurements.

WORK THIS PERIOD Letters of inquiry to ascertain the current regulatory status have been sent to the appropriate Federal, state, and municipal agencies. Replies received so far indicate a considerable awareness of the problem among those states where sealed-source applications are concentrated. In general, state regulations tend to be equally or more restrictive than Federal regulations.

Similar inquiries have been sent to advisory technical groups, and to insurance and standards associations with interests in radiation protection, to establish the current state of technology and efforts in the area of sealed sources. Although safety performance criteria for sealed sources are not under current investigation by any of the organizations contacted, the consensus seems to be that such a program is needed.

The search for already available standard test procedures which might be suitable for application to the testing of sealed sources has been continued.

PLANS FOR FUTURE WORK A number of source and device manufacturers are to be visited to develop more detailed information on source designs, fabrication techniques, current testing procedures, and failure-experience data than that furnished by the replies to the questionnaires. With this information, evaluation of the applicability of potential test methods will begin.

ASSISTANCE TO AEC-EURATOM PROGRAM

H. M. Epstein and D. L. Keller

Studies concerned with obtaining information on void-content and heat-transfer relationships in forced-convection two-phase flow in light-water systems and with the development of uranium mononitride as a possible fuel material are under way for the Joint U. S. -Euratom Research and Development Board. Both programs are directed toward obtaining data that will be useful in efforts to achieve more economical nuclear power.

The most important property of two-phase flow for the reactor designer is the boiling-void distribution since the amount and distribution of the vapor will have a major effect on the reactor kinetics as well as on the critical dimensions. Since no general correlation of the void distribution has been proven reliable over the wide range of reactor variables, data from the study of boiling-void distribution will be interesting to those working in this field.

Uranium mononitride is a high-melting-point compound possessing a particularly high uranium density. As a dispersion fuel in stainless steel its behavior during irradiation is similar to UO_2 . However, little is known about its irradiation resistance in bulk form or about practical methods of fabricating the material into dense bodies. Therefore, the program on uranium mononitride is concerned with establishing the basic feasibility of this material as a reactor fuel. It will include an evaluation of the most promising methods of fabricating UN, the determination of several physical and mechanical properties of UN, and the preparation, irradiation, and evaluation of UN bodies (both clad and unclad) of three different enrichments.

VOID-DISTRIBUTION AND HEAT-TRANSFER STUDIES

R. O. Wooton, F. G. Peter, J. J. Foglia,
H. M. Epstein, and J. W. Chastain

OBJECTIVE To investigate axial void distribution and heat transfer for rectangular coolant passages over a range of experimental conditions of interest in light-water reactors.

PROGRAM APPROACH A positive-displacement pump is used to circulate distilled water in a closed, pressurized loop consisting of piping, accumulator, preheater, heat exchanger, test section, condenser, and sump.

The void distribution in the test section is measured using a beta-ray attenuation technique. The experimental void fractions are correlated in terms of the significant heat-transfer parameters such as mass flow rate, fluid temperature, heat flux, slip ratio, and quality.

PROGRESS REPORTED PREVIOUSLY Test runs were made in the pressure range from 700 to 1300 psi, with mass flows of 550, 800, and 950 lb per hr.

Calculations of slip ratio with d-c power heating the test section indicated that there was less scattering than with a-c power.

A heat exchanger was designed and installed to correct variations in temperatures due to power fluctuations in the line.

WORK THIS PERIOD Tests with d-c power were continued and concentrated in the pressure range from 900 to 1000 psi with mass flows of 800 and 950 lb per hr.

The results indicated that the use of a heat exchanger guarantees the stability of the inlet temperature to the test section.

PLANS FOR FUTURE WORK Preparation of a topical report presenting data and correlations is in progress.

DEVELOPMENT OF URANIUM MONONITRIDE

Powder-Metallurgy Studies

S. J. Paprocki, D. L. Keller, H. J. Stoecker, and E. O. Speidel

OBJECTIVE To develop a method for fabricating high-density uranium mononitride bodies suitable for property measurements and irradiation testing.

PROGRAM APPROACH Cold pressing and sintering, isostatic hot pressing by the gas-pressure-bonding technique, and rotary swaging are the primary fabrication techniques being investigated.

PROGRESS REPORTED PREVIOUSLY Little densification of UN powder by vacuum sintering has been effected at temperatures low enough to prevent decomposition of the UN. At apparent temperatures of 1800 C and above, a free-uranium liquid phase occurs.

Rotary swaging of pellets in stainless steel cans consolidates the powder up to 85 per cent of theoretical density but no interparticle bonding is achieved.

The maximum density obtainable by isostatic hot pressing in stainless steel cans for 3 hr at 10,000 psi at temperatures up to 1290 C appears to be about 87 per cent.

WORK THIS PERIOD Two specimens isostatically hot pressed in Armco iron cans at 1340 C and 5 tsi for 3 hr reached densities of 11.5 and 12.4 g per cm³ or 80 and 86 per cent of theoretical. A specimen pressed in niobium at 1425 C at the same pressure and time reached a density of 13.4 g per cm³ or 93.5 per cent of theoretical. Molybdenum-canned specimens pressed at 1480 C under the same conditions exhibited densities up to 13.6 g per cm³ or 95.0 per cent of theoretical.

There were reactions between the UN cores and the cladding all cases, but none was severe.

The dense cores pressed in the molybdenum cans could not be removed intact because of numerous thin cracks in the cores. These cracks are believed to result from tensile stresses produced in the UN cores during cooling by the difference in thermal expansion of the UN and molybdenum. The molybdenum cladding loses ductility and becomes very brittle.

Hardness traverses across this dense UN both longitudinally and transversely gave Knoop hardness numbers ranging from 582 to 644 with an average of 607. This brittle UN shatters into numerous smaller particles when impacted.

Two approximately 0.5-g samples were immersed in water, one in room-temperature water and one in boiling water, for 89 hr with no apparent attack other than darkening of the specimen in the hot water. These data are quite encouraging in that they furnish an indication that UN will not be significantly attacked by moisture in the air. This could reduce substantially some of the storage problems. A larger specimen of about 2.4 g in saturated steam at 500 F for 24 hr fractured into six small pieces. There was oxidation and some powdering of the surface of the pieces. These specimens are being examined further by metallography. Molybdenum-clad UN core assemblies sheathed in Type 304 stainless steel were swaged at 600 and 1800 F through about 30 per cent reduction in area, but the molybdenum failed. Wrinkles and longitudinal cracks extending the length of the tubing were imparted to the molybdenum.

PLANS FOR FUTURE WORK Uranium mononitride cores swaged in Type 304 stainless steel to about 80 to 85 per cent of theoretical density are being hot pressed. Cores in both molybdenum and niobium cans have been hot pressed at 1480 C and are being evaluated. The amount of densification appears comparable. Less cracking of the UN cores is expected in the niobium.

Melting and Casting Studies

R. W. Endebrock, J. Bugl, E. L. Foster, and R. F. Dickerson

OBJECTIVE To produce by melting and casting techniques a limited number of dense UN bodies to be used for the determination of physical and mechanical properties and for irradiation tests.

PROGRAM APPROACH The conversion of uranium metal to the mononitride in a nitrogen atmosphere is the basis of an arc-melting process under study. Calculations from existing thermochemical data indicate that the UN system is sensitive to relatively minor changes in pressure and temperature at or above the melting point of UN. Consequently, the program approach requires that the relationships must first be established in order to produce sound specimens, and then specimens must be prepared for physical-property determinations and irradiation studies.

PROGRESS REPORTED PREVIOUSLY Reaction is viturally complete after 10 min of arc melting uranium in nitrogen at 3 atm of pressure. Nitrogen content of buttons was shown to vary widely with arc amperage and, therefore, temperature. By reducing the arc amperage at the end of the melt the nitrogen content of the button was raised 15 per cent. An investigation of the effect of pressure has shown that the nitrogen content varied from 3.15 w/o in a button produced at

1/4 atm to 4.82 w/o in one produced at 3 atm. Extrapolation of the data indicates that stoichiometric material can be produced by direct arc-melting procedures at about 10 atm of nitrogen pressure. However, exploratory tests in the 10 to 24-atm pressure range did not increase the nitrogen content of buttons significantly above the nitrogen content of buttons prepared at 3 atm. As pressure was raised, the distance from the electrode to the melt became much less, the melting area became smaller, and "smoke" completely obscured the arc.

Attempts to attain stoichiometry by heating substoichiometric bars of UN by induction heating at or just below the melting point of UN produced a thick UN surface coating, but the process appeared to be too slow to be practical.

WORK THIS PERIOD Various melting tests were conducted during this period in an attempt to define the variables of arc and furnace control at high nitrogen pressures. In one test, heat losses were reduced by stacking insulating blocks around the arc zone and the hearth. The metallographic structure of a button produced by arc melting under 10 atm of nitrogen pressure and at 350 to 400 amp and 40 v was compared with one produced without insulation. The button prepared with insulation contained much less second-phase uranium, and consequently more nitrogen, than the one prepared without insulation. Large striated bands of nearly pure UN were observed in the button prepared using the insulating block.

A high-frequency arc voltage starter was superimposed on the direct-current arc during the preparation of a button in an attempt to ionize nitrogen in the melt area and to give a more stable arc. Metallographic inspection of the button generated in this test showed a structure containing considerably more uranium than when the high-frequency arc was not used.

It is of interest that at a 10-atm or higher nitrogen pressure during arc melting of uranium the arc disappears from view because of the formation of a dense smoke that is formed during melting and which collects on the furnace sidewalls as a finely divided, brownish-black powder. This powder was analyzed by X-ray diffraction and was found to be composed of about 70 to 80 per cent UN₂, 10 to 15 per cent UN, and 5 to 10 per cent of a third phase tentatively identified as tungsten nitride (from the tungsten electrode).

Since arc melting uranium under 1/2 atm of nitrogen produces a substoichiometric material containing at least 3.5 w/o nitrogen or 63 w/o UN, a test was conducted to determine whether an alloy of UN and UC could be produced under 1/2 atm of nitrogen pressure which would result in a single-phase U(C,N) alloy. Carbon was first added to the uranium to produce a button containing 46 w/o UC. This button was then melted for 10 min under 1/2 atm of nitrogen in an effort to produce a 54 w/o UN-46 w/o UC solid-solution alloy. The material produced was relatively homogeneous, but still contained uranium metal. Analysis showed that the button contained only 1.54 w/o nitrogen (or about 30 w/o UN) instead of the 3.0 w/o nitrogen expected.

PLANS FOR FUTURE WORK More tests are planned to help define the parameters required to attain stoichiometric UN in the arc-melting process. A series of buttons is to be produced under 10 atm of nitrogen at 350 to 400 amp but with arc potentials of 20, 40, and 80 v to determine the effect of electrode distance on homogeneity and UN stoichiometry. Certain additives, such as hydrogen to the nitrogen atmosphere or such as tin to the charge metal are to be investigated as aids for producing a longer, more stable arc. In addition, UN powder compacts are to be

melted under high nitrogen pressures to compare the dissociation of UN with the reaction kinetics of the uranium-nitrogen reaction.

Irradiation of UN Specimens

P. B. Shumaker, G. E. Raines, and J. H. Stang

OBJECTIVE To investigate the integrity of UN bodies irradiated to high burnups in capsules designed to minimize specimen temperatures in-pile.

PROGRAM APPROACH Six noninstrumented capsules are being prepared for irradiation of UN specimens containing depleted (approximately 0.3 per cent uranium-235) and natural (approximately 0.7 per cent uranium-235) uranium and uranium enriched approximately 5 per cent. The capsules will be irradiated at the Materials Testing Reactor for approximately 6 months in thermal-neutron fluxes selected to provide specimen-effective fluxes of approximately 1×10^{14} nv. This exposure will produce in the specimens (1) uranium-235 burnups of approximately 60 per cent, (2) a fairly wide range of fractional burnup of all the uranium atoms originally present, and (3) a fairly constant amount of matrix hydrogen as a result of the (n,p) reaction with nitrogen. The combination of (2) and (3) is desired to gain semiquantitative information relative to irradiation-damage effects owing to hydrogen accumulation in the UN.

PROGRESS REPORTED PREVIOUSLY Preliminary heat-transfer calculations were made to ascertain specimen-surface temperature conditions during irradiation as a function of flux and enrichments. These early computations were based on the use of sodium as the capsule heat-transfer medium and indicated that, in the maximum heat-generation cases (i. e., specimens enriched to 5 per cent), the surface temperature of unclad 0.30-in.-diameter specimens receiving an effective flux of 1×10^{14} nv will be approximately 500 F. Recently, sodium has been abandoned in favor of NaK, and, as a result, temperatures now estimated (see below) are somewhat higher than these prior estimates.

Brief laboratory experiments were initiated to examine the compatibility of the UN-NaK-aluminum combination at 500 and 900 F.

WORK THIS PERIOD Final plans were made for the capsule-irradiation program. Among the modifications to plans made earlier are the following:

- (1) NaK will be substituted for sodium as the heat-transfer medium to minimize the handling problems during the postirradiation examinations.
- (2) One capsule containing 5 per cent enriched specimens will be irradiated with a specimen-effective thermal-neutron flux of approximately 5×10^{13} nv. The remaining capsules will adhere to the original 1×10^{14} nv specification.
- (3) Several specimens will be clad either with stainless steel or with molybdenum.

Further study was made of specimen-temperature levels with results listed in Table I-1. These estimates are based on the following assumptions:

- (1) A cladding thermal conductivity of 12 Btu/(hr)(ft)(F)
- (2) A specimen diameter of 0.3 in.
- (3) An effective thermal-neutron flux of 1×10^{14} nv
- (4) No gamma heat production in the specimen or aluminum capsule
- (5) A reactor water temperature of 120 F.

TABLE I-1. ESTIMATED FUEL-SURFACE TEMPERATURES WITH UN SPECIMEN RECEIVING AN EFFECTIVE FLUX OF 1×10^{14} nv

Type of Specimen	Uranium-235 Content, per cent	Fuel-Surface Temperature, F
Unclad specimens		
Enriched	5.0	720
Enriched (in a flux of 5×10^{13} nvt)	5.0	420
Natural	0.72	215
Depleted	0.30	165
Clad specimens		
Enriched	5.0	757
Enriched (in a flux 5×10^{13} nvt)	5.0	435
Natural	0.72	220
Depleted	0.30	167

The capsule design was completed during February. While not provided with thermal instrumentation, the capsules will be well dosimetered. In addition to conventional internal dosimeter wires immediately adjacent to the specimens, removable dosimeter wires will be attached to the outer surface of each capsule. One or two of these outside dosimeters will be removed periodically to determine the accumulated exposure. Since the cobalt content of these wires will be relatively low (0.1 w/o cobalt in aluminum), they will not become activated to the point that their analysis will require remote manipulations.

The UN specimens exposed at 500 F for approximately 1000 hr in the NaK-aluminum-UN compatibility study were removed and examined. Preliminary observations have indicated no gross attack. A black residue found on the wall of the aluminum liner is being analyzed spectrographically. Another pair of specimens is being exposed at 900 F; this experiment is still in progress.

PLANS FOR FUTURE WORK Capsule parts will be fabricated during March and the first capsule should be assembled early in April, provided specimens are available. The remaining capsules will be constructed during April and May.

The remaining compatibility test will be terminated in March and the specimens examined.

MATERIALS DEVELOPMENT AND EVALUATION (HAPO)

F. R. Shober

Research and development is being conducted on materials to be used in conjunction with construction of the NPR (New Production Reactor) and operation of the PRTR (Plutonium Recycle Test Reactor) at the Hanford Atomic Products Operation. The creep properties of Zircaloy-2 at elevated temperatures are being studied in an effort to determine the feasibility and advisability of using Zircaloy-2 for process-tube material. Changes in thermal and electrical properties of UO_2 resulting from irradiation and fabrication techniques are important in relation to the operational characteristics of the PRTR. Also in support of the PRTR program studies to develop a metallic container material for the HAPO fused chloride-electrolytic fuel-recovery process are in progress. These three studies, although not directly related, contribute to the over-all program at HAPO.

Mechanical Properties of Zirconium Alloys

J. A. VanECHO

OBJECTIVE To obtain creep and creep-rupture data, especially long-term creep (25,000 to 30,000 hr), on annealed and cold-worked Zircaloy-2 sheet and to evaluate the effect of stress and/or temperature cycle on the creep properties of this material.

PROGRAM APPROACH All tests are made in vacuum in standard Battelle creep machines and furnaces. Temperatures of interest include 550, 650, and 750 F. Creep measurements are taken daily by means of an optical system. In all respects, the tests meet or exceed the requirements for creep testing specified in ASTM Standard E139-58T.

PROGRESS REPORTED PREVIOUSLY Twenty creep tests are in progress. All except one of these tests have been in progress for times ranging from about 4,000 to 28,000 hr. Therefore, test results on 19 tests have been reported from time to time in the past. The monthly report for December, 1960, (BMI-1489) contains a table of results as of the end of that month. Since all are long-time creep tests, there is little change in creep rate or total deformation from month to month.

WORK THIS PERIOD The 19 creep tests mentioned in the previous section have been continued through February. Except for incremental changes in creep rate and total deformation, the results as of the end of February are largely the same as reported in BMI-1489. There is, of course, an additional accumulation of 672 hr of test time to each test. The tests in progress include:

- (1) Two long-time (26,000 to 28,000 hr) creep tests on 15 per cent cold-worked Zircaloy-2 sheet at 650 and 700 F
- (2) Twelve long-time (10,000 to 17,000 hr) creep tests on annealed Zircaloy-2 sheet at 550, 650, and 750 F

- (3) Five creep tests (4000 to 7000 hr) on annealed sheet at 550 and 650 F with both stress and temperature cycled to zero and room-temperature 1 day a week
- (4) One test just started at 550 F and 20,000 psi on a specimen taken from an annealed section of a PRTR pressure tube.

PLANS FOR FUTURE WORK The 20 creep tests described above are scheduled to continue through March. When it is evident that no additional information can be gained, the tests will be discontinued one by one. Emphasis will then be placed on starting more tests on the PRTR pressure tube at 450 F as well as at 550 F. Similar work is also tentatively planned on sections of the NPR pressure tubing.

Thermal Conductivity and Electrical Conductivity of UO_2

H. W. Deem and C. F. Lucks

OBJECTIVE To measure the thermal and electrical conductivity of irradiated and unirradiated UO_2 .

PROGRAM APPROACH An apparatus based on a steady-state, absolute, thermal-conductivity method has been assembled for the thermal-conductivity measurements of the irradiated UO_2 . Existing Battelle equipment is being used for the unirradiated thermal- and electrical-conductivity measurements.

PROGRESS REPORTED PREVIOUSLY Details concerning the assembly of a thermal-conductivity apparatus, its calibration, and the measurements of four control UO_2 specimens were summarized in BMI-1448(Rev). Included in the report are data on the thermal conductivity of an irradiated UO_2 specimen with a burnup of 0.005 a/o. Also included in the summary are data on the electrical conductivity of the four control specimens.

Tentative thermal-conductivity data were reported for an irradiated UO_2 specimen having a burnup of 0.016 a/o in BMI-1455.

Final thermal-conductivity data were reported for a sintered UO_2 disk specimen, identified as Fabrication Specimen A, in BMI-1489. Interpolated values at 200, 800, and 1400 C were 0.067, 0.034, and 0.025 w/(cm)(C), respectively, for 100 per cent theoretical density.

Techniques have been worked out for making thermal-conductivity measurements on vibrationally compacted powder UO_2 specimens.

WORK THIS PERIOD Work is continuing on the thermocouple repairs of the thermal-conductivity apparatus at the hot cells. All components of the electrical-resistivity-measuring apparatus have been assembled and are being put together for measuring the electrical resistivities of the irradiated UO_2 specimens. Additional unirradiated specimens have been received from HAPO.

PLANS FOR FUTURE WORK During the next work period measurements will begin on the unirradiated UO_2 specimens. The electrical-resistivity assembly will be completed and measurements begun on the irradiated UO_2 specimens. Thermal-conductivity measurements will also begin on the 0.0615 a/o burnup specimen.

Materials of Construction for the
Fused Chloride-Electrolytic UO_2 Process

E. L. White, P. D. Miller, D. C. Drennen, C. H. Lund,
A. M. Hall, and W. K. Boyd

OBJECTIVE To develop a metallic container material for the HAPO fused chloride-electrolytic fuel-recovery process.

PROGRAM APPROACH Several commercially available metals and alloys were screened as candidate materials of construction by using a bench-scale apparatus employing chlorine to produce uranyl chloride from uranium oxide. At present, a series of experimental iron- and nickel-base alloys, designed for this application on the basis of the results of the screening program, are being evaluated by weight changes during exposure to a 750 to 800 C equimolar solution of sodium and potassium chlorides containing U_3O_8 and sparged with chlorine.

PROGRESS REPORTED PREVIOUSLY Fourteen experimental-alloy compositions were melted, cast and cut into pieces for corrosion evaluation.

WORK THIS PERIOD The iron- and nickel-base alloys listed in Table J-1 in BMI-1496 have been exposed for 8 hr to the conditions noted above. The results are tabulated in Table J-1, along with the values for the four materials reported

TABLE J-1. CORROSION RATES OF EXPERIMENTAL ALLOYS IN FUSED-CHLORIDE
METALS SPARGED WITH CHLORINE AT 750 TO 800 C

Material	Corrosion Rate, mils per month		
	Below Sparge	Near Sparge	Interface
68Ni-32Al	40	50	70
Alloy 1	100	400	700
Alloy 2	60	3	20
Alloy 3	50	70	300
Alnico 3B	200	300	400
Alloy 4	200	100	100
Alloy 5	100	200	500
Alloy 6	500	400	1300
Alloy 7	80	300	800
Unitemp 600	200	300	600
Alloy 8	200	200	400
Alloy 9	200	500	1900
Alloy 10	300	300	1500
Alloy 11	300	500	800
Alloy 12	200	200	1000
Hastelloy B	200	500	200
Alloy 13	100	100	100
Alloy 14	600	1400	3100

previously which were the basis for the choice of the new alloys. It can be seen that Alloys 2 and 3 confirm the effectiveness of nickel-aluminum combinations in reducing corrosion. In addition, the results for Alloy 4 show that an increase in the aluminum content of the Alnico 3B type also increases the resistance to corrosion. Additions of copper and molybdenum did not improve this type of alloy.

The modified superalloys (Alloys 8 through 11) did not show any marked improvement in corrosion resistance. However, the removal of the chromium from the Unitemp 600 composition did increase the resistance to attack by almost 30 per cent.

Alloy 13, which represents the addition of aluminum to the Hastelloy B type, showed a decided increase in corrosion resistance.

PLANS FOR FUTURE WORK Additional experimental-alloy compositions are being planned as a result of the work just completed.

COATED-PARTICLE FUEL MATERIALS (AEC-DRD)

R. W. Dayton and J. H. Oxley

This program is being carried out to determine the characteristics of various coated-particle fuels and to develop optimum materials for specific reactor applications. Various combinations of fissionable-core, protective-coating, and matrix-support materials are to be evaluated in terms of fission-product retention as a function of burnup and operating temperature.

There have been five tasks outlined within the scope of this development program. Tasks I, II, and III concern the optimization of the full capabilities of the three most promising coating materials, alumina, and pyrolytic carbon. Investigation of other possible coatings will be carried out during Task IV, while Task V will involve the evaluation of coated-particle materials produced commercially.

The immediate objective of Task I of this program is to evaluate fully a fuel material containing approximately 125- μ uranium dioxide particles coated with 40 μ of alumina. Limited evaluation of irradiated material of this type from the Sanderson & Porter program has been authorized and is in progress. In addition, preliminary experimental studies are being carried out on carbon-coated fissile materials. These studies are currently aimed at developing coating methods and studying the radiation behavior of the materials.

EVALUATION OF COMMERCIAL PRODUCTS

T. S. Elleman and D. N. Sunderman

OBJECTIVE To provide information on the availability and quality of coated fuel particles from commercial sources.

PROGRAM APPROACH Interested manufacturers of coated particles who request information on the Coated-Particle Program are sent a standard form letter and summary of the evaluation procedures presently used for coated particles. Battelle is authorized to purchase 100-g lots of coated fuel particles at a price of \$1 per g and to report the results of an evaluation of this material in this section of the report.

PROGRESS REPORTED PREVIOUSLY Requests for information on this program from 16 interested commercial firms have been received and answered.

WORK THIS PERIOD A request for information on this program from one additional interested commercial firm was received and answered.

PLANS FOR FUTURE WORK No future work is contemplated until offers of commercial products are received.

COATING STUDIES

Al₂O₃ Coatings on Fuel Particles

M. F. Browning, V. M. Secrest, and
J. M. Blocher, Jr.

OBJECTIVE To establish the conditions and equipment for coating fuel particles with Al₂O₃ of optimum quality.

PROGRAM APPROACH Alumina is being deposited on UO₂ particles by hydrolysis of Al₂Cl₆ vapor in a fluidized bed. The coatings are being evaluated by microscopic examination, measurement of physical properties, alpha counting, and fission-gas release on postirradiation heating. Promising materials will be evaluated by in-pile tests at elevated temperatures.

PROGRESS REPORTED PREVIOUSLY A general summary of the experimental work on Al₂O₃-coated particles prepared prior to this program is given in BMI-1471.* Modifications of the fluidized-bed reactor design and water-vaporizer system have improved process control and have extended the operating time to permit deposition of coatings of the desired thickness without interruption. The following specific samples for in-pile evaluation have been prepared:

<u>Lot</u>	<u>Type</u>
17682-78-715A	Dense Al ₂ O ₃ on dense UO ₂
17847-8-717B	Dense Al ₂ O ₃ on porous UO ₂
17652-64-612A	Dense Al ₂ O ₃ over porous Al ₂ O ₃ on porous UO ₂

WORK THIS PERIOD Coated-particle lots listed above were subjected to a series of screening tests to evaluate their suitability for in-pile testing. Process and evaluation data for these materials are summarized in Table L-1.

An effort was made to up-grade the three lots of coated particles for in-pile study. Materials were screened, the particles greater than 210 μ in diameter were leached in hot concentrated HNO₃, and samples were chosen to minimize the occurrence of thinly coated and uncoated particles.

Lot 715A satisfactorily passed the screening tests and samples have been submitted for incorporation in specimens for in-pile evaluation. Certain of the out-of-pile evaluations have not been completed, but only those evaluations that have not been shown to be critical in ascertaining the suitability of the coated materials for in-pile evaluation are still incomplete.

The dense Al₂O₃-coated porous UO₂, Lot 717B, was found to be somewhat inferior to Lot 715A on the basis of postirradiation fission-gas release above 1230 C. It was

*Browning, M. F., Veigel, N. D., Cook, T. E., Diethorn, W. S., and Blocher, J. M., Jr., "Alumina Coating of UO₂ Shot by Hydrolysis of Aluminum Chloride Vapor", BMI-1471 (October 25, 1960), pp 1-12.

suspected that the inferior results obtained in the activation test were caused by the failure of isolated particles. A 20-g sample of Lot 717B was thermal cycled five times to 1350 C in helium and oxidized 48 hr in oxygen at 1100 C to crack any weak particles. This treatment was followed by a HNO_3 leach to dissolve exposed UO_2 . A portion of this sample has been alpha counted and is now being checked for fission-gas release after activation. The remainder will be considered for in-pile evaluation after the fission-gas release results are available. The neutron-activation test should be completed by March 6.

Lot 612A, dense Al_2O_3 over porous Al_2O_3 -coated porous UO_2 , was found to have fission-gas-release properties inferior to those of both Lots 715A and 717B above 1070 C. The additional evaluation tests indicated that conditions other than defects in isolated particles caused the cracking and excessive fission-gas release. It is suspected that the transition of porous amorphous Al_2O_3 at elevated temperatures to crystalline Al_2O_3 is a factor. This assumption is being investigated further. It should be noted that the temperature at which Lot 612A showed excessive fission-gas release is above the temperature expected in the in-pile tests. However, the maximum temperature used in fabrication of the graphite-matrix specimens is 1230 C and, therefore, if coating failure is due to a temperature effect, further experimentation may be required to solve this problem.

PLANS FOR FUTURE WORK Evaluation of the Al_2O_3 -coated enriched UO_2 materials and additional coating studies, if necessary, will be continued. Experimental work to further improve the Al_2O_3 coating procedure will be carried on at a reduced rate of effort. Temperature and rate of coating application are the variables of immediate interest.

TABLE L-1. SUMMARY OF EVALUATION TESTS

Lot ^(a)	Base Material	Coating Temperature, C	Coating Thickness, μ	UO ₂ ^(b) , w/o	Treatment	Knoop Hardness (50-G Load)	Effect of Thermal Cycling ^(c)	Crush Test ^(d)		
								Average Coating Thickness, μ	Particle Diameter, μ	Average Strength, g
17652-64-612A	Product 716A and 612J-01-JK 127 $\pm$ 22- μ enriched UO ₂ ; crush strength, 120 g	Dense, 1000; porous, 700	Dense, 7-12; porous, 7-12, and dense, 15-23	42.2	As prepared	Dense, 2000-2300; porous, 200-600	--	40	240	750
					4-hr leach in HNO ₃	--	Some discoloration	--	--	--
					Leached, thermal cycled	--	--	--	--	--
					Leached, oxidized	--	--	--	--	--
17682-78-715A	Product 715 K-01-JX 127 $\pm$ 22- μ enriched UO ₂ ; crush strength, 160 g	1000	40-50	34.9	As prepared	2300-2600	No effect	45	260	2101
					4-hr leach in HNO ₃	--	--	--	--	--
					Thermal cycled	--	--	--	--	--
17847-8-717B	Product 717 and 717A J-01-JX 127 $\pm$ 22- μ enriched UO ₂ ; crush strength, 120 g	1000	35-50	34.1	As prepared	2050-2400	--	50	290	1800
					4-hr leach in HNO ₃	--	No effect	--	--	--
					Leached, thermal cycled	--	--	--	--	--
					Leached, oxidized	--	--	--	--	--
					Thermal cycled, oxidized, leached	--	--	--	--	--

(a) UO₂ was flashed with 6 μ of Al₂O₃, acid leached, and the coating continued in clean equipment to prevent uranium contamination of coating.

(b) Determined by chemical analysis.

(c) Thermal cycled between 200 C and 1350 C five times in a dry helium atmosphere with 10 min at each temperature. Evaluation by microscopic examination.

(d) Average load necessary to crush a single particle. Largest diameter particles selected so the coating thickness could be assumed to be a maximum average. Surface irregularities of the coating prevented an accurate measurement of the diameter of the unsectioned coated particle.

(e) Determined spectrographically.

(f) Activity ratio is defined as the weight of uranium detected by radiochemical analysis of the coated particles divided by the weight of contained uranium within the coated particles.

(g) Indirect gamma assay consists of suspending the particles in high-purity silica gel, irradiating the mixture, separating the particles from the gel, and analyzing the gel for recoiled fission fragments by gamma-ray spectroscopy.

4

Carbon Coatings on Fuel Particles

A. C. Secrest, R. B. Landrigan, V. M. Secrest,
M. F. Browning, and J. M. Blocher, Jr.

OBJECTIVE To establish conditions for coating fuel particles with pyrolytic carbon of optimum quality.

PROGRAM APPROACH Pyrolytic-carbon coatings are being applied by the decomposition of hydrocarbons in a tumbling-bed reactor at temperatures above 1500 C, as well as in a fluidized bed of particles at temperatures below 1500 C. The coatings are being evaluated by means of microscopic examination, measurement of physical properties, direct alpha counting, and fission-gas release on post-irradiation heating. Promising materials will be evaluated by in-pile tests at elevated temperatures.

PROGRESS REPORTED PREVIOUSLY In a previous program, pyrolytic-carbon coatings were applied to UC, UC₂, and UO₂ by pyrolysis of hydrocarbons in a fluidized bed of the powders at temperatures up to 1500 C. Promising coatings have been obtained, although there is some indication of mechanical failure of the coated particles at operating temperatures above the coating temperature.

In the present program, a tumbling-bed reactor has been used to coat particles at temperatures between 1500 and 1750 C. These particles were of nonuniform coating thickness and a considerable fraction of the particles adhered to the wall of the reactor.

Alterations of the nozzle design improved the uniformity but failed to eliminate agglomeration and adherence to the walls.

The fluidized-bed reactor design for coating temperatures under 1500 C was altered to eliminate the occurrence of poorly coated particles due to inadequate fluidization. Precoating the particles with a thin layer of carbon, and transferring them to a clean reactor was initiated for the purpose of minimizing contamination of the coating with dust associated with the original charge of fissile material.

WORK THIS PERIOD Several lots of depleted UO_2 were coated with pyrolytic carbon in a fluidized bed of the particles to study the effect of temperature and deposition rate on the coating. In addition, a batch of UO_2 was coated with approximately 36 μ of carbon at 1400 C for a postirradiation fission-gas-release study. Excellent fission-gas-release results (1.6×10^{-6} xenon-133 released at 1320°C during 130 min) were obtained.

Preliminary results indicate that both deposition rate and coating temperature effect the occurrence of a columnar structure in the coating, but additional data are needed to define the conditions.

The experimental work on deposition of pyrolytic-carbon coatings at temperatures above 1500 C in a tumbling-bed reactor was concluded. Despite modifications of equipment and procedure, coatings continued to be nonuniform in thickness, and particle agglomeration as well as particle adherence to the reactor wall were major problems. It is believed that the current effort would be better spent in obtaining information on coatings prepared at temperatures of 1500 C and below.

PLANS FOR FUTURE WORK Establishment of conditions for depositing both dense and porous coatings at temperatures below 1500 C in a fluidized bed will be continued. It is the immediate aim of this program to prepare coatings during March, suitable for in-pile evaluation. The effect of temperature and coating rate on coating structure will be determined. Investigation of coatings prepared at temperatures above 1500 C will be deferred until the present effort is concluded or additional funding becomes available.

CERAMIC-MATRIX STUDIES

Graphite-Matrix Fuel Elements

M. C. Brockway, D. J. Bowers, and W. H. Duckworth

OBJECTIVE To prepare and characterize graphite-matrix bodies containing coated fuel particles.

PROGRAM APPROACH For initial tests, bodies which are representative of current graphite technology are desired. Specimens are to be prepared with the minimum of development studies. The development work is to be carried out only to the extent needed to achieve reasonable physical properties, reproducibility, and fuel dispersion. Later, improvements in these qualities will be sought.

PROGRESS REPORTED PREVIOUSLY Processing conditions were established for unfueled specimens made from AGOT graphite flour and medium-hard coal-tar pitch. Processing conditions which yielded the highest density (1.65 g per cm^3) then were used in an investigation of methods to disperse Al_2O_3 -clad depleted UO_2 in graphite.

Two general methods were investigated for dispersing fuel. In one, the fuel was introduced into an entire batch at the matrix-solvent mixing step; in the other, specimen quantities of fuel and graphite batch were mixed together just prior to molding each specimen.

WORK THIS PERIOD Baked specimens prepared last month by dispersing fuel at the solvent-mixing step were partially characterized this month. These specimens contained 0.326 g of Al_2O_3 -clad depleted UO_2 (0.153 g of UO_2) per cm^3 after baking up to a maximum temperature. The average density was 1.81 g per cm^3 . The average tensile strength of five cylindrical specimens, 0.22 in. long by 0.21 in. diameter, was 1590 psi and that of three disk specimens, 0.08 in. long by 0.21 in. diameter, was 1300 psi . In both cases, strength with the grain was measured by the diametral-compression test. The average value of electrical resistivity against the grain was $3.05 \times 10^{-3} \text{ ohm-cm.}$

Also, specimens were prepared containing dense Al_2O_3 -clad enriched UO_2 by mixing fuel and matrix in specimen quantities. The two ingredients were dry mixed by tumbling and further mixed with a Micro-stirrer in the heated die cavity (where the graphite mix is slightly sticky). This procedure assured precise fueling of each specimen, and radiographs revealed fair uniformity of dispersion within most of the specimens.

PLANS FOR FUTURE WORK Property data will be obtained for the enriched fuel specimens. Other types of Al_2O_3 -clad enriched UO_2 (dense Al_2O_3 on porous UO_2 , and dense Al_2O_3 over porous Al_2O_3 on porous UO_2) will be dispersed in graphite. Further improvement in dispersion methods will be sought.

Oxide-Matrix Fuel Elements

A. K. Smalley, D. J. Bowers, and W. H. Duckworth

OBJECTIVE To develop fuel-element bodies consisting of dispersions of oxide-coated UO_2 particles in an oxide matrix and possessing a high degree of fission-product retention and oxidation resistance.

PROGRAM APPROACH The effects of fuel-particle content, type of matrix, and processing variables on the qualities and microstructures of composite bodies will be investigated.

PROGRESS REPORTED PREVIOUSLY An early experiment demonstrated that the non-shrinking character of the fuel particles interfered seriously with densification of the composite bodies. Two approaches to this problem were made. One method was to coat the fuel particles prior to incorporating them into the matrix with an organic resin which would volatilize during the early stages of

sintering and provide space into which the matrix could shrink. The other approach was to use a small amount of a glassy phase in the matrix oxide. The glass phase would impart some high-temperature plasticity to the matrix and possibly would minimize stresses resulting from the mismatched shrinkages of fuel particles and matrix. Initial studies on both these approaches were completed during February.

WORK THIS PERIOD A fluxed matrix material was prepared from a finely ground mixture of T-61 Al_2O_3 and 5 w/o of Yellowstone talc. In this powder were dispersed 25, 50, and 75 w/o additions of $127 \pm 22\text{-}\mu$ -diameter fused Al_2O_3 grains, to simulate fuel particles. The mixtures were compacted into pellets at 40,000 psi and then sintered at a temperature of 1650 C for 1 hr in flowing hydrogen.

These bodies were unsatisfactory for a number of reasons. Their bulk densities ranged from about 70 to 82 per cent of theoretical. Examination of their microstructures revealed both gross and micro porosity in the matrix phase. Moreover, the fused Al_2O_3 particles were attacked extensively by the fluxed matrix. The matrix would also, presumably, attack vapor-deposited Al_2O_3 coatings. The choice of this particular matrix body probably was a poor one. Other bodies would sinter to more nearly theoretical density and would possibly exhibit less reactivity with the Al_2O_3 particles.

The feasibility of applying an organic burnout layer to coated fuel particles and the effects of such a layer on the sintering behavior of a composite body were investigated during February. Particles used in this experiment were $127 \pm 22\text{-}\mu$ -diameter, natural UO_2 , coated by vapor deposition with about $6\text{ }\mu$ of Al_2O_3 . Coating the particles with an acrylic resin (Acryloid A-21, Rohm and Haas) was achieved by spraying a solution of the resin into a fluidized bed of particles. Three samples of organic-coated particles were prepared in which the average particle diameter was increased by 8, 14, and 20 per cent, nominally. These double-coated UO_2 particles were then mixed with a sinterable Al_2O_3 powder, compacted into pellets at 40,000 psi, and sintered for 1 hr at a temperature of 1540 C in flowing hydrogen. The nominal fuel loading of the pellets was 20 volume per cent of UO_2 . Based on this assumption, the bulk densities of the sintered pellets averaged 85.7, 86.7, and 87.4 per cent of theoretical for groups in which the fuel particles had been coated with resin to increase their diameters by 8, 14, and 20 per cent, respectively. Examination of polished sections of these pellets showed the porosity to be general throughout the matrices. Voids were not necessarily adjacent to the fuel particles, and did not consist of cracks.

PLANS FOR FUTURE WORK The fuel-containing pellets will be evaluated for oxidation resistance by heating in air at 1650 C and by leaching in hot HNO_3 . The effects of resin-coated fuel particles on the sinterability and microstructure of composite fueled bodies will be investigated further.

Attention will be given to techniques for forming fuel-containing bodies without damaging the particle coatings. Also, a problem may exist in the effect of sintering the fueled bodies at temperatures from 500 to 700 C higher than the temperature at which the Al_2O_3 coatings were deposited. This will be explored through thermal-cycle testing.

FUEL-IRRADIATION STUDIES

Capsule Irradiations

W. J. Zielenbach, G. E. Raines, N. E. Miller,
and W. H. Goldthwaite

OBJECTIVE To evaluate coated-fuel-particle materials in irradiation-capsule experiments where temperature and burnup levels will reach those anticipated in conventional power-producing reactors.

PROGRAM APPROACH Both static and sweep-gas capsule experiments are planned for core-position exposures at the Battelle Research Reactor. In the static system, several canned fuel specimens will be irradiated simultaneously in a single capsule and radiation damage will be assessed as a function of temperature of burnup in postirradiation hot-cell examinations. In the sweep-capsule experiments, the fission gas released by a fuel specimen will be continually removed from the capsule during the irradiation and periodically analyzed to determine the fission-gas-release characteristics as a function of burnup.

PROGRESS REPORTED PREVIOUSLY Alumina-Coated Uranium Dioxide Particles. Capsule SP-5. A summary of the experimental results from this capsule for the in-pile fission-gas-release behavior of the specimen containing alumina-coated particles (No. 471) and the graphite specimen fueled with uncoated UC particles (E8-7) was presented in BMI-1480. A correlation of the fission-product-release data from the coated-particle specimen with respect to the disintegration constants of the various species and a discussion of plausible release mechanisms were reported in BMI-1496 along with data from the final daughter-trap sample from the E8-7 specimen.

Capsules CFP-1A, -1B, 1C, and -1D. A discussion of the purpose and design of these capsules was presented in BMI-1489 and BMI-1496.

Carbon-Coated Uranium Dicarbide Particles. Capsule CFP-S-2. The design of this sweep capsule, for fission gas release studies, was discussed in BMI-1496.

WORK THIS PERIOD Alumina-Coated Uranium Dioxide Particles. Capsules CFP-1A, -1B, -1C, and -1D. The irradiation of this series of capsules has been detained by the specimen-fabrication delay.

Carbon-Coated Uranium Dicarbide Particles. Capsule CFP-S-2. The out-of-pile thermal mock-up of this capsule has been fabricated and is being prepared for operation. The construction of the out-of-pile sweep-gas facilities has continued during this period.

PLANS FOR FUTURE WORK Alumina-Coated Uranium Dioxide Particles. Capsules CFP-1A, -1B, -1C, and -1D. The irradiation of this series of capsule is anticipated to begin late in March, 1961.

Carbon-Coated Uranium Dicarbide Particles. Capsule CFP-S-2. The thermal mock-up of this capsule will be operated during the next report period. The sweep-capsule experiment is tentatively scheduled to begin in April, 1961.

Beam-Tube Irradiation Facility

J. B. Melehan, F. A. Rough, and R. F. Dickerson

OBJECTIVE To design and construct a beam-tube furnace for irradiation of coated-particle fuels at temperatures up to 2200 C which, with supporting equipment, will provide for the collection and analysis of fission products released during irradiation.

PROGRAM APPROACH An apparatus developed to study the in-pile release of fission gases from refractory fuels consists of a carrier-gas purifier, an r-f induction furnace for operation in a BRR 8-in. beam tube, and a fission-gas collection system. During irradiation, the specimen, heated to desired temperature by the induction furnace, releases fission gases which are swept into the collection system by the carrier gas and are accumulated on refrigerated charcoal for gamma-ray spectrometric analysis. Inadequate lead-coil insulation has prevented elevated-temperature operation. Modifications are under way to eliminate this deficiency and to make possible operation at a temperature level up to 2200 C. Additional problems associated with development of high-temperature potential involve selection of suitable, durable, and compatible thermocouples and furnace refractories.

PROGRESS REPORTED PREVIOUSLY Preparations were under way to evaluate various coil-furnace configurations.

WORK THIS PERIOD Experiments were begun to evaluate alternative induction coil-susceptor configurations for electrical and thermal efficiency, durability, and compatibility of materials. By way of brief explanation, the beam-tube furnace proper consists of a vacuumtight specimen container or plug designed for easy insertion into or removal from the beam tube. It is approximately 2-1/2 in. in diameter by 9 ft long and extends through the reactor shielding to the core face. Several of the specimen-container components are an induction susceptor, aluminum thermal insulators, thermocouples, tubulation to introduce and exhaust carrier gas, and high-density concrete and lead shielding. The plug end directly adjacent to the reactor core is a Vycor vacuum enclosure approximately 3 ft long fastened to the remainder of the plug by O-ring vacuum seals. External to the Vycor enclosure is the induction coil installed semipermanently in the beam tube and requiring removal only for maintenance.

An out-of-reactor furnace test was conducted at a temperature of 1650 C for 24 hr. The major problem encountered was mechanical failure of insulating refractories. By changing refractory shape it may be possible to reduce the thermal stresses and thereby minimize these mechanical failures.

PLANS FOR FUTURE WORK Evaluation of furnace designs will continue with the temperature objective of up to 2200 C for extended periods of time. Susceptors and ceramics will be selected for mutual compatibility and for usefulness with proposed furnace atmospheres, thermocouples, and irradiation samples. Concurrently, efforts will be made to improve the vacuum system.

POSTIRRADIATION STUDIES

R. J. Burian, M. S. Farkas, J. E. Gates,
and R. F. Dickerson

OBJECTIVE To evaluate the properties of coated fuel particles and matrix materials after irradiation.

PROGRAM APPROACH Uranium compounds with oxygen and carbon are being coated with various ceramic materials including alumina, and pyrolytic carbon. These particles will be irradiated separately and in compacts of graphite to varying burnups at various temperatures. In-pile fission-gas sampling and postirradiation examination, including metallographic inspection, X-ray studies, and strength tests, will be used to evaluate the suitability of the particles for use in a reactor.

PROGRESS REPORTED PREVIOUSLY Two 1.5-in.-diameter graphite spheres fueled with about 10 w/o fully enriched 127- μ -diameter UO_2 particles, coated with 40 μ of Al_2O_3 , were examined after irradiation to an estimated burnup of about 6 per cent of the uranium-235 at 500 to 650 C in Capsule SP-5. The spheres appeared clean, and evidence of cracks or other structural failures was not observed. However, a roughened area on one sphere, irradiated in the sweep section of the capsule, presumably caused by erosion of the sweep gas, was found. The spheres exhibited contraction and a greater loss of weight than was expected. The reason for this is not known. Detailed results of this examination were presented in BMI-1496.

Four other graphite spheres fueled with bare UO_2 particles were also examined. These spheres, clad with silicon-SiC or pyrolytic carbon, experienced burnups of about 3 to 6.5 per cent of the uranium-235 at irradiation temperatures of 500 to 650 C. The cladding on three spheres was cracked. Dimensional and weight changes were about as was expected considering the cracked condition and poor structural strength of the spheres. The results of the examination of these spheres were also presented in BMI-1496.

WORK THIS PERIOD Sphere 470, recovered from the static (nonsweep) section of Capsule SP-5, was subjected to a compression test. It was tested in a Riehle Model PH-30 universal tester at a strain rate of about 0.01 in. per min to an ultimate load of 4520 lb. This is about 800 lb greater than the ultimate loads achieved during compression tests of other irradiated and unirradiated spheres of similar design and fuel loading but fueled with bare particles (BMI-1483). Compression-strength data on unirradiated spheres fueled with coated particles are not available. Except for a short period at the initiation of the test, the slope of the load-deflection curve was constant throughout the test at 69,000 lb per in. There was no indication of a yield point on the load-deflection curve. The total deflection exhibited by the sphere was

0.0725 in. A linear relationship between the load and the deflection during most of the test and the absence of a yield point on the load-deflection curve are typical of other tests on spherical specimens fueled with bare particles. Because of the spherical geometry of the specimen, a complex stress pattern exists in the sphere and it is not feasible at present to obtain a stress-strain relationship from the load-deflection data.

Sphere 471, irradiated in the sweep section of the capsule, was sectioned to obtain samples for metallographic examination. Two spherical wedge-shaped specimens, each approximately about one-eighth of the sphere, were examined on the faces exposed by the sectioning cut. The examination revealed that, except for cracks which were present in the Al_2O_3 coating on some of the fuel particles, the particles were similar to particles observed during the metallographic examination of specimens sectioned from an unirradiated sphere. The 127- μ -diameter UO_2 was closely surrounded by a dense 8- μ -thick Al_2O_3 shell. This shell was separated from a second coating of dense Al_2O_3 , about 40 μ thick, by a 7- μ -thick shell of porous Al_2O_3 . This porous shell was probably the result of a temporary change in conditions during the coating procedure.

By means of a grid system, selected areas of the metallographically prepared surfaces of the two irradiated specimens were examined for occurrence and distribution of particles with cracked coatings. The results of these examinations indicated that about 8 to 11 per cent of the particles had cracked coatings after irradiation and that almost all of these were situated between the midradius and the surface of the sphere. In a similarly prepared unirradiated metallographic specimen, particles with cracked Al_2O_3 coatings were not observed. Assuming no change in material properties, gas pressure within the fuel particle and thermal-expansion differences between the UO_2 and the Al_2O_3 have been tentatively eliminated as primary causes of the cracking. Several other possibilities exist, however, which must still be investigated. One possibility is that some of the cracking occurred during irradiation because of forces applied by the graphite matrix. Another possible cause is that radiation caused weakening and/or embrittlement of the coating to such a degree that relatively small forces (such as from fission-gas pressure within the particle or from handling during postirradiation examination) were sufficient to crack the coating. Results of calculations and flux determinations indicate that the flux at the center of the sphere was about 0.7 the flux at the surface. It is therefore possible that the greater number of fission fragments attenuated in the Al_2O_3 coatings on particles near the surface of the sphere (roughly proportional to the flux level) was sufficient to promote cracking.

Samples from the center and surface of Sphere 470 are being analyzed by mass spectrographic techniques to determine fuel burnup. Analysis of dosimeter wires recovered from the irradiation capsule has been initiated.

PLANS FOR FUTURE WORK The particles in a sample cut from along a radius of Sphere 471 will be separated from the graphite matrix in increments by an electrolytic separation method developed for this purpose and described in BMI-1489. These particles will then be subjected to additional metallographic examinations and acid-leach tests to determine the degree and distribution of the cracked coatings. Heat treatment of the particles will be conducted to determine fission-gas-retention properties of the coating. The Al_2O_3 coating will be studied by X-ray diffraction techniques to determine the changes in the structure due to fission-recoil fragments.

PHYSICS AND ENGINEERING GUIDANCE

R. O. Wooton, H. M. Epstein, and J. W. Chastain

OBJECTIVE To investigate the importance of effects of coated fuel particles on the physics and engineering characteristics of reactor systems which may utilize these coated particles.

PROGRAM APPROACH Reactor systems previously designed by other laboratories are selected and examined to determine the effects of substituting coated fuel particles for the given fuel. Parameters investigated are coating material, coating thickness, particle size, fuel and moderator loading, and reactor size. The calculation techniques are based on the simplest analysis available consistent with the program objectives. Other miscellaneous problems for which solutions will assist the total program are also considered.

PROGRESS REPORTED PREVIOUSLY A literature survey was completed to assist in evaluating the amount of fission-product release which can be tolerated in a system without interfering with the normal reactor maintenance. Plans were made to study the effects of fuel-particle coatings on the physics of several typical gas-cooled graphite-moderated reactors. Some of the results of a study of a pebble-bed reactor were reported.

WORK THIS PERIOD An investigation of the effects of coated fuel particles on the reactivity of a pebble-bed reactor (PBR) has been completed. The reactivity effects were determined from perturbation-type calculations where the unperturbed reference core is described in NYO-2373, Section 3, page 76. The conclusions of this study are stated here.

The use of coated fuel particles in place of the reference PBR fuel will cause significant reactivity perturbations. The magnitude and direction of the perturbations depend on the coating material and thickness. Using a fuel particle 125 μ in diameter coated with 40 μ of Al_2O_3 perturbs the PBR reference core by an amount $\Delta k = -2.50$ per cent. The core will appear to be unperturbed ($\Delta k = 0$) with this coated particle if the carbon-moderator density is increased by 4.2 per cent (that is, from 1.70 g per cm^3 to 1.77 g per cm^3), or the thorium-to-uranium atom ratio is decreased from 14.2 to 12.55, or the core radius is increased from 4.5 ft to 4.82 ft. To those not accustomed to thinking in terms of reactivity, a decrease in reactivity of 2.5 per cent would require an increase of 12 per cent in the uranium loading.

PLANS FOR FUTURE WORK A study will be started to assemble information on weight per cent fuel loadings which will be required for reactors presently designed. Also, a criticality analysis will be made to determine the maximum size chemical reactor of cylindrical geometry which can be used to coat 125- μ -diameter fuel particles with Al_2O_3 , or carbon.

FISSION-GAS-RELEASE STUDIES

Fission-Gas Analytical Techniques

R. L. Ritzman, T. S. Elleman, and D. N. Sunderman

OBJECTIVE To develop improved techniques for the analysis of fission-gas mixtures.

PROGRAM APPROACH The measurement of fission-gas-release rates from in-pile fuel specimens requires accurate sampling of the off-gas and a suitable method for analyzing the fission gases. Using the gamma-ray-spectrum analysis method, it is necessary to know the size of the gas sample collected, the efficiency of the gamma-ray spectrometer for the various fission-gas gamma rays, and the accuracy with which the gamma-ray spectrum can be resolved into contributions from individual fission gases. The present program is directed toward the improvement and expansion of current techniques for fission-gas analysis. The retention time of fission gases on charcoal traps will be measured to determine the maximum sampling times in collecting gas samples. Fission gases with gamma-ray photopeaks in the energy range from 80 to 230 kev will be standardized in the gamma-ray spectrometer to check the presently used efficiency values for this energy range. New techniques for resolving complex gamma-ray spectra will be studied as possible replacements for present methods.

PROGRESS REPORTED PREVIOUSLY Previous progress reports have discussed the construction of new sampling traps for fission gases and the use of these in gathering helium elution data for krypton and xenon from charcoal traps at liquid-nitrogen and dry-ice temperatures. Also, a 4π beta- and gamma-ray standardized solution of iodine-133 provided known concentrations of xenon-133 and xenon-133m for determining the gamma-ray spectrometer detection efficiencies of these radionuclides on charcoal traps.

WORK THIS PERIOD Uncompleted calculations of gamma-ray spectrometer detection efficiencies for xenon-133 and xenon-133m on charcoal traps indicate good agreement with presently used values for these radionuclides. Equipment has been constructed for the final experiment in this program, which is the development of new techniques for analyzing complex gamma-ray spectra. Krypton and xenon fission-gas mixtures, produced by irradiating uranium foil, will be separated by gas chromatography and adsorbed on charcoal traps. Resolution of the gamma-ray spectra from each fraction will then be studied.

PLANS FOR FUTURE WORK The krypton and xenon gas fractions obtained from the uranium-foil irradiations will be scanned repeatedly with a gamma-ray spectrometer to yield plots of observed counting rate versus the gamma-ray energy. The spectrometer scans will be divided into a number of energy increments and the number of counts in each energy range will be determined for each scan. The contribution of each fission gas to each energy range (in terms of counts per minute) will be determined by plotting the counts in a given energy range versus time and fitting the experimental curve with the theoretical decay equation for a mixture of radioisotopes. Once the counting rate for each radioisotope has been measured for each energy range,

the information can in principle be applied to resolving unknown fission-gas scans into the contribution from each fission gas. The accuracy of this technique will be studied.

Fission-Gas-Diffusion Studies

R. H. Barnes, J. C. Smith, T. S. Elleman,
and D. N. Sunderman

OBJECTIVE To determine diffusion coefficients in the absence of radiation for rare-gas fission products in alumina, pyrolytic carbon, and other potential coating materials for nuclear fuel particles.

PROGRAM APPROACH Small particles of the coating material of interest are dispersed in uranium dioxide powder and are irradiated at low temperatures in the Battelle Research Reactor. These particles, which contain fission products recoiled from surrounding uranium dioxide powder during irradiation, are separated from the powder and heated at constant temperature in a flowing helium stream. The fission gases released from the particles during heating are collected from the helium on activated charcoal at liquid-nitrogen temperature and radioassayed. The results of the measurements are then used to determine fission-gas diffusion coefficients.

WORK THIS PERIOD A series of measurements of xenon-133 diffusion from alpha alumina have been performed using 1-mm-diameter alpha alumina spheres which were obtained from the Linde Company. The spheres were packed in natural uranium dioxide powder and irradiated for 10 hr in a thermal-neutron flux of 1.7×10^{13} nv. Fission-gas release during postirradiation heating was measured at a number of temperatures. The results of the diffusion measurements, expressed in terms of diffusion coefficients, are summarized in Table L-2. These results are tentative, and further analysis of the data is continuing. A second series of experiments is currently in progress. In these experiments xenon-133 diffusion from a vapor-deposited coating of 60 w/o alpha alumina-40 w/o gamma alumina on Linde Company 1-mm-diameter spheres is being measured at temperatures ranging from 800 to 1600 C.

TABLE L-2. XENON-133 DIFFUSION FROM
ALPHA ALUMINA

Diffusion Temperature, C	Diffusion Coefficient, cm ² per sec
807	5.8×10^{-18}
1000	1.3×10^{-16}
1210	1.3×10^{-15}
1300	5.5×10^{-15}
1400	2.6×10^{-14}
1495	6.0×10^{-14}

PLANS FOR FUTURE WORK Further diffusion experiments with alpha alumina are planned. Additional xenon-133 diffusion measurements

will be made using uncoated alpha alumina spheres and alpha alumina spheres with a pure-phase alpha alumina coating formed by vapor deposition. Other studies will be performed to measure krypton-85 diffusion from alpha alumina and to measure xenon-133 release during postirradiation heating from alpha alumina irradiated in contact with uranium dioxide for about 8 weeks in a thermal-neutron flux of 1×10^{13} nv.

Preparations of pyrolytic carbon material for diffusion studies are planned.

Particle-Separation Techniques

R. A. Ewing, T. S. Elleman, and D. N. Sunderman

OBJECTIVE To develop techniques for the separation of coated fuel particles from graphite matrices for postirradiation examination.

PROGRAM APPROACH Chemical separation methods are being investigated, including disintegration of the graphite matrix with boiling fuming nitric acid and electrolysis. Efficiency of separation is evaluated by visual observations. Assessments of freedom from physical damage and extent of chemical damage are based primarily on the amount of uranium dissolved during the separation.

PROGRESS REPORTED PREVIOUSLY It has been shown that $\text{Al}_2\text{O}_3\text{-UO}_2$ coated particles can be separated from the graphite matrix by boiling in fuming nitric acid and by application of the electrolytic technique. The electrolytic method is convenient to use but, like nitric acid dissolution, results in some dissolution of exposed UO_2 . In evaluating coated-particle systems, it would be desirable to recover exposed particles intact, and experiments have been carried out to determine if this can be accomplished with the electrolytic technique. The use of dilute sulfuric acid or dilute nitric acid electrolytes resulted in lower uranium oxide dissolution than was observed with concentrated acid electrolytes, but the quantity dissolved was still higher than desired.

WORK THIS PERIOD Limited studies have been conducted to evaluate the effects of the electrolytes investigated to date upon uncoated UO_2 spheres, and to develop less aggressive electrolytes. Potassium chromate appears to be more satisfactory than either chromic or sulfuric acids as indicated by the data on leaching of 250 to 300- μ -diameter high-fired, uncoated UO_2 spheres listed in Table L-3. Attack on fractured or cracked coated particles during their liberation would be expected to be negligible at rates of a few hundredths of a per cent per hour.

TABLE L-3. ELECTROLYTE ATTACK ON HIGH-FIRED UO_2 SPHERES

Electrolyte	Temperature, C	Uranium Dissolved, per cent	
		30 Min	1 Hr
7-1/2 per cent chromic acid	~95	1.72	5.48
20 per cent sulfuric acid	~95	0.025	0.041
20 per cent potassium chromate	~95	--	0.014

Disintegration rates of graphite bodies containing Al_2O_3 - UO_2 coated particles with a 20 per cent potassium chromate electrolyte were somewhat lower than those obtained earlier with 7.5 per cent chromic acid. Even lower rates were found for 20 per cent potassium dichromate or sodium sulfate. No data are available on uranium solubilities for the latter two electrolytes.

PLANS FOR FUTURE WORK The effects of electrolysis on the dissolution of uncoated UO_2 particles are to be investigated by a limited series of experiments.

FUEL-COMPATIBILITY STUDIES

G. W. Cunningham, D. C. Carmichael, J. J. Ward,
and S. J. Paprocki

OBJECTIVE To investigate reactions which may affect the maximum operating time or temperature of coated fuel particles.

PROGRAM APPROACH The stability of Al_2O_3 -coated UO_2 particles in an oxidizing atmosphere will be studied by measuring weight changes and determination of changes in oxygen content of the UO_2 in the temperature range of 1500 to 1800 C. Specimens will be examined by metallographic and X-ray diffraction techniques and the results compared to weight changes obtained on a recording micro-balance. Initial studies on the Al_2O_3 -carbon reaction will involve the use of standard diffusion couples. Later studies will require the measurement of gas pressures. Both resin-bonded and pitch-bonded graphites as well as pyrolytic carbon will be reacted at temperatures of 1000 to 1800 C. Diffusion of uranium through pyrolytic carbon coatings of UC, UC_2 , and UO_2 particles will be investigated by annealing coated particles of fully enriched uranium compounds at temperatures of 1000 to 1800 C for various times and determining the distribution of uranium in the carbon coating by a combination of metallographic, autoradiographic, and alpha counting of the coating surfaces.

PROGRESS REPORTED PREVIOUSLY Particles of UO_2 with a 53- μ -thick coating of Al_2O_3 and an overcoating of 120- μ -thick pyrolytic carbon showed no indication of reaction after 2 hr at a temperature of 1800 C in vacuo. Particles of UO_2 -coated with 7- μ -thick pyrolytic carbon showed cracking and severe reaction after 2 hr in vacuo at temperature levels of both 1600 and 1800 C.

WORK THIS PERIOD The reaction between Al_2O_3 and carbon is being investigated using massive couples of these materials and using UO_2 particles coated with Al_2O_3 and overcoated with pyrolytic carbon. Metallographic examination of fuel particles of this type which were heated in vacuum at a temperature of 1800 C for 4 hr showed no visible reaction between the Al_2O_3 and the carbon coatings, nor between the Al_2O_3 and UO_2 . The results were essentially the same as those reported previously for a treatment for 2 hr at a temperature of 1800 C in vacuum. No cracks had developed in the coatings, and excessive grain growth and some isolated voids occurred in both the UO_2 and the Al_2O_3 . For the studies using massive couples, graphite clamps have been machined for performing the diffusion treatments and suitable samples of high-purity Al_2O_3 are being prepared.

The reaction between UO_2 and graphite coatings to form UC or UC_2 is being investigated by heating the coated particles in vacuum. Particles of UO_2 with 38- μ -thick coatings of pyrolytic carbon have been heat treated at a temperature of 1800 C for 2 hr in graphite and alumina boats. For comparison, particles with 7- μ -thick coating which had previously showed considerable reaction at temperatures of 1600 and 1800 C were also run. Evaluation of these samples is in progress.

Fully enriched UC powder has been prepared and coated with 55- or 100- μ coatings of pyrolytic carbon for use in studying the diffusion of uranium through the coating. A sample of each of these particles has been heat treated at a temperature of 1400 C for 2 hr in vacuum and is being evaluated.

PLANS FOR FUTURE WORK Particles of UO_2 coated with Al_2O_3 of three thicknesses (5 to 10, 22 to 29, and 52 μ) will be run 48 hr at a temperature of 1600 C in 1 atm of oxygen as soon as the furnace equipment is repaired. Samples of reactor-grade, resin-bonded, and pitch-bonded graphites, and pyrolytic carbon will be held in contact with Al_2O_3 under slight pressure and diffusion annealed at temperatures of 1200 and 1400 C. Diffusion anneals of UC particles with carbon coatings will be continued at a temperature level of 1400 C, and techniques will be developed for evaluating the results.

COOLANT-COMPATIBILITY STUDIES

J. F. Foster and A. Levy

OBJECTIVES To collect and appraise the information available in the technical literature on potential reactions between gas coolants and ceramic materials for use in gas-cooled reactors and to define experimental studies that should contribute missing data on the use of the most promising combinations.

PROGRAM APPROACH The solid materials included in this study perform three functions, as fuel particles, particle coatings, and matrix materials:

<u>Fuels</u>	<u>Coatings</u>	<u>Matrices</u>
Oxides, nitrides, or carbides of uranium, thorium, or plutonium	C Al_2O_3 MgO ZrO_2	C SiC ZrC

The gas coolants are CO_2 , air, nitrogen, H_2O , CO, hydrogen, and helium. Since helium is the preferred coolant at present, it is included primarily for comparison with the other gases. Trace impurities that may be carried by the primary gas coolant are also considered, but the likely impurities are mostly those already listed as possible primary coolants.

To establish qualitatively the compatibility of the above coolants and ceramics the literature is being combed for pertinent thermodynamic kinetic, and radiation data. Quantitative estimates of rates of reaction and evaporation of ceramic materials are

carried out by applying available free-energy data to assumed corrosion reactions. With the aid of free-energy data, equilibrium partial pressures of volatile species are calculated; rates of evaporation are then calculated from the Knudsen expression. These calculations ignore any kinetic control of the rate of evaporation and in this sense yield estimated rates of volatilization which would never be lower than the experimental rates. As such, the estimates give maximum values and mean that higher temperature limits should be attainable in practice.

PROGRESS REPORTED PREVIOUSLY Data sources were surveyed, and a considerable number of pertinent references were selected. Calculations were made by thermodynamic methods, with relatively simple kinetic assumptions, of the rates of loss of oxide ceramics in low-pressure atmospheres.

WORK THIS PERIOD Following the thermodynamic calculations made last month, where only standard-state conditions were considered, calculations were carried out this month on the corrosion rates of Al_2O_3 , and MgO in the presence of air, nitrogen, steam, and carbon dioxide at a 100-atm pressure. The results are summarized as follows:

Al_2O_3 . Corrosion rates are negligible with high-pressure (100 atm) air, nitrogen, and carbon dioxide at 1230 C. With 100-atm steam, corrosion rates are tolerable to approximately 1100 C.

MgO . Corrosion rates are negligible in high-pressure air or nitrogen at temperatures of 1100 C. The approximate allowable temperature for MgO in the presence of steam at 100 atm is 800 C.

The present results show that high-pressure steam as a coolant reduces the useful temperature range of magnesia appreciably, and alumina relatively slightly.

PLANS FOR FUTURE WORK Calculations will be made for other ceramic fuels and coatings, and further interpretations will be made.

RADIATION-DAMAGE STUDIES

T. G. Knorr and C. M. Schwartz

OBJECTIVE To study fission-recoil damage in nonfissionable ceramic materials.

PROGRAM APPROACH Decoration procedures are being incorporated to allow observation of the fission tracks with optical, X-ray, or

electron microscopic or diffraction techniques. Alpha Al_2O_3 will ultimately be the material studied, but the alkali-halides will be investigated initially because of ease of handling and the comparative results already available.

PROGRESS REPORTED PREVIOUSLY Plastic-replica techniques were developed for cleaved surfaces of NaCl, KI, KBr, KCl, and LiF. Three concentrations of fuel (UO_2) were prepared for the reactor irradiations of the above salts.

WORK THIS PERIOD Four irradiations have been performed with the following results. Because the cleavage faces show so much structure it would be impossible to observe the fission tracks, KI will be eliminated from further experiments. Most of the data have been obtained for NaCl and KBr. Some type of damage has been observed after irradiation. A final check is being completed to verify the cause of this damage.

The plastic replicas were temporarily abandoned in favor of a direct carbon (pre-shadowed with platinum) replica which would show a higher resolution. The use of these replicas requires the destruction of the crystal to remove the replica. As of now, this is not objectionable. A new method of fueling was also incorporated. Natural UO_2 was suspended in a solution of the plastic and solvent used to make the plastic replicas. A drop of this mixture was then allowed to dry on the cleavage face. Such a method of introducing the fuel assured a more positive contact with the crystal.

An analysis of various X-ray methods resulted in a decision to postpone their use because of more promising experiments with electron and optical techniques.

PLANS FOR FUTURE WORK The cause of the damage is to be verified, and an analysis program based on this verification will be completed. Alumina will also be investigated.

THERMAL-CONDUCTIVITY STUDIES

H. W. Deem, S. D. Beck, and C. F. Lucks

OBJECTIVE To select a method and to design and assemble an apparatus for making thermal-conductivity (thermal-diffusivity) measurements on unirradiated and irradiated specimens containing coated fuel particles.

PROGRAM APPROACH The problem was approached through a literature survey of methods for measuring thermal conductivity at elevated temperatures.

PROGRESS REPORTED PREVIOUSLY This program has been directed toward the selection of a method suitable for measuring the thermal diffusivity of specimens of a size dictated by coated-particle size, encapsulation considerations, and irradiation conditions. A breadboard setup was planned in order to check out certain ideas for making the measurements.

WORK THIS PERIOD The program during February was directed toward further considerations of methods for making the measurements and to making a breadboard arrangement to help evaluate some instrumentation problems.

In BMI-1496 emphasis was given to the idea of measuring specimen back-surface temperatures using small thermocouple probes or beads. This idea is now, however, considered less promising than measuring the specimen back-surface temperature by a total radiation receiver or photometric arrangement.

According to preliminary calculations there will be an attenuation in a heat wave of 0.1 at a frequency of about 25 cps and 0.01 for a frequency of about 100 cps through 0.08 in. of graphite assuming a diffusivity of 0.6 cm^2 per sec. The method of calculating thermal conductivity involves the varying attenuation of heat waves in the specimen with different frequencies. The use of small thermocouple probes or beads to measure temperatures may present some serious complications. The problem is that all such devices have thermal mass and hence thermal inertia, and there would be an increasing but unknown attenuation between the temperature of the specimen surface and the measuring device with frequency.

The possibilities of measuring temperatures by a phototube or photomultiplier type tube are now being explored. Such measurements would be relatively independent of frequency, provided a suitable amplifier and recording system is used. There would be a problem of measuring small differences in a high total input to the tube. This might be handled in part by a bias. Also, phototubes designed to work at longer wavelengths (lower temperatures) lack sensitivity, so obtaining data at low specimen temperatures would be a problem.

A breadboard device was set up and is ready for use in testing photometric responses and amplification-recording systems.

The general design of an apparatus for making the measurements is worked out, and sources of supply for certain items have been located. Orders will be placed and assembly started when basic details of the method to be used are clear.

PLANS FOR FUTURE WORK Future plans involve testing various receivers with associated amplification and recording systems using the breadboard arrangement. An investigation will be made into photometric receivers such as lead sulfide cells which reportedly have a response time of microseconds and which are sensitive to about 6μ . Use of such a receiver may permit photometric-type temperature measurements below the visible range.

PROBLEMS ASSOCIATED WITH THE RECOVERY OF SPENT REACTOR FUEL ELEMENTS (ORNL)

R. A. Ewing and C. L. Peterson

Two problem areas associated with the recovery of spent reactor fuels are under study in support of the work on fuel reprocessing being carried on by the Chemical Technology Division at ORNL. Corrosion problems are common to all chemical reprocessing schemes yet suggested, and are under continuing investigation. Also being studied are the effects of fuel-element irradiation upon the chemical processes used in aqueous head-end treatments of spent reactor fuels.

The Fluoride-Volatility process, originally intended for fuel elements clad with zirconium or containing zirconium as a diluent, involves a hydrofluorination step during which the fuel elements are dissolved in a fused-salt melt by an HF sparge. This is followed by a fluorination with elemental fluorine which separates uranium as the volatile hexafluoride.

The corrosion of various process vessels and equipment removed from service in the ORNL Fluoride-Volatility pilot plant is being evaluated at BMI, chiefly by metallographic techniques.

Research at ORNL has indicated that oxide-type fuels might also be recovered by the Fluoride-Volatility process. Bench-scale hydrofluorinations are being made at BMI simulating the conditions anticipated with oxide-type fuels (containing UO_2 , BeO , ZrO_2 , or combinations thereof) in order that materials of construction may be evaluated. Of primary interest will be the behavior of the alloy INOR-8 (Hastelloy N or INCO 806). Bench-scale fluorinations will also be studied.

A number of aqueous head-end treatment processes have been devised for the several types of power-reactor fuels of the present generation of power reactors. Two of these processes were developed for stainless steel-clad ThO_2 - UO_2 fuels of the type to be employed in the Consolidated Edison reactor at Indian Point, New York. Both are two-step processes, designed to remove the stainless steel cladding for separate disposal. One, the Darex-Thorex process, utilizes dilute aqua regia for decladding, while the Sulfex-Thorex process employs sulfuric acid for this operation. Both processes rely on fluoride-catalyzed nitric acid for dissolution of the declad fuel core.

A considerable fund of information is already available on the performance of both processes on unirradiated fuels, primarily derived from the extensive development work which has been conducted on each. However, comparable data for irradiated fuels are relatively meager, especially for fuels at high burnups. Since significant radiation effects may be encountered in processing such spent fuels, laboratory investigations are being conducted to identify and evaluate these effects.

Corrosion Studies of the Fluoride-Volatility Process

P. D. Miller, E. L. White, E. F. Stephan, and C. L. Peterson

OBJECTIVE To evaluate materials of construction for various components of the Fluoride-Volatility process.

PROGRAM APPROACH Candidate metals and alloys are being subjected to hydrofluorination and fluorination conditions in bench-scale equipment. Also, components from the ORNL Fluoride-Volatility pilot plant are being evaluated by metallographic techniques.

PROGRESS REPORTED PREVIOUSLY Preparations for hydrofluorination of ZrO_2 were reported last month in BMI-1496.

WORK THIS PERIOD Scheduling difficulties prevented proceeding with the hydrofluorination of ZrO_2 in a NaF-LiF melt as planned last month.

In place of this, a combined hydrofluorination-corrosion study with BeO has been in progress. An Inconel container loaded with a salt composition of 53 mole per cent NaF -47 mole per cent ZrF_4 was used at 570 C. The corrosion coupons were flat strips of INOR-8 suspended on tubes of the same material. The molten salt was sparged with 10 g per hr of HF . The beryllium oxide was added in 100-g increments to a total of 576 g. The progress of the dissolution was followed by collecting and analyzing the liquid condensed by copper condensers in the effluent line. The condensate was about 89 per cent hydrofluoric acid.

Material-balance calculations indicated that about 50 per cent of the BeO was dissolved after 120 hr. At this time the sparge tube was completely severed near the top of the container from corrosion, probably by concentrated hydrofluoric acid condensed at this area. The salt was cooled and the INOR-8 corrosion specimens were cleaned and examined. The over-all corrosion on the specimens was relatively low and no preferential attack was seen at the interface areas.

PLANS FOR FUTURE WORK The BeO dissolution studies will be continued with the same corrosion specimens.

Equipment will be assembled to conduct corrosion studies on materials under fluorination conditions.

Study of the Effects of Irradiation on Cladding- and Core-Dissolution Processes

R. A. Ewing, H. B. Brugger, and D. N. Sunderman

OBJECTIVE To investigate the significance of radiation effects upon the chemical processes used in head-end treatments in the recovery of spent reactor fuels of the Consolidated Edison type.

PROGRAM APPROACH Irradiated prototype fuel pins, in the 20,000-MWD/T burnup range, are being dissolved according to the standard Darex-Thorex and Sulfex-Thorex flowsheets. Principal radiation effects being evaluated are losses of fuel and fertile material to decladding solutions during dissolution of the stainless steel jackets, extent of core fracturing, and the ease of dissolution of the dejacketed cores.

PROGRESS REPORTED PREVIOUSLY Results of the first year's work, upon generally low-burnup and nonspecification Consolidated Edison fuel specimens, were reported in BMI-1427. Recent work has dealt with two B&W pin remains and two ORR pins, in the 6,000 to 25,000-MWD/T range, which more nearly approach design burnups, and has shown the superiority of Sulfex over Darex decladding with respect to uranium losses. Losses to the Sulfex decladding solution of both thorium and uranium were low for the 6,000- and moderate for the 12,000-MWD/T B&W pin. Thorium losses were likewise low with the Darex decladding of the higher burnup ORR pins. However, uranium losses for these were excessive, confirming the results obtained on the first high-burnup ORR pin declad by the Darex process and reported in BMI-1496. The consistency of these results suggests that a real and significant radiation effect is involved.

Difficulty was encountered in attempts to dissolve the core of the 6000-MWD/T B&W pin using the standard Thorex process. Three core passes succeeded in dissolving only 94 per cent of the core. Further attempts to dissolve the core residue were postponed to the present hot-cell campaign. Density determination of the core after decladding indicated a density of 9.74 g per cm³, which approaches 100 per cent of theoretical density, and may be significant in accounting for the difficulty in dissolution.

WORK THIS PERIOD Two B&W pin remains from postirradiation studies and two ORR pins, all having burnups in the 20,000-MWD/T range, were dissolved by the standard Sulfex-Thorex and Darex-Thorex processes. One B&W specimen and one ORR pin were dissolved by each system. Decladding of all four irradiated pins in 3-hr runs and dissolution of their cores in 5-hr runs was essentially complete. Density determinations of the two B&W cores ranged from 9.20 to 9.57 g per cm³. Further passes to dissolve the core residue to the 6000-MWD/T B&W pin remaining from the previous hot-cell campaign were attempted, but no significant dissolution of the core residue was observed. Attempts to reconfirm the density of this core residue were unsuccessful.

PLANS FOR FUTURE WORK March will be devoted to analysis of the solutions from the four dissolution experiments.

EVALUATION OF FUELED-GRAPHITE ELEMENTS FOR THE PEBBLE-BED REACTOR (S & P)

A. K. Smalley and B. W. Dunnington

OBJECTIVE To develop and evaluate ceramic materials for use in the Pebble-Bed reactor.

BACKGROUND Materials have been under development in support of the Pebble-Bed Reactor program being conducted for the AEC by Sanderson & Porter. The retention of fission products within fuel particles in a ceramic matrix by the use of coatings on the particles has been a major objective of the work.

PROGRAM APPROACH Aluminum-coated UO_2 and pyrolytic carbon-coated UC_2 particles are being incorporated into graphite spheres as fuel elements for the Pebble-Bed Reactor. Laboratory evaluations include HNO_3 leaching, alpha-emission measurements, determination of oxidation resistance in the case of oxide particles, evaluation of thermal-cycling resistance, neutron activation, and metallographic examinations.

PROGRESS REPORTED PREVIOUSLY Evaluation of the pyrolytic carbon-coated UC_2 particles received from the Minnesota Mining & Manufacturing Company and from High-Temperature Materials, Incorporated, were continued. Density distribution of the leached pyrolytic carbon-coated UC_2 particles by a heavy-liquid float-sink method was initiated.

WORK THIS PERIOD Alpha emission of pyrolytic carbon-coated UC_2 particles received from American Metal Products and National Carbon Company was measured. Pyrolytic carbon-coated UC_2 particles (Sample 16564-SP-6), produced at Battelle and shipped to 3M were returned to Battelle and alpha-emission data were obtained on them. These three samples were then leached in 1:1 HNO_3 , and alpha emission was measured after leaching. These data are given in Table P-1. The net alpha count increased on all samples except Sample 16564-SP-6 after acid leaching. The leach solutions were analyzed for uranium content by fluorescence measurements. These results are reported as the percentage of the particle uranium content in the leach solution, and are given in Table P-2. In all tests, the starting solution was 8.0 ml of 1:1 HNO_3 , and the sample weight was 0.050 g. These data are not consistent with alpha-emission data.

TABLE P-1. SURFACE URANIUM CONTAMINATION OF PYROLITIC CARBON COATED FUEL PARTICLES

Sample	Vendor	Specimen Condition	Net Alpha Counting Rate per G of Clad Particles, cpm	Uranium Concentration on Surface per G of Clad Particles, mg
16684-52-1	AMP	As received	19.5 ± 3.8	0.026 - 0.052
16684-52-1	AMP	Acid leached	20.5 ± 6.5	0.027 - 0.054
16684-52-2	AMP	As received	43.0 ± 4.8	0.057 - 0.11
16684-52-2	AMP	Acid leached	76.8 ± 9.9	0.10 - 0.20
16684-53	National Carbon	As received	38.2 ± 5.2	0.050 - 0.10
16684-53	National Carbon	Acid leached	45.4 ± 8.4	0.060 - 0.12
16564-SP-6	BMI	As received	12.1 ± 2.9	0.016 - 0.032
16564-SP-6	BMI	Acid leached	2.5 ± 2.2	0.0033

TABLE P-2. LEACH-TEST RESULTS OF PYROLYTIC CARBON-COATED UC₂ PARTICLES

Sample	Vendor	Uranium Content, w/o	Coating Thickness, μ	Amount of Original Uranium in Leach Solution, per cent
16684-52-1	AMP	64.0	(a)	1.05×10^{-3}
16684-52-2	AMP	64.0	(a)	1.00×10^{-3}
16684-53	National Carbon	59.3	80	0.27×10^{-3}
16564-SP-6	BMI	52.7	80	3.94×10^{-3}
16762-74-1	3M	79.0	80 ^(b)	0.32×10^{-3}
16684-22-5	HTM	58.1	80 ^(b)	0.28×10^{-3}

(a) Not available.

(b) Estimated.

Experiments were completed on particle separation by the heavy-liquid float-sink method. The leached particle density distribution of Sample 16762-74-1 received from 3M and Sample 16684-22-5 received from HTM were calculated. These data are given in Table P-3. From these data, the weight percentage of the 3M material above 3.0 g per cm³ is 81.7 per cent and for the HTM material it is 75.0 per cent, but in the density range of 3.5 to 4.05 g per cm³ the HTM material has a larger amount. No future work is planned, on these particles.

TABLE P-3. PARTICLE DENSITY DISTRIBUTION OF LEACHED PYROLYTIC CARBON-COATED UC₂

Sample	Vendor	Amount Having Density in Indicated Range, w/o				
		2.0 - 2.5 ^(a) G per Cm ³	2.5 - 3.0 G per Cm ³	3.0 - 3.5 G per Cm ³	3.5 - 4.05 G per Cm ³	4.05 G per Cm ³
16684-22-5	HTM	2.4	22.6	37.7	23.5	13.8
16762-74-1	3M	3.2	15.1	59.9	15.6	6.2

(a) No particles had a density of less than 2.0 g per cm³.

The Al₂O₃-coated UO₂ particles (NUMEC) were alpha counted after being subjected to oxidation in static laboratory air for 5 hr at 1200 F. The net alpha count per g of clad particles was 3.2 ± 4.3 cpm. There was no increase due to the oxidation testing of the particles. Neutron-activation testing of these particles indicated a high degree of xenon-133 containment at up to 2500 F. The conditions and results of this test are shown in Table P-4.

TABLE P-4. RESULTS OF NEUTRON ACTIVATION OF Al_2O_3 -COATED UO_2 PARTICLES SUPPLIED BY NUMEC

Test Temperature, F	Postirradiation Heat Treatment		Incremental Release, per cent of xenon-133
	Time to Temperature, min	Time at Temperature, min	
1600	5	60	5.1×10^{-4}
1800	4	70	5.1×10^{-4}
2000	3	80	1.3×10^{-4}
2200	3	65	1.3×10^{-4}
2500	10	130	1.3×10^{-3}

Note: Results are from Sample 16684-32, weighing 9.94 g. Batch consisted of 105 to 150- μ normal UO_2 particles coated by vapor deposition with about 40 μ of Al_2O_3 . UO_2 content was 43 w/o.

Sample was irradiated to 1.89×10^{15} nvt and cooled for 4 days prior to heat treatment.

PLANS FOR FUTURE WORK Laboratory evaluations have been discontinued.

DEVELOPMENT OF FABRICATION PROCESSES FOR COLD BONDING OF ZIRCALOY-2 TO TYPE 410 STAINLESS STEEL (SRO)

S. W. Porembka

In assistance to the CANDU reactor program, a study of fabrication processes for cold joining Zircaloy-2 pressure tubes to Type 410 stainless steel headers was established. It is desirable that the methods developed in this program produce metallurgical bonding and also have the potential of being performed in-pile in order to facilitate tube replacement. Techniques considered in this investigation have been limited to those which will produce only a limited amount of diffusion, since the two materials readily form brittle compounds on alloying. Three approaches which are currently being studied include friction techniques, the effects of surface preparation in roll forming, and explosive joining. In each approach, the operations are performed at ambient temperatures, thereby limiting diffusion. Both direct joining and transition joining of these materials are being considered through dissimilar metal joints and self-bonds with particular emphasis on the dissimilar metal joints.

Friction Bonding

S. J. Paprocki, E. S. Hodge, and H. D. Hanes

OBJECTIVE To study joining of Type 410 stainless steel to Zircaloy-2 by friction techniques.

PROGRAM APPROACH Current studies of friction bonding concern both direct joining and bonding through a transitional member. Joint design, pressure, rotational velocity, time, and surface preparation are the variables being investigated in joining Zircaloy-2 to stainless steel by the two approaches. Metallographic techniques are presently employed as the primary method of evaluation. Satisfactorily joined specimens are subsequently corrosion tested in 750 F steam and their mechanical properties determined.

PROGRESS REPORTED PREVIOUSLY Successful bonding of rod-type specimens was reported in BMI-1489. Major emphasis was then shifted to joining tube-type specimens. A major problem encountered with tube joints concerns the upsetting of Zircaloy into the bore of the stainless steel tubing, as reported in BMI-1496.

WORK THIS PERIOD In an effort to minimize inward flow of the Zircaloy members, several variations of joint design were attempted. One consisted of utilizing a 30-deg taper joint with the stainless steel as the male member. Upsetting was controlled in this case; however, poor bonds were attained. The lack of bonding was attributed to the limited pressure available in the present apparatus. Another technique, which also proved unsuccessful, provided void space in the joint to accommodate Zircaloy flow during the friction-bonding operation. The most promising method for controlling material upset employed the use of a mild-steel mandrel which was located in the bore of the mating materials during the bonding operation. This technique is now being used for all specimens.

An additional problem became evident with the introduction of a mandrel into the specimens. It appears that the Zircaloy adheres readily to the stainless steel early in the bonding cycle with a subsequent shearing action in the Zircaloy-2. This behavior indicates that the loss of strength in the Zircaloy, due to the moderate heating, leads to failure in the Zircaloy rather than in the bond. This effect was noted earlier in specimens with poor bonds. It would appear that an initial heating cycle in which the surfaces are heated but not bonded, followed by the simultaneous increase in pressure and reduction in power would eliminate the shearing in Zircaloy. Although a recent experiment did not substantiate this, the pressure was limited to approximately 3000 psi by the present apparatus. It should be noted that this pressure is below the 10,000 psi found necessary for Zircaloy-to-Zircaloy bonding in previous rod-type samples.

Good bonding with only a slight amount of shearing was obtained in a specimen with a multiple-taper joint and a mandrel. The stainless steel female member was tapered 45 deg while the Zircaloy had a double 40- and 50-deg taper with the apex at the center of the wall. The specimen was bonded in 6 sec at a rotational velocity of 12.6 in. per sec, and a normal interfacial pressure of 1500 psi. Upsetting into the bore of the tubing was controlled by the mandrel, but some metal flow occurred in the outward direction. Also, a relatively large heat-affected zone was noted in the stainless steels.

PLANS FOR FUTURE WORK The study of the multiple-taper joints will be continued. Also, a two-step bonding cycle including the preheat and high-pressure steps will be studied on rod-type samples.

Effects of Surface Preparation in Roll Forming

S. J. Paprocki, R. J. Carlson, C. C. Simons, and E. G. Smith, Jr.

OBJECTIVE To investigate the effects of prior surface preparation on cold bonding Zircaloy-2 to Type 410 stainless steel using roll-bonding techniques.

PROGRAM APPROACH Flat-plate couples of stainless steel and Zircaloy-2 have been utilized for the preliminary cold-rolling studies. Surface preparation as well as groove design and rolling reductions have been investigated to determine their effect on the degree of bonding achieved. The program approach will now be concentrated on achieving a joint through roll-forming techniques using Zircaloy and stainless steel components of the size employed at CANDU.

PROGRESS REPORTED PREVIOUSLY Studies to date have indicated that machined surfaces yield a greater degree of apparent bonding than those subjected to either belt abrading or commercial chemical etches. Cold reductions of 45 to 50 per cent or greater in a single pass were required to achieve bonding between Zircaloy and stainless steel. The most successful surface preparations consisted of a 300- μ in. rms finish on the mating faces which were subsequently scrubbed with a MgO-NaCO₃ solution. The use of TiC powder as an intermediate layer in cold rolling assemblies did not appear to offer much advantage in the extent of bonding obtained.

WORK THIS PERIOD Cold-rolled specimens have been heat treated at 1600 F for 4 hr to promote diffusion across the bonded interface. Metallographic examination of these specimens to determine the extent and uniformity of diffusion is not yet complete.

Several specimens were cold rolled employing a groove design to concentrate deformation over a small portion of the contact area. Difficulty was encountered in rolling flat-plate couples with a projection in the Zircaloy plate because stresses at the projection caused the material to rupture before complete deformation could be attained. No bonding was evident in these couples. These specimen failures were attributed to the tensile forces characteristic of the rolling process. It would appear that the use of projections on the bonding faces would be more successful in the roll-forming process where the stresses are primarily compressive.

A brief study was made of relative component reduction to determine where bonding could most easily be achieved. A tapered design was employed on both the Zircaloy and stainless steel mating surfaces. Thickness measurements made at intervals along the taper of the specimen both before and after the 55 per cent total cold reduction gave the relative amounts of reduction that occurred in each component. In all cases, the Zircaloy reduced more than stainless steel. Toward the ends of the specimen where the relative component thicknesses were a maximum, no bonding occurred and severe rupturing of the materials resulted. Where the components were of almost equal thickness, some bonding took place with very little damage to the materials. This corresponded to reductions of 55 to 60 per cent in the Zircaloy and 37 to 40 per cent in the stainless steel.

PLANS FOR FUTURE WORK The preliminary cold-bonding studies have now been completed. The results obtained during this study will be applied to future studies on roll forming the Zircaloy-stainless steel joint. Full-scale components will be used and major emphasis will be placed on groove design to achieve the desired metallurgical bonding.

Metallographic examination of cold-rolled and heat-treated specimens will be completed during the next reporting period.

Explosive Joining

S. J. Paprocki, R. J. Carlson, and C. C. Simons

OBJECTIVE To determine the feasibility of achieving mechanical and metallurgical bonding between Zircaloy-2 and Type 410 stainless steel by explosive techniques.

PROGRAM APPROACH Explosive techniques are being employed to bond Zircaloy-2 to Type 410 stainless steel. Evaluation is based upon bond strength as determined by metallographic examination and mechanical testing.

PROGRESS REPORTED PREVIOUSLY Several flat-plate assemblies have been explosively joined. The results of this testing are reported in BMI-1489. Currently, attempts are being made to explosively butt weld Zircaloy-2 to Type 410 stainless steel. Results of the initial butt-welding experiments are given in BMI-1496.

WORK THIS PERIOD The metallographic examination of the explosively joined flat-plate assemblies has been completed. This examination revealed that the best bonding was achieved with a 16-g charge of PETN placed in direct contact with the assembly. It was also found from the metallographic examination that pockets of an iron-zirconium intermetallic had been formed at the interface during impact. It is suspected that this was due to an incomplete evacuation of the assembly, and that during impacting the entrapped air was forced into pockets. A sufficient amount of heat was generated from the compression of the air in these pockets to permit the formation of an iron-zirconium intermetallic. It is felt that this can be eliminated by modifying the assembly design to insure its complete evacuation before impacting.

Several additional butt-welding tests have been conducted. Various butt-joint designs were used during this testing. The results of these experiments are given in Table Q-1, where it can be seen that bonding was not achieved in any of these tests. Therefore, no further butt-welding experiments will be conducted.

PLANS FOR FUTURE WORK Additional flat-plate assemblies will be joined in an effort to produce a good weld which does not contain any intermetallics at the interface.

Preparations are also being made to investigate the feasibility of explosively joining tube-type specimens of Zircaloy-2 to Type 410 stainless steel.

TABLE Q-1. DATA FROM EXPLOSIVE BUTT-WELDING EXPERIMENTS WITH ZIRCALOY-2 AND TYPE 410 STAINLESS STEEL

Specimen	PETN Charge, g	Butt-Joint Design	Remarks
1	3	Flat edges on both the Type 410 stainless steel and Zircaloy-2	Assembly was detonated in air; no bonding was achieved
2	6	Edge of the stainless steel machined to a point	Explosive was placed in carton filled with water which was placed on top of the stainless steel and the charge detonated; some bonding achieved, but the bond was easily separated by hand.
3	7.5	Edge of stainless steel machined to a point with a corresponding groove in the edge of the Zircaloy-2	Same charge arrangement as for Specimen 2; stainless steel bent to one side on impact and did not come in complete contact with Zircaloy-2
4	6	Same as Specimen 3	A mild-steel buffer was placed on top of the stainless steel with the charge being placed on top of the mild steel; assembly was detonated in air; no bonding was achieved and the Zircaloy-2 ruptured at the interface
5	6	Same as Specimen 3	A mild-steel buffer was placed on top of the stainless steel and the explosive charge was placed in a carton filled with water which was placed on top of the mild steel and the charge detonated; no bonding was achieved and the Zircaloy-2 ruptured at the interface
6	6	Edges of both the Zircaloy-2 and stainless steel machined to a 45-deg angle	A mild-steel buffer was placed on top of the stainless steel and the assembly was placed in a sack of Gooch tubing and then submerged in a barrel filled with water; the charge was placed on the Gooch tubing over the mild steel and detonated; no bonding was achieved, the Zircaloy-2 did not rupture.
7	6	Same as Specimen 3	Same charge arrangements as for Specimen 4; no bonding was achieved, and the Zircaloy-2 ruptured at the interface

RADIATION-EFFECTS STUDY OF CANDIDATE FUEL MATERIALS FOR THE MGCR (GA)

N. E. Miller, P. Steinback, J. E. Gates, and W. H. Goldthwaite

OBJECTIVE To determine the irradiation stability of selected ceramic-matrix fuels under conditions of temperature and burnup similar to those anticipated in the MGCR.

BACKGROUND Battelle has assisted General Atomic in the development and evaluation of core materials for the Maritime Gas-Cooled Reactor and the High-Temperature Gas Reactor. This work has included research and development of ceramic-matrix dispersion-type fuels and fuel-particle coatings and study of coolant-core material compatibility in an irradiation environment. At the present time, with the emphasis on the BeO-moderated, helium-cooled concept for the MGCR, Battelle is conducting studies of the irradiation damage of BeO-matrix fuels up to relatively high burnups.

PROGRAM APPROACH Clad fuel pellets are irradiated in capsules which are equipped with thermocouples and auxiliary electric heaters and designed to maintain specimen-surface temperatures in the 1500 to 1700 F range primarily by fission heating. Target burnups range from 1 to approximately 50 per cent of the uranium-235 atoms originally present. Data concerning specimen burnup, swelling, fission-gas release, and microstructural changes are obtained in post-irradiation hot-cell examinations.

PROGRESS REPORTED PREVIOUSLY Capsules GA-BRR-1 and BMI-31-1, -2 and -3.
Each of these four capsules contains two specimens of the following three fuel compositions: 20 volume per cent UO_2 in BeO, 20 volume per cent uranium monocarbide in graphite, and 20 volume per cent uranium dicarbide in graphite; the uranium enrichment in each of the 31-series capsules is 30 per cent, whereas in the GA-BRR-1 capsules it was 93 per cent. The fuel pellets are canned in Type 316 stainless steel tubing under a helium atmosphere.

One of the four capsules, GA-BRR-1, was irradiated in the Battelle Research Reactor to specimen burnups ranging from 1.0 to about 1.7 a/o with specimen-surface temperatures ranging from 1275 to 1560 F. Postirradiation examinations at the Battelle Hot-Cell Facility indicated that all three types of specimens were in good physical condition.

The three remaining capsules were irradiated at the Materials Testing Reactor. Two of these three, BMI-31-2 and BMI-31-3, were discharged from the reactor (at the end of Cycle 144 and 129, respectively) and returned to the GA hot cells for post-irradiation examinations. The estimated specimen burnups for Capsule BMI-31-2 range from 16 to 20 a/o; for specimens in Capsule BMI-31-3 this range is from about 17 to 22 a/o.

Capsule BMI-36-1. This capsule is being prepared for the irradiation at the MTR of pellets of 30 volume per cent UO_2 (12 per cent enriched) in BeO encased in Hastelloy X. Target irradiation conditions include a specimen-surface temperature of 1700 F and an in-pile period of about 18 months at a specimen-effective peak flux

of about 2×10^{13} nv. These exposure conditions will yield a peak burnup in the neighborhood of 50 a/o.

The fueled pellets for this irradiation are to be furnished by General Atomic.

WORK THIS PERIOD Capsule BMI-31-1. The irradiation of this capsule in the MTR was completed on February 27, 1961, following 28 cycles. During this irradiation, the surface temperature of the peak-flux specimens was maintained near 1500 F with the aid of auxiliary electrical heat. The maximum fission burnup expected is approximately 40 a/o.

Capsule BMI-36-1. Preparation of this capsule is awaiting receipt of the fuel pellets from General Atomic.

PLANS FOR FUTURE WORK Capsule BMI-31-1. This capsule will be shipped to the General Atomic hot cells during the latter part of March.

Capsule BMI-36-1. Assembly of the capsule will start upon receipt of the fuel pellets.

RADIATION STUDIES OF SM-2 FUELS (ALCO)

J. H. Stang, J. F. Lagedrost,
and W. H. Goldthwaite

OBJECTIVE The effects of irradiation on stainless steel-clad dispersions of UO_2 (nominally 26 w/o, high enriched) and certain burnable poisons in Type 347 stainless steel are being investigated.

BACKGROUND This study is being conducted in assistance to ALCO Products to develop satisfactory fuel materials for Army pressurized-water reactors. Reference and alternate SM-2-type specimens have been fabricated and are being irradiated in the ETR.

PROGRAM APPROACH Capsules containing five to eight specimens each are being irradiated or have been irradiated in the MTR or the ETR. Desired experimental conditions include nominal specimen-surface temperatures of 600 F and burnups of 37 and 70 per cent of the total uranium-235 atoms. The program includes seven instrumented (heaters and thermocouples) and three noninstrumented capsules; the latter were designed for irradiation in MTR core-lattice positions, the former for irradiation in ETR beryllium-reflector positions. This capsule group is identified as the BMI-32 series.

PROGRESS REPORTED PREVIOUSLY Irradiations of the first four capsules were completed early in 1960; irradiation histories and results of specimen analyses were reported in BMI-1442, BMI-1448 and BMI-1464.

The irradiation status of Capsules BMI-32-5 through BMI-32-10 in the ETR, including estimates of specimen burnups, was reported in BMI-1489 and BMI-1496. It was pointed out that peak-flux specimens in all capsules have exceeded burnups of 30 per cent of the original uranium-235 atoms and that target burnups of 70 a/o will be reached by mid-1961 with routine reactor operation.

WORK THIS PERIOD Irradiations of the six in-pile capsules were continued in the ETR. Cycle 34 ended on February 14, Cycle 35 will end on March 6. Temperature performance of the capsules continues to be generally satisfactory; 21 of the 24 thermocouples are still functioning, and the auxiliary heaters in all capsules except BMI-32-8 are operable. It is believed, however, that the heaters in this capsule can be restored to operation through a check-out of the external circuits. This will be done during reactor shutdown.

A study of the effect of specimen burnup on the temperature difference between the surface of the specimen and the reference thermocouple was completed. Information from this study is being utilized to regulate the auxiliary heat input to the in-pile capsules so that specimen-surface temperatures of approximately 600 F are maintained as burnup progresses. However, because of the heat-transfer characteristics of the capsule and the limitations of the electric heaters, it will not be possible to maintain the 600 F level after the specimens have reached approximately 50 a/o burnup unless reactor fluxes exceed those for which the capsules were designed.

PLANS FOR FUTURE WORK The ETR irradiations of BMI-32-5 through BMI-32-10 will be continued toward the 70 a/o target specimen burnups.

GAS-COOLED REACTOR PROGRAM (AGN)

D. L. Keller

The Army Reactor Branch (ARB) is developing small portable reactor systems for military applications. Aerojet-General Nucleonics (AGN) is the prime contractor under the Army Gas-Cooled Reactor Systems Program (AGCRSP) and is charged with the design, construction, and operation of the GCRE and ML-1. The object of the ML-1 program is to produce a prototype mobile nuclear plant suitable for military field use.

The programs reported in the following sections are in support of this ML-1 program and are concerned primarily with fuel-element development.

Advanced ML-1 Fuel Pellets

J. W. Lennon and A. K. Smalley

OBJECTIVE To develop oxidation-resistant ceramic fuel pellets of UO_2 and Al_2O_3 , or other suitable oxide, the content of UO_2 being at least 60 volume per cent.

PROGRAM APPROACH Dense UO_2 particles are being coated with Al_2O_3 by vapor deposition. The coated shot is mixed with powdered Al_2O_3 , and the mixture is compacted and sintered to form pellets. Oxidation resistance at elevated temperatures, mechanical soundness, and sintered bulk density are the criteria by which the experimental pellets are evaluated.

PROGRESS REPORTED PREVIOUSLY Steel-die pressing at 40,000 psi of coated particle-matrix powder mixtures containing more than 25 volume per cent of UO_2 fractured the particle coatings. This was evidenced by the ease with which the pressed specimens disintegrated when up to 40 volume per cent of UO_2 were oxidation resistant at 1200 F in air. In no cases were sintered specimens oxidation resistant. Damage to the vapor-deposited coatings during forming and failure of the coatings during sintering were indicated as difficulties to be resolved.

WORK THIS PERIOD The batch compositions of mixtures of coated shot and powder-matrix Al_2O_3 yielding pellets with 60 volume per cent UO_2 were as follows:

<u>UO_2 Average Diameter, μ</u>	<u>Al_2O_3 Coating Thickness, μ</u>	<u>Pellet Composition, w/o</u>	
		<u>Al_2O_3-Coated UO_2</u>	<u>Matrix Al_2O_3</u>
715	11.5	83	17
415	11.0	85	15
127	6.0	90	10
59	5.5	100	0

An investigation of the effects of forming pressure on the oxidation resistance of pressed pellets containing about 50 to 60 volume per cent UO_2 were made. Coated 415- μ shot was used rather than the 715- μ shot because the coating on the former was felt to be more reliable, and the advantage in using 715- μ shot for the purpose of incorporating more matrix Al_2O_3 is slight.

Pellets pressed at 20,000, 10,000, or 5,000 psi, using beeswax as binder-plasticizer, were not oxidation resistant after pressing. Using a water, glycerine, and starch combination as the plasticizer-binder, the same compositions were pressed at 2000, 1000, or 500 psi with similar results. The pressed pellets disintegrated during the oxidation treatment at 1200 F.

In earlier work, compacts of low UO_2 content which did not oxidize after pressing were found to oxidize after being sintered at 3000 F in hydrogen. To determine if this might be due to failure of the vapor-deposited coating during sintering, a sample of coated shot was heated for 1 hr at 3000 F in hydrogen and, after firing, evaluated for oxidation resistance. The coated shot oxidized during heating in air at 1200 F for 1 hr. The failure of the coating is attributed to the difference in thermal expansion of the UO_2 and Al_2O_3 ; the expansion of the shot is higher than that of the coating. At the temperature at which the coating was deposited (1830 F) it would be free of strain but would be put in tension on heating above this temperature.

Concurrent with the above study, preliminary experiments were conducted on the use of an inorganic "burnout" coating on the Al_2O_3 -coated shot. It was anticipated that such a coating would be necessary to provide space, after burning out, for the matrix Al_2O_3 to shrink around the shot during sintering. Limited tests indicated that burnout coating provided some protection or cushioning for the Al_2O_3 deposited coating during pressing. Minor increases in sintered pellet density also resulted.

It does not appear feasible to make oxidation-resistant bodies containing 60 volume per cent of UO_2 using the techniques employed in this work. The high UO_2 content specified did not permit the use of enough matrix Al_2O_3 to cushion the coated particles during pressing. An organic coating on the particles appeared to help in protecting the particles during pressing, but did not eliminate the problem.

An even greater problem is the failure of the particle coatings during sintering. This difficulty is receiving attention in another program.

PLANS FOR FUTURE WORK No further work is planned at this time.

An Alternate Method of Fabricating Advanced ML-1 Fuels

S. J. Paprocki and D. L. Keller

OBJECTIVE To investigate the simultaneous densification and cladding of Al_2O_3 -coated UO_2 as a method of obtaining a high-density oxidation-resistant fuel material.

PROGRAM APPROACH It has been demonstrated that the oxidation resistance of UO_2 powder can be significantly improved by protecting the powder with a thin coating of Al_2O_3 . In this program, the coated powder will be used as a starting material. Various methods of packing the coated powder into stainless steel tubes will be investigated. The steel tubes will be evacuated and under isostatic pressure collapsed around the ceramic core. The resulting densification will be accomplished at temperatures around 2300 F. The maximum Al_2O_3 diluent is restricted to about 40 volume per cent. The main concern is the retention of coating integrity during densification. This will be evaluated by nitric acid leach tests, oxidation tests, and metallographic studies.

PROGRESS REPORTED PREVIOUSLY Spherical UO_2 particles of 150 and 50 μ in average diameter have been coated by a vapor-deposition method with from 5 to 10 μ of Al_2O_3 . Six cylindrical specimens were prepared from mixtures of these coated particles by hot pressing in mild steel tubes at 2300 F for 3 hr under an isostatic pressure of 10,000 psi.

WORK THIS PERIOD Samples of the coated UO_2 powder used to prepare the six specimens were examined metallographically to determine the coating thickness. The results are shown in Table U-1.

TABLE U-1. DESCRIPTION OF Al_2O_3 -COATED UO_2 POWDER USED IN HOT-PRESSING EXPERIMENTS

Specimen	Average UO_2 Particle Diameter, μ	Average Al_2O_3 Coating Thickness, μ	Calculated Loading of UO_2	
			Weight Per Cent	Volume Per Cent
A-6	150	6.5	90.5	78
A-9A	50	6.0	77.8	56

Mixtures of the two sizes of coated particles were blended together in a ratio which should provide the best packing density. In several cases, very fine Al_2O_3 powder was blended with the coated particles in hopes of preventing coating breakup during fabrication. Six specimens were prepared for hot isostatic pressing with five of these made from cold-pressed pellets. Some of the more pertinent details are shown in Table U-2.

The specimens prepared from cold-pressed pellets contained three or four pellets of the indicated composition which were bonded into a continuous cylindrical specimen during hot isostatic pressing. Radiographs of the six specimens showed Specimens 7 and 8 to be somewhat segregated. The data in Table U-2 indicate that Specimen 5 probably leaked during hot pressing, since no densification occurred. This also means that any cracking of the Al_2O_3 coating which might have occurred during cold pressing could not have healed during hot pressing. The final densities obtained with Specimens 9, 10, and 11 seem directly related to the green density.

TABLE U-2. DESCRIPTION OF Al_2O_3 -COATED SPECIMENS HOT PRESSED AT 2300 F FOR 3 HR AT 10,000 PSI

Specimen	Powder Constituents, w/o	UO ₂ Phase		Cold Compacting Pressure, tsi	Approximate Density, per cent of theoretical	
		Weight Per Cent	Volume Per Cent		Green	Pressed
5	90 A-6 and 10 A-9A	89.5	88.0	50	72	72
7	80 A-6, 7 A-9A, and 13 Al_2O_3	78.0	56.2	50	61	--
8	Ditto	Ditto	Ditto	25	61	--
9	85 A-6, 8 A-9A, and 7 Al_2O_3	83.2	64.3	50	71	85
10	Ditto	Ditto	Ditto	15	64	80
11	90 A-6 and 10 A-9A	89.5	88.0	Tamp Packed	52	70

After hot pressing, transverse sections of Specimens 9 and 11 were examined metallographically. The UO_2 was well distributed in both cases, and there was no evidence at all of cracks in the Al_2O_3 coating in either specimen. The density of Specimen 9 was obviously higher than Specimen 11.

The mild steel cladding was then removed from each of the specimens by dissolving in a hot acid solution of 50 HNO_3 -50 H_2O . As soon as the cladding was removed, Specimens 5, 9, 10, and 11 were returned to fresh acid for a period of 3 hr and the weight loss measured. Specimen 5 lost 48 per cent of the UO_2 present, Specimen 11 lost 30 per cent, Specimen 10 lost 10 per cent, and Specimen 9 lost 5 per cent. A sample of a mixture of A-9A and A-6 coated powders was also measured, and it lost approximately 1 per cent of the UO_2 present.

Specimens 9, 10, and 11 were then placed in an air furnace at 1500 F. A visual examination after 2 hr revealed that Specimens 9 and 10 were still intact; however, after 4 hr, all specimens had disintegrated into a mixture of U_3O_8 and Al_2O_3 powder.

Specimen 8 was placed in an air furnace at 1200 F and the weight gain continually measured on a thermogravimetric balance. There was a nearly linear weight increase with time during the first hour. During that period, approximately 80 per cent of the UO_2 was oxidized to U_3O_8 as indicated by the weight gained.

A sample of the mixed coated powders, A-9A and A-6, was also tested in air at 1200 and 1500 F for a period of 4 hr during which time about 1 per cent of the UO_2 was oxidized to U_3O_8 in both cases. The sample tested at 1200 F had previously been tested in the nitric acid solution, and the results were described earlier.

The most significant factors which seem to be indicated by the results during January are:

- (1) The coated powder used in these studies is resistant to both nitric acid and air oxidation.

- (2) After hot isostatic pressing, the maximum density obtained was approximately 85 per cent of theoretical. Higher densities can likely be obtained by increasing the hot-pressing temperature or increasing the amount of "active" Al_2O_3 (that alumina added as a powder as opposed to that added as a vapor-deposited coating).
- (3) Metallographic examination of two specimens made before the cladding was removed revealed no cracks in the Al_2O_3 phase.
- (4) Dissolution tests in a nitric acid solution showed a varying degree of attack on four unclad specimens. Two of these specimens showed some resistance to air oxidation in that the specimens were still intact after 2 hr at 1500 F. Specimen 8 gained weight rapidly at 1200 F and had disintegrated to powder after 1 hr.
- (5) These results suggest that the Al_2O_3 is failing either when the cladding is removed or when the specimens are rapidly heated to temperature prior to oxidation testing.

PLANS FOR FUTURE WORK An effort will be made to determine at exactly what stage of fabrication or testing the Al_2O_3 coatings are failing.

Additional specimens will be prepared and some of these will be tested as de-fected pins rather than as unclad cores.

Encapsulation Studies

W. J. Zielenbach, J. F. Lagedrost, and J. H. Stang

OBJECTIVE To investigate the elevated-temperature radiation stability of Hastelloy X-clad compacts of highly enriched UO_2 , both alone and dispersed in a BeO matrix.

PROGRAM APPROACH Two capsules, each containing six clad specimens based on highly enriched UO_2 , are being irradiated, one capsule at the Materials Testing Reactor and the other at the Battelle Research Reactor. The specimens in the MTR capsule consist of 70 and 80 w/o UO_2 dispersed in BeO; there is no diluent in the specimens being irradiated at BRR. The peak burnup levels presently desired are 9 per cent of the original uranium-235 atoms for the former specimens, and 3.5 per cent for the latter. The desired specimen cladding-surface temperature is 1725 F in both cases.

PROGRESS REPORTED PREVIOUSLY The irradiation history of these capsules was reported in BMI-1480, BMI-1489, and BMI-1496. Performance and monitoring of the MTR capsule (BMI-38-1) was hampered by failures of auxiliary heaters and thermocouples during recent cycles. As of February 1, 1961, all thermocouples and two of three heaters had failed. Performance of the BRR capsule was satisfactory.

WORK THIS PERIOD Capsule BMI-38-1 completed its eighth cycle in the MTR. Although failure of the thermocouples and heaters has eliminated direct temperature monitoring and control, estimates of current performance are being made on the basis of previous data. It is likely that the peak-temperature specimen surface is currently near 1550 F, and that its burnup rate is approximately 1 per cent of the original uranium-235 atoms per reactor cycle. This burnup rate, which is based on a detailed heat-transfer and temperature analysis recently completed, is slightly higher than that estimated previously.

Capsule AGN-III has completed its eleventh cycle in the BRR; the estimated accumulated burnup of the peak-flux specimen is 2.5 per cent of the original uranium-235 atoms. This capsule has been rescheduled for an additional five cycles to comply with a recent modification of the burnup goal from an initial 2.0 a/o to 3.5 a/o. The peak-temperature specimen surface was maintained at the desired 1725 F for most of this period with the addition of approximately 900 w of auxiliary electric heat.

PLANS FOR FUTURE WORK The MTR capsule will be discharged early in May. The BRR capsule will be transferred to a different core position (because of previously scheduled space commitments) during March, and will remain in the new position until about May 1. Neutron fluxes in this new position are expected to be about 10 per cent lower than the current levels.

High-Temperature Fatigue Evaluation of Nonirradiated Hastelloy X Tubing

G. M. McClure, H. J. Grover, and A. R. Duffy

OBJECTIVE To evaluate the fatigue characteristics of Hastelloy X tubing at elevated temperatures.

PROGRAM APPROACH An experimental program is being conducted to evaluate the fatigue performance of Hastelloy X tubing at temperatures of 1400, 1600, 1800, and 2000 F. Krouse axial-load fatigue machines are being used to develop S-N curves out to 10^6 cycles for each of the temperature levels. Four stress ratios are being studied in order to establish a Goodman-type diagram based on failure at 10^6 cycles. These ratios are $A = 0$, $A = 0.25$, $A = 1.0$, and $A = \infty$. The 1/4-in.-diameter tubing is being tested at a cyclic speed of 1725 cpm, which produces 10^6 cycles in about 10 hr.

WORK PREVIOUSLY REPORTED It has been previously reported that there were slight dimensional and metallurgical differences between the original and new supplies of tubing used for this investigation. These slight differences have resulted in distinct and clearly defined variations in the fatigue performance of the two supplies. For a stress ratio of $A = 1$, the maximum stress required to instigate failure in 10^6 cycles was 18,500, 5,300, and 2,500 psi for 1600, 1800, and 2000 F, respectively, for the original tube supply. For the same stress ratio of $A = 1$, the maximum stress required for failure in 10^6 cycles for the new supply of tubing was 22,500, 8,200, and 3,200 psi, for 1600, 1800, and 2000 F, respectively. No such comparison can be made for the tests at 1400 F, or for other stress ratios since only the new supply of tubing was available for these tests. For a

stress ratio of $A = 1$, the maximum stress required for 10^6 -cycle failure at 1400 F was 37,000 psi.

Also previously reported were the preliminary results for the stress ratio of $A = 0.25$. For $A = 0.25$, maximum stresses of 34,000, 15,400, 6,100, and 2,700 psi are required to promote failure at 10^6 cycles for 1400, 1600, 1800, and 2000 F, respectively.

WORK THIS PERIOD The metallurgical study, designed to indicate whether the differences in the fatigue behavior of the two supplies of tubing could be explained by microstructural differences, has been completed. It is concluded from this brief examination that the fatigue behavior of the Hastelloy tubing is related to the structure prior to testing and that an examination of a tube structure would indicate whether its fatigue life would be similar to the original or the new supply of tubes. It would have to be determined by some further study into the problem, but it is likely that with a slight modification or control of the processing details of the tubes (including the cold working and subsequent heat treating) maximum fatigue life could be achieved.

During February, 24 specimens have been failed at a stress ratio of $A = \infty$. Preliminary reduction of data indicates that maximum stresses of 30,000 and 11,500 psi are necessary to promote 10^6 -cycle failure at 1400 and 2000 F, respectively. The results for 1600 and 1800 F are, as yet, not conclusive.

PLANS FOR FUTURE WORK Plans for March are to conduct more tests for the stress ratio of $A = \infty$ for 1600 and 1800 F and thereby complete the experimental program. Also, a final report will be written during March to summarize the findings of the present phase of the project.

CORROSION OF THORIUM AND URANIUM UNDER STORAGE CONDITIONS (LIVERMORE)

P. D. Miller

Thorium, uranium, and their alloys are being considered by the Lawrence Radiation Laboratories and by the Sandia Corporation for applications which may require exposure to a variety of atmospheric conditions. Two research programs, aimed at enlarging the information concerning the corrosion resistance of these metals, are under way at Battelle.

In one study, procedures are being developed for applying corrosion-resistant electroplated coatings to thorium.

A fairly extensive corrosion evaluation is also being conducted under a variety of conditions on bare and coated specimens of the above-mentioned metals and their alloys.

Electrodeposited Coatings for Thorium (SC)

J. G. Beach and C. L. Faust

OBJECTIVE To develop a coating for thorium that prevents corrosion.

PROGRAM APPROACH The various factors for producing sound, protective electroplated coatings on thorium are being studied: (1) prefinishing, to remove surface contamination and defective basis metal; (2) activating, to provide maximum adherence of the plated coating; (3) coating system, to provide the needed protection and/or surface properties; and (4) postplating treatment, to improve the properties of the composite system. Metallography, bond tests, and corrosion tests are being used to evaluate the coated thorium.

PROGRESS REPORTED PREVIOUSLY Nickel (1 to 2 mils) plus chromium (0.035 mil) protected as-plated thorium samples, but blistering occurred.

WORK THIS PERIOD Metallographic examination of as-plated thorium samples that blistered during exposure to water-saturated air at 200 F showed the failure to have occurred within the thorium metal and not at the thorium-nickel interface. Thus, the adherence of the plated coatings was satisfactory, but hydrogen gas could collect in the thorium, at voids or inclusions, and result in failure of electroplate-thorium composite.

Outgassing of the plated thorium by "slow" heating to 500 F in vacuum, with a holding period at 200, 300, 400, and 500 F, prevented subsequent blistering of nickel-plus-chromium plated thorium. Apparently hydrogen, in the atomic form, can be removed through the plated coatings by outgassing. But if the hydrogen is allowed to collect and form molecular hydrogen in voids or inclusions within the thorium, the pressure built up will blister surface layers of thorium along with the plated coatings.

Eight additional samples were coated with nickel-plus-chromium plates for the UCRL corrosion evaluation: exposure to water-saturated air at 120 F and exposure to storage conditions at Columbus, Ohio, and at Daytona Beach, Florida. These samples will provide corrosion data to compare the pretreating, plating, and outgassing techniques developed thus far with the technique available in September, 1960.

PLANS FOR FUTURE WORK Evaluation of electrochemically produced films (thorium phosphate or phosphate sulfate) on thorium as a basis for adhesive bonding is to be made.

Comparison of various types of thorium metal as to the quality of fabricated sheet and to plating characteristics is planned.

Corrosion Evaluation (LRL)

E. F. Stephan, P. D. Miller, and F. W. Fink

OBJECTIVE To determine the durability of thorium, uranium, and related alloys under storage conditions.

PROGRAM APPROACH Bare and coated coupons of the metals are being exposed under simulated storage conditions and under accelerated laboratory conditions.

PROGRESS REPORTED PREVIOUSLY Thorium, uranium, and uranium-10 w/o molybdenum-alloy specimens were exposed to three accelerated laboratory conditions, as summarized in BMI-1469. The attack was localized and resulted in some pitting. The uranium was the most severely attacked. In general, the alloy was the most durable of the materials studied.

WORK THIS PERIOD A Phase II study has been completed, involving exposure of materials to 100 per cent relative humidity at 120 F for 2500 hr. Thorium, uranium, and uranium-10 w/o molybdenum alloy were combined by soldering and welding to form specimens about 1/2 by 2 in. Crevice specimens of about the same size were formed by joining two pieces by a metal screw. In this group, the above metals were combined and also thorium was joined to aluminum, beryllium, magnesium, stainless steel, and titanium.

The soldered joints involving uranium were not durable, and some were separated after only about 500 hr of exposure.

The welded coupons showed no effects that could be attributed to the welds.

There was no evidence of marked galvanic attack at the couples of dissimilar metals. The magnesium was covered with a heavy white scale and the beryllium was partially covered with a thin white deposit. The aluminum looks good, except for a fine "salt-and-pepper" effect. The stainless steel and the titanium were in excellent condition.

In general, the uranium was severely corroded and pitted. The thorium was covered with the typical white gelatinous corrosion product. Small nodules above shallow pits were scattered at random over most of the pieces. Scrubbed pieces showed these nodules, but otherwise the surface looked unaffected. The uranium-10 w/o molybdenum alloy specimens were covered with a thin colored tarnish film. No corrosion was evident, except for a very few isolated pits on some pieces.

Bare 2 by 3-in. panels of thorium, uranium, and the alloy were corroded much in the normal manner. The corrosion was somewhat worse on one alloy specimen which has been pickled prior to exposure.

The nickel-plated thorium showed good resistance, except at the plating-contact areas.

Blisters formed on the panels covered with the organic coating.

Severe corrosion occurred on the aluminum-plated uranium panels. One panel was removed after 1000 hr because the coating was almost completely loosened.

PLANS FOR FUTURE WORK The Phase III program described in BMI-1473 will be continued.

GAS-PRESSURE BONDING OF BERYLLIUM-CLAD ELEMENTS (ORNL)

S. J. Paprocki, E. S. Hodge, and J. S. Perrin

OBJECTIVE To develop fabrication techniques for cladding uranium dioxide fuel cores with beryllium.

BACKGROUND The gas-pressure-bonding process is valuable as a fabrication technique because in this process the components undergo a minimum of deformation. The process is thus particularly suited for use with materials, such as beryllium, that have directional properties. In addition, the technique will enable cladding of brittle fuel core materials, such as uranium dioxide, to be accomplished without producing fragmentation. Beryllium-clad uranium dioxide is of interest in ORNL's studies on potential materials for gas-cooled reactors, and program reported here is in support of this work at ORNL.

PROGRAM APPROACH The gas-pressure-bonding technique is being used to fabricate specimens. Evaluation is based upon bond and cladding properties after bonding as determined by metallographic examination and mechanical testing.

PROGRESS REPORTED PREVIOUSLY Studies of the effect of surface condition and bonding parameters on the self-bonding of beryllium are being conducted. Studies of the self-bonding of beryllium components similar in design to those contained in compartmented fuel elements have been made. Beryllium specimens containing UO_2 cores have been bonded at various parameters to determine the compatibility of beryllium and UO_2 .

WORK THIS PERIOD Specimens containing beryllium in contact with coated UO_2 cores were bonded at 1650 F for 4 hr at 10,000 psi and metallographically examined. One of the cores was coated with pyrolytic carbon and the other with graphite. A reaction occurred between the beryllium and the core coated with graphite. No reaction was observed between the beryllium and the core coated with pyrolytic carbon. A specimen containing a pyrolytic carbon-coated core in contact with beryllium is being bonded at 1750 F for 4 hr at 10,000 psi to determine if a reaction occurs under these bonding conditions.

PLANS FOR FUTURE WORK Fabrication of specimens to study the self-bonding characteristics of beryllium and the compatibility of UO_2 with beryllium will continue.

RWD:CRT/all