NUCLEAR FUELS AND MATERIALS DEVELOPMENT

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I. PREFACE

Within the United States Atomic Energy Commission, materials research is supported by the Division of Research (1), the Division of Reactor Development and Technology, and by others, such as the Division of Military Application. The Division of Reactor Development and Technology funds materials research via three routes. The major program is that sponsored through the Fuels and Materials Development Branch (2). Materials research is also funded under the terms of the Joint U.S.-Euratom Research and Development Program (3). Finally, materials research is performed under the various reactor projects to obtain materials to meet the individual design requirements.

This report is a summary of work being done under the Advanced Reactor Technology program of the Division of Reactor Development and Technology. It includes discussions of several materials projects, authorized by the U.S.-Euratom Joint Research and Development Board, for which the Fuels and Materials Development Branch is technical point of contact.

The fuels and materials research supported under the Advanced Reactor Technology program provides a technical base of information necessary for establishing the capabilities and limitations of reactor materials. This effort includes the synthesis, fabrication, and testing of prototype fuels and fuel elements aimed specifically at improving nuclear reactor output and life. The program supplies data on physical and mechanical properties of metals, alloys, and materials required by reactor designers. Where testing criteria are vague, attempts are made to develop more meaningful testing procedures which would provide data for use in design of nuclear systems.

This document highlights some of the more interesting developments in fuels and materials research during calendar year 1964. Certain work at the General Electric Company's Atomic Power Equipment Department is included because of its relationship to uranium dioxide fuel technology, even though the work is not funded under the fuels and materials program. The format for this issue is not the same as in previous editions. Work is identified by site, rather than topic. Thus, it is necessary to refer to the Subject Index in order to determine what work may be reported on a particular fuel or material. Little attempt is made to provide the rationale for performance of the various research programs, as this would have required appreciable expansion of the report. It is thus assumed that the reader is familiar with reactor materials requirements. Such information has been provided in detail in the literature, in general discussions (4,5) and in more specialized publications (6,7,8).

The report has been compiled from material provided by the individual contract sites. To maintain brevity, actual technical data have been kept to a minimum. The reader should therefore consult the reports issued by the individual organizations for detailed coverage of the material presented.

Ames Laboratory, Iowa State University, Ames, Iowa

The principal objective of this work is the development of materials with more desirable properties for nuclear application. This includes preparation of higher purity metals or compounds, discovery of new alloys and a better understanding of the processing methods of materials of interest and their behavior under conditions imposed by their intended use.

New Technique Developed for Purifying Thorium and Yttrium Metals

The transport rates of various impurities in thorium and yttrium under the influence of a direct current are being measured at various temperatures. Carbon, oxygen and nitrogen have been found to move at appreciable rates in both metals and this knowledge is being used to prepare them in very high purity. Chemical analyses, hardness and electrical resistivity values for thorium thus treated indicate that previously unattained degrees of purity are attainable by this method. While the technique has previously been applied to yttrium with only limited success, the process developed at the Ames Laboratory shows considerable promise and may have application to other metals such as lutetium, vanadium and chromium.

New Process for Preparing Metal Chlorides

The conversion of an oxide salt to the chloride is usually carried out by the reaction of chlorine gas with a mixture of the oxide with carbon. This generally results in a product with some residual carbon which is often difficult to remove and is transferred to the metal during reduction of the chloride. The use of phosgene gas as the chlorinating agent circumvents this problem and has been used successfully to prepare high quality thorium and yttrium chlorides. These salts can be reduced rather simply to yield metal of a quality suitable for most reactor applications.

Oxidation Mechanism of MoSi_2

The oxidation mechanism of MoSi_2 has been established. Below 800°C SiO_2 and MoO_3 are the final products while above this temperature Mo_5Si_3 and SiO_2 are formed. The reaction kinetics are governed by diffusion of the reactants.

Computer Program for Indexing X-ray Powder Data

A computer program for determining the crystal class and lattice constants of a phase from x-ray powder data has been worked out. The satisfactory application of the program was demonstrated by processing trial problems for various crystal symmetries.

Alloy Investigations

Work on determination of phase diagrams has been completed and published in the scientific literature during the past year for the following alloy systems: yttrium-oxygen, yttrium-cobalt, ytterbium-magnesium, cerium-zinc, magnesium-cobalt, calcium-ytterbium, hafnium-cobalt and the niobium-rich end of the niobium-zirconium-oxygen ternary system.

Adiabatic Heating During High-Energy-Rate Forming

Among the several recent innovations in forming methods, high-energy-rate extrusion particularly shows considerable promise for forming refractory metals. Because the deformation rate is extremely rapid, the heat generated does not have time to dissipate. A temperature rise associated with such adiabatic processes has been proposed to explain the improved formability of refractory metals during high-energy-rate extrusion. A technique has been developed for measuring the adiabatic temperature rise in the deformation zone during the forming operation. Preliminary results indicate that the temperature increase is not sufficient, per se, to account for the enhanced formability.

A Universal Electropolishing Procedure for Metals

A method whereby almost any metal can be electropolished with a single electrolyte has been developed. The electrolyte is perchloric acid in methanol that has been cooled to approximately -70°C . There are a few metals and many alloys on which the method has not been tried, of course, but it has proven a successful electropolishing technique for a large number. It may also have applications in analytical chemistry as a general procedure for dissolving an alloy and in studying the mechanisms of electropolishing and electroplating.

Argonne National Laboratory

Work at Argonne National Laboratory supported by the Fuels and Materials Development Branch can be classified into the following general areas:

1. Ceramic Fuels Development. This work includes preparation of various compounds of (U,Pu,Th) with (C,P,S,O,As,Te,Sb,Se) and the determination of physical and thermal properties of the more interesting compositions.
2. Metallic Fuels Development. Emphasis in this area has been on alloys containing plutonium, most recently in the Th-U-Pu system.
3. Cladding Materials Development. Work in this area has centered on studies of the mechanical properties of refractory metal alloys in the temperature range 500-1000°C.
4. Irradiation Studies. The most promising reactor materials are irradiated under temperature controlled conditions to determine the influence of irradiation and irradiation temperature on important material properties.
5. Corrosion Studies. Liquid metal corrosion experiments are performed on potential cladding materials in order to determine the important variables in both the liquid metal environment and in the test material that affect corrosion and mass transfer rates.
6. Nondestructive Testing Development. Work in this area has been concentrated on developing new and more effective inspection techniques utilizing infrared radiation, ultrasonic imaging, neutron imaging, and rotating electromagnetic fields.

Significant accomplishments in the above areas of research and development are summarized in the following sections:

Sintering of UC-PuC

Mixtures of UC-PuC were prepared by arc-melting the elements. Buttons formed were crushed in a nitrogen atmosphere, containing about 0.005 w/o O_2 and 0.01 w/o H_2O . Pellets prepared from powder with a particle size of $<8\mu$ attained densities of 80 to 85% of theoretical when sintered in argon for 2 hours at 1600°C and 90% of theoretical when the temperature was increased to 2000°C for 2 hours. The fine particle size of the powder was apparently conducive to oxygen pickup since these pellets contained from 1 to 2 w/o O_2 oxygen. Powder having a particle size of $<4\mu$ was pressed at 2100 kg/cm² and sintered to 90% of theoretical in argon at 2100°C for 2 hours. Examination of these pellets showed only a solid solution of (U,Pu)C,

and there was no detectable loss of plutonium from sintering under argon at this temperature.

Plutonium Monosulphide

Plutonium monosulphide prepared by the gas-metal reaction was crushed to $<44 \mu$, pressed into pellets and sintered in vacuum or in an argon atmosphere. Densities of about 94% of theoretical were obtained at temperatures of 1600°C . The theoretical density of PuS_2 , calculated for a stoichiometric compound with a lattice constant of $5.540\text{\AA}$ was 10.59 g/cc . The melting point of PuS was determined as 2330°C and the average linear thermal expansion coefficient for the temperature range of 18 to 960°C was found to be $18.54 \times 10^{-6}/^{\circ}\text{C}$. The average value for room temperature electrical resistivity was $2450 \pm 150 \text{ micro-ohm-cm}$. This value is considerably higher than the range of 112-359 micro-ohm-cm for US.

Thorium and Plutonium Phosphides

Thorium phosphide like uranium phosphide is a refractory compound, and may be of interest for some reactor applications. It is prepared by the gas-metal reaction, and is dark blue in color. It has a calculated density of 8.83 g/cc , and a melting point of $2900 \pm 50^{\circ}\text{C}$. Pellets pressed from this material sintered to 70-78% of theoretical at 1800°C . Only a slight increase in density was obtained by increasing the sintering temperature to 2200°C .

Plutonium phosphide, prepared by the gas-metal reaction, and crushed to $<44 \mu$, sintered to densities of 88% of theoretical at a temperature of 1600°C . At higher sintering temperatures the vaporization loss increased rapidly with only a slight increase in sintered density. The melting point of this compound under two atmospheres of pressure appeared to be about 2900°C , however, additional work is needed to determine the exact melting point. The melting point of PuP probably lies between the melting point of UP (2540°C) and that of ThP ($2900 \pm 50^{\circ}\text{C}$).

Uranium Mixed Anion Systems

The system UC-US and US-UP are being investigated. The preliminary phase diagram of UC-US indicated that no compounds were formed. This diagram showed the presence of two solid solution regions, a UC(S) which has a maximum of 40 m/o US in solution at 1600°C , and US(C) which contains 40 m/o UC at 1600°C . The region between is composed of two saturated solid solutions.

Melting temperature determinations indicated a maximum liquidus temperature for the composition 40 m/o UC-60 m/o US. The temperature 2540°C is higher than the melting point of US (2460°C) or UC (2410°C).

In the system US-UP complete mutual solubility was found between the end members. The preliminary phase diagram showed a melting point maximum at 70 w/o UP-30 w/o US, and a minimum at 10 w/o UP-90 w/o US.

Mechanical Properties of UO_2

Uranium compounds have many suitable properties for application as reactor fuel materials, but little quantitative information is available to assist design from the structural strength standpoint. The modulus of rupture of UO_2 is being studied to gain some insight as to the effect of processing variables (i.e., density) strain rate and temperature on the strength of UO_2 .

High density UO_2 (95% plus, theoretical density) shows a modulus of rupture of the order of $850\text{--}900 \text{ kg/cm}^2$, at room temperature, with a brittle fracture, i.e., showing little evidence of plastic deformation. At 1000°C , the breaking strength increases to around 1200 kg/cm^2 for high density and slow straining. A decrease in density to 92% of theoretical and an increase in strain rate lowers the strength to about 1000 kg/cm^2 . At 1000°C some indication of deformation is noticed.

At 1250°C the breaking strength increases to about 1750 kg/cm^2 . Deformation is mainly elastic, with a value of Young's Modulus of 1900 kilobars.

At 1500°C the material begins to behave in a similar manner to a ductile metal when slowly strained. Load-deflection curves show an initial elastic portion of Young's Modulus roughly 200-250 kilobars. The breaking strength is lowered at 1500°C to about 1000 kg/cm^2 . Lower densities have little influence on strength, but gives higher ductility.

Thorium-Uranium-Plutonium Fuel Alloy Development

It has been found that thorium alloys containing up to about 20% uranium and 10% plutonium are potentially useful fuel alloys. They have solidus temperatures of greater than 900°C and are two-phase alloys in which the uranium-plutonium phase is completely surrounded and contained by the structurally desirable thorium. On the other hand, it was established that those thorium alloys that are high in plutonium (20% or more) and low in uranium (1 to 4%) are metallurgically undesirable because of the presence of a low-melting plutonium phase.

The alloys were successfully fabricated by rolling and swaging from metals of commercial purity.

Compatibility tests showed that vanadium-20% titanium alloy is a suitable cladding material for the thorium-uranium-plutonium alloys whereas stainless steel is not. Ultimate evaluation of the promising Th-20U-10Pu and Th-10U-10Pu alloys must await the outcome of the irradiation tests which are in progress.

Mechanical Properties of Refractory Metal Jacketing Alloys

Alloys based on the refractory metals vanadium, niobium, and molybdenum are potentially useful in conjunction with plutonium-bearing alloy fuels. Comparative tests on alloys selected from these systems show that

V-20w/oTi alloy has a creep strength superior to Type 304 stainless steel at 650°C. It also exhibits a high uniform elongation capability which will permit it to deform in a ductile manner in the form of a pressurized tube. Other alloys studied have been Nb-1w/oZr and Mo-0.5w/oTi-0.08w/oZr. At test temperatures of 650-700°C these alloys deform locally and fracture at low strain values in a tubular geometry. The mechanical properties of V-20w/oTi alloy are sensitive to fabrication method and heat treatment. Rod extruded at 1100°C has a 0.002 offset yield stress of 46 kg mm⁻² at 650°C whereas the sheet, recrystallized at 900°C, has a corresponding value of only 33 kg mm⁻². Sheet recrystallized at 900°C was found to have a minimum creep rate about 1/4 that of sheet that had been stress relieved at 700°C. Further improvements are being sought in the vanadium base alloy system through alloying and heat treatment.

Irradiation Behavior of US

The microstructures of high density (90% of theoretical) and low density (80% of theoretical) US pellets show a considerable difference in appearance after irradiation to high burnups at elevated temperatures. Significant changes do not occur in the high density material, but marked alterations in structure are noted in low density pellets. It appears that most of these changes are the result of high central temperatures and temperature gradients that are caused by the lower thermal conductivity of the more porous material. Central void formation has been observed, along with extensive migration of UOS phase to the cooler periphery of the pellet. Any free oxygen present results in the formation of UOS on crystallographic planes and the conversion of some of the UOS to UO₂.

Additional specimens of pressed and sintered US are under irradiation. These specimens have achieved burnups ranging up to 5×10^{20} fissions/cm³ at cladding temperatures as high as 800°C with no indication of failure or other operating difficulty. Target burnups are near 2×10^{21} fissions/cm³.

Irradiation Behavior of Vibratory-Compacted UC-PuC

UC and PuC powders, vibratorily compacted into Nb-1w/oZr alloy tubes, appear to have excellent potential as a high burnup, high temperature fuel element design. Specimens of UC-20w/oPuC powder mixtures in Nb-1w/oZr alloy tubing with a thickness of 0.23 mm (0.009 in.) have reached burnups near 1.4×10^{21} fissions/cm³ at a cladding temperature of 650°C (1200°F) without indication of failure or other operating difficulty. Target burnup for these specimens is 2.6×10^{21} fissions/cm³. Other specimens being irradiated under similar conditions are scheduled for burnups of 4×10^{21} fissions/cm³.

Irradiation Behavior of Glass-B₄C Dispersions

Dispersions of B₄C in glass as a control rod material offer the important advantages of corrosion resistance and low cost fabrication into complex shapes by extrusion. The first irradiations of this material have shown unusual dimensional stability. Pellets of 15 w/o B₄C dispersed in a

soda-potash glass were jacketed with 0.5 mm thick Type 321 stainless steel and irradiated to exposures up to 4×10^{21} neutrons/cm² at temperatures as high as 550°C. No dimensional or density changes resulted.

Irradiation Behavior of Co-Dy₂O₃ Dispersions

Co-Dy₂O₃ dispersions offer a new approach to a long-lived control rod material which, because of Co⁶⁰ buildup, would also have appreciable monetary value after removal from reactor service. The initial irradiation behavior of this material has been very favorable. Pellets of Co-30w/o Dy₂O₃ irradiated in 0.5 mm thick Type 304 stainless steel jackets to an exposure of 8×10^{21} neutrons/cm² at 300°C showed diameter increases of about 1%.

Zirconium Alloys for Use in Superheated Steam

The metallurgical condition for optimum corrosion resistance varies with alloy composition. For example, Zr-3w/oNi-0.5w/oFe, one of the better alloys, has the lowest corrosion rate when exposed in the as-cast condition. (This last statement is of course restricted to comparison among the conditions studied.) However, material exposed to steam in the as-cast condition is subject to formation of surface blisters, thought to be related to local physical defects in the metal. Moderate cold deformation (about 10% diameter reduction) produced by the Magneform Process, a high-energy forming technique, did not destroy the as-cast structure but did apparently eliminate the cause of surface defects. Zr-3w/oNi-0.5w/oFe exposed to steam at 540°C and 42.2 kg/cm² for 128 days formed a smooth, dark, adherent corrosion film free of surface blisters. The rate of weight gain, 3 mdd (linear approximation for the period 35-128 days) was appreciably lower than for hot rolled material. (Hot rolling is an alternate method of reducing surface blistering.) This development is significant in that a technique adaptable to fuel element fabrication retains a desirable metallurgical condition which is stable in the exposure environment. The behavior of Zr-3w/oNi-0.5w/oFe is in contrast to that of ternaries containing copper and iron, for which the preferred structure, produced by beta quenching, is not retained during long time exposure at 540°C.

Corrosion rates at 650°C of the better alloy₃ are not affected if the pressure is reduced from 42.2 kg/cm² to 1.35×10^{-3} kg/cm² (1 torr). This result may be of practical significance and is of theoretical importance because it lends validity to extrapolation of the results of electrical measurements made at the lower pressure (for reasons of experimental convenience) to the higher pressures of practical interest. Such measurements lend support to previous suggestions that the reduction in absorption of corrosion product hydrogen as the exposure temperature is increased from 540° to 650°C is related to temperature sensitive surface electrical properties.

Corrosion of Stainless Steels and Nickel Base Alloys in Superheated Steam

The high general corrosion rates at 650°C and sensitivity of rates to surface preparation of the 300 series stainless steels and Incoloy 800

have been noted in previous reports. Addition of aluminum or silicon (up to about 4 w/o) markedly reduced corrosion rates of material tested in the electropolished condition (the condition which has been shown to have the highest corrosion rates). Although problems of brittleness can arise as the result of alloying with aluminum or silicon, material has been commercially produced which is ductile, fabricable, and weldable, and which contains aluminum or silicon in concentrations great enough to significantly reduce corrosion rates. Examples are Type 302B stainless steel (essentially 304 with 2 w/o silicon) and modified Incoloy-800 containing 2.9 w/o aluminum.

At 750°C, under static conditions, the behavior of these materials is qualitatively similar to the behavior at 650°C. The relative corrosion resistance (one material compared to another) is unchanged. Except for Type 406 stainless steel, all materials showed slightly increased metal losses for equivalent exposure times as compared with exposure at 650°C. Type 406 showed decreasing metal loss with the increase in temperature, a continuation of the trend noted earlier. The pronounced effect of pre-exposure surface treatment on corrosion behavior was again observed.

Experimental evidence indicates that the improved corrosion resistance associated with cold worked surfaces is related to partial conversion to ferrite rather than to the effects of residual stresses.

Corrosion Mechanism in Liquid Metal Environments

The kinetics of the dissolution of Type 304 stainless steel in bismuth-tin eutectic alloy has been investigated using the rotating disk technique. This study, considered as preliminary to the investigation of refractory metal-alkali metal systems was undertaken to demonstrate the validity of the theoretical approach. If it develops that the results are similar for systems of widely differing chemical characteristics, an important generalization will have been demonstrated.

The effect of Reynolds number (as determined by rotational speed of the disk) was studied over a range of 1.3×10^3 to 1×10^5 at 860°C. Below a Reynolds number of 2×10^4 , the rate of dissolution was a function of the angular velocity of the disk and the data show that the process is liquid diffusion controlled. Above a Reynolds number of 2×10^4 , the rate of dissolution is independent of angular velocity and the process is surface reaction controlled.

Temperature also affects the dissolution mechanism. For example, above about 700°C and at a Reynolds number of 6.6×10^3 , the process is controlled by liquid diffusion, as stated above. However, if the temperature is reduced below about 650°C (at a constant Reynolds number) the process becomes surface reaction controlled.

These results tend to confirm that as the temperature is increased, systems tend toward diffusion control and diffusion control becomes operative over wider ranges of Reynolds numbers.

Polarization Studies in Liquid Metal Environment

Surface electrical phenomena in alkali metal systems are being studied chiefly because it is thought the results of such studies may give insight into mechanisms. Results to date indicate that impressed voltages can, in fact, affect the behavior of the zirconium-oxygen-sodium system at 540°C and that aspects of the corrosion process may be monitored by electrical means.

Determination of Elastic Moduli of High Temperature Materials by Ultrasonics

The object of this program is to measure the temperature dependence of the elastic moduli of materials which show promise in high temperature reactor applications. Any of the elastic moduli, e.g., Young's Modulus, Poisson's Ratio, Shear Modulus, can be determined if the sound velocities are known. A technique for measuring two sound velocities with one type of sound wave makes use of the waveguide effects which are present when sound is propagated in a long, narrow, bar. Threading the bar greatly reduces the amplitude of disturbing trailing pulses in the sample, a fact originally reported elsewhere, and confirmed by this work. Although the temperature limitation of the present equipment, about 1150°C, is comparable to other available equipment for these measurements, the successful operation of, and experience with this equipment is expected to be of value in the design of the 2000°C and higher temperature range equipment which is of primary interest.

Ultrasonic Imaging

A significant advance in the use of the continuous-wave ultrasound closed circuit television system used for viewing ultrasonic images has been made during the past year. This has come about by the realization that relatively thin flat inspection objects used in a direct-shadowing technique (no lenses used in the ultrasonic imaging system) should be oriented to excite a first-order Lamb wave mode in the object. With the proper orientation for Lamb wave excitation, standing waves are eliminated, the intensity of ultrasonic energy transmitted through the inspection object is increased, and the sensitivity to internal defects is maintained at a high level. The television imaging system used with a Lamb wave object orientation appears particularly attractive for inspections of flat reactor fuel elements. Such objects can be inspected with excellent sensitivity to defects normally of interest with ultrasonic inspection, and with improved resolution and inspection speed as compared to mechanical scan ultrasonic techniques. As an example of this latter advantage, a Borax-V superheater type fuel plate can be inspected in 10 mins. or less as opposed to an average time of 45 to 60 mins. required by a mechanical scan method.

Correlation of the Sound Transmission and Heat Transfer Properties of A Bond

The acceptance or rejection of a bonded element which has been tested by ultrasonic methods has been made on the basis of the ability of the bond to transmit or reflect ultrasonic energy, with only occasional

reference to destructive evaluation of the bond. The criteria for acceptance are often poorly defined, as the tests do not provide any information about the serviceability of the element, i.e., its ability to transmit heat, because it is not known what correlation, if any exists between the heat transfer and ultrasonic transmission properties. Thermal diffusivity and thermal conductivity measurements on mechanical bonds (brazed bonded copper) and roll bonds (sections of Borax fuel plates) were made utilizing a thermal pulse method. The method proved itself to be very sensitive to variations of bonding, and great differences in thermal properties were found in closely spaced (about 1 mm apart) small areas (1 mm^2). Ultrasonic tests using the through-transmission method were also made by a point-by-point scan of the specimens, so that a comparison of the amplitude of the transmitted ultrasonic pulse and the thermal diffusivity and thermal conductivity could be made at each point on the specimen. Although complete results from this program are not yet available, this study has shown a general correlation between thermal conductivity and ultrasonic transmission in bonded test samples. This in itself is a significant result. In addition, the thermal method proved itself so well that plans are now underway to perform thermal conductivity measurements on irradiated samples.

Neutron Image Intensification

A neutron imaging system which presents an immediate televised picture of a thermal neutron image has been placed in operation at Argonne's Juggernaut reactor. The neutron system provides such advantages as low object dose per picture, reduced shielding problems, and, most important, the capability for observing movement within the inspection object. The image intensifier tube which converts the neutron image into a visible signal is a vacuum tube type intensifier. The input target is 22 cm in diameter and is a combination neutron-scintillator, photoemissive target which provides an electron image of an incident thermal neutron signal. Amplification is provided by a 30 kv acceleration of these electrons toward a 2.5 cm diameter, output phosphor screen. The brightness of the output phosphor is greater than 10 ft-Lamberts for an incident thermal neutron intensity of $10^7 \text{ n/cm}^2\text{-sec}$. The closed circuit vidicon television system now used with the intensifier provides a televised image for thermal neutron intensities of $10^5 \text{ n/cm}^2\text{-sec}$ or higher, demonstrates thickness changes in materials such as steel and uranium having values as small as 4 percent, has a resolution of about 0.5 mm and has the capability for following high contrast object movements at least as fast as 5 m/min. The low gamma radiation response of the present system permits televised neutron images of reasonably radioactive objects to be obtained. In the latter part of 1964, preparations were being made to use the television system for examinations of irradiated jacketed fuel samples while the samples were being heated. The capability for observing fuel expansion and/or jacket rupture using such postirradiation annealing methods is expected to yield important information. Also of importance for the potential industrial application of neutron inspection methods is the excellent sensitivity of the neutron intensifier. Detection capability at thermal neutron intensities as low as $10^3 \text{ n/cm}^2\text{-sec}$ makes non-reactor neutron sources practical for the first time in such neutron inspection systems.

Infrared Imaging

An infrared sensitive television system employing a vidicon camera tube sensitive to radiation in the 0.8 to 2.7 μ wavelength region has been placed in operation. The lowest object temperature which has been observed through the system is 170°C. Variations in object temperature which can be observed with the system vary from 10°C for an object temperature of 200°C, to 3°C for object temperatures 350°C or higher. For nondestructive testing applications, the system is attractive because a reasonably large object area can be continuously observed and because the speed of the image presentation enhances the possibility of detecting thermal transients on the object surfaces.

ATOMICS INTERNATIONAL

The fuels and materials studies underway at Atomics International are directed towards obtaining a detailed understanding of the processes and mechanisms controlling the response of materials under irradiation and the application of this knowledge to the development of improved reactor core materials. The research investigations are primarily concerned with material parameters associated with crystal lattice defect generation, motion, and recovery and rare gas atom behavior in fissile and non-fissile materials. Programmatically the work is oriented to: a) structure, properties and fission effects in uranium carbide type interstitial compounds, b) synthesis, structure and fission effects in transition metal hydrides, c) properties, structure, and radiation effects in beryllium oxide, and d) studies of fission effects in metal fuels.

Preparation and Characterization of Stabilized UC Containing Second Phase Particles

Tungsten has been incorporated into UC in the form of a fine dispersion of second phase particles to provide fission gas trapping sites which should stabilize the UC against swelling at high temperature-high burnup levels. Research samples are being prepared as follows: a) procurement of arc cast UC rods, b) pre-forming 0.005" or 0.010" diameter tungsten wire into a long helix of slightly larger diameter than the UC rod, c) spacing the tungsten helix around the UC rod to give a predetermined average concentration of tungsten per unit length of the rod, and d) incorporation of the tungsten into the UC utilizing an induction zone refiner with the molten zone traverse rate ranging from 1" to 4" per hour in an argon atmosphere.

Starting with hypostoichiometric UC, the resulting material is nearly stoichiometric and metallographic, X-ray diffraction, electron microscopic, and electron microprobe examination has shown that the tungsten is dispersed throughout the UC as small second phase metallic particles. Macroscopically, the concentration of tungsten is uniform in the radial direction but an axial concentration gradient is established with the tungsten content gradually increasing from the bottom to the top of the sample until the final solidified region is reached which contains a much higher concentration of tungsten. The axial gradient is small, 0.6 to 0.8 wt % W, over a 3" length of a nominal 1 wt % sample. The homogeneity within short sections is satisfactory. One very noticeable characteristic of this material is the very irregular "snake-like" grain boundaries suggesting surface adsorption during crystal growth from the melt.

Utilizing replication electron microscopic techniques, the tungsten particle size has been observed to be in the range of 0.1 to 1.0 microns with a few "large" particles present 3 to 10 microns in size. The concentration is in the range 10^{12} to 10^{13} particles/cc. The particle size and density approach the desired 10^{13} particles/cc of 0.1 micron particles. These tungsten particles are thermally stable to at least 1900°C. Heat treatments to develop a finer dispersion are being studied.

Composition Control of UC by Zone-refining

It has been found that zone-refining can be used to both purify uranium carbide and to control stoichiometry. When zone-melting is performed in a vacuum, volatile impurities are removed but vaporization of uranium causes a strong shift to a hyperstoichiometric composition. Using an argon atmosphere to suppress uranium evaporation, it has been observed that the excess uranium or UC_2 is concentrated in the molten zone. The resultant zone-refined rod approaches single-phase UC containing ~ 4.8 wt % C regardless of whether the starting rod is hypo- or hyperstoichiometric. Removal of the excess constituent is more effective the slower the rate of traverse and in many cases the product is stoichiometric, single phase UC.

Hardness of UC as Affected by Temperature, Composition, and Impurity Content

Hardness of a substance as a function of temperature is easily measured and is qualitatively related to the strength and rigidity of the crystal structure. Hardness measurements with a diamond pyramid indenter for a group of UC preparations are given in the table below, covering the temperature range from room temperature to 800°C.

Although several variables are operating, the observed trends are believed significant. One of these is the effect of metallic impurity content. The sample with an exceptionally large metallic impurity content had the highest room temperature hardness, perhaps due to the existence of the impurities as a dispersed phase. The softest room temperature value was obtained on the sample with the lowest metallic impurity content, in spite of the fact that this was slightly hyperstoichiometric. Those with the lowest hardness at high temperature were the most hypostoichiometric samples, with appreciable quantities of free uranium. Thus, hardness at room temperature is particularly sensitive to metallic impurities, while hardness at elevated temperature is sensitive to the presence of free uranium. A correlation with oxygen and nitrogen content could not be made.

Hardness of Uranium Carbide

Carbon Content wt % C	Metallic Impurities, ppm	Oxygen Content, ppm	Nitrogen Content ppm	Diamond Pyramid Hardness, Kg/mm (0.4 Kg load)			
				25°C	500°C	700°C	800°C
4.85	100	<100	<150	540	400	350	230
4.59-4.63	6500*	140	900	1050	550	320	210
4.76-4.81	-	140	900	700	480	300	270
3.94	-	100	770	713	405	123	53
4.19	1000	100	250	770	505	147	73
4.60	800	200	180	865	470	203	115
4.75	500	50	130	720	400	136	97

*Principally 0.39% Si and 0.24% Mo.

Ternary Hydride Preparation and Characterization

Ternary compounds of the type metal-hydrogen-non-metal are being studied as potential high temperature moderating materials, as species that may be present as impurities in metal hydrides, and as compounds with a potentially unique type of bonding. On investigation of the ternary zirconium-hydrogen-non-metal systems, where the non-metal may be B, C, N, or O, the existence of a ternary compound $ZrC \cdot ZrH_x$ has been confirmed and a similar compound $ZrN \cdot ZrH_x$ discovered. These compounds exist over a range of compositions, with the subscript x for hydrogen approaching the value 2 as a maximum. The crystal lattice cell constants of these compounds compared with alpha zirconium are:

<u>Material</u>	<u>a_o</u>	<u>c_o</u>	<u>c_o/a_o</u>
α Zr	3.232A	5.147A	1.593
$ZrN \cdot ZrH_x$	3.288A	5.468A	1.663
$ZrC \cdot ZrH_x$	3.347A	5.469A	1.634

In preparing these compounds by heating mixtures of zirconium hydride and zirconium nitride or carbide in hydrogen, it appears that a degree of substoichiometry in the starting nitride or carbide is essential. Attempts to form ternaries in the system Zr-H-B, Zr-H-O, Ti-H-N, and Zr-H-Si have been unsuccessful, possibly because the starting binary compounds are not sufficiently substoichiometric.

Crystal Structure of $NiZrH_3$

To establish the hydrogen atom positions in $NiZrH_3$, neutron diffraction studies have been carried out on powder samples of both $NiZrH_3$ and $NiZrD_3$ in collaboration with workers at Washington State University. The previously reported space group and heavy

atom positions determined by X-ray techniques were confirmed. The hydrogen atoms in NiZrH_3 are located in 4-fold and 8-fold positions of the orthorhombic space group Cmcm . The 8-fold hydrogen atoms have three Zr atoms and one Ni atom as close neighbors, while the 4-fold hydrogen atoms have an approximate 5-fold coordination.

BeO Crystal Growth Mechanisms

Earlier studies on BeO crystal growth led to recommended procedures for production of usable crystals and these procedures have been followed to produce a supply of crystals with size and quality appropriate to experimental use. Selected crystals grown from the $\text{Li}_2\text{MoO}_4 - \text{MoO}_3$ system were studied by X-ray diffraction topography. It was determined that a screw dislocation contributes to significant growth rates at low supersaturation, as previously predicted. Internal lattice strain patterns revealed by the topography studies have contributed considerably to insight into crystal growth kinetics, habit, and inversion twinning; and the production procedures have been improved as a result of these investigations.

Crystal Structures of BeO

Application of the Translation-Permutation Operator Crystal Algebra to BeO crystal growth has resulted in a first correlation between theory and experiment leading to the prediction of interstice lattice stacking faults (ILSF). Observations of the inversion twins in BeO crystals have provided the first clear-cut examples of the hypothesized structures.

Calculations of the electrostatic energy, E_e , and the overlap repulsion energy, $E_r = br^{-n}$ (where r = radius and b, n are constants), have been carried out for the wurtzite-BeO crystal structure, now called α -BeO. A combination of the two calculations defines a "potential energy valley" in an $E-(c_0/a_0)-u$ space (where u is a measure of the MX bond length parallel to c_0) within which all wurtzite compounds are constrained to lie. Thus these two factors alone, E_e and E_r , are sufficient to explain the gross features of the distortions away-from-ideality that are observed in BeO and AlN. However, further work will still be required to bring in the polarization and covalency factors in order to explain some of the fine-detail features of the observed distortions.

The crystal structure for BeO at high temperature ($> 2100^\circ\text{C}$), termed the β -phase, has been established in collaboration with workers at Livermore Research Laboratory. The structure is tetragonal, derived from the hexagonal structure of α -BeO by specific, identified atomic shifts. Although β -BeO cannot be retained by quenching normal, massive samples, it has been found possible to produce β -BeO by beam-heating in the electron microscope, and to retain it when the sample is quenched by removing the heat-producing beam. The quench-retention of very small volumes of β -BeO may be significant to radiation damage since β -BeO has been observed in very small pieces of irradiated and crushed BeO.

Self-diffusion in BeO

The self-diffusion studies have been continued during this year, with emphasis upon the use of oriented single crystals. The results of the now-completed cation diffusion studies, coupled with prior cation diffusion measurements in polycrystalline BeO, have been used to determine the cation diffusion mechanism. No enhancement of diffusion rates in grain boundaries is evident, nor is Be diffusion appreciably anisotropic. The data are interpreted in terms of cation diffusion via vacancies. The observed diffusion coefficients indicate extrinsic behavior, with the vacancy concentration dependent upon the concentration and type of dissolved aliovalent impurities. Additionally, the fraction of these vacancies that are mobile and can contribute to cation diffusion is temperature-dependent. Association-dissociation equilibria between aliovalent impurity atoms and their corresponding lattice vacancies have been invoked to explain the peculiar temperature dependence of beryllium self-diffusion, which was observed in both polycrystalline and single crystal specimens.

Irradiation Damage in Single Crystal BeO

Radiation damage studies with BeO have progressed to an interpretation of the damage structure developed in the lattice during low-temperature irradiation ($< 100^{\circ}\text{C}$). It is believed that most of the displaced atoms recombine with vacancies, while a small fraction (on the order of one percent) remain in the lattice as interstitials, probably as BeO molecules; and an even smaller fraction coalesce into the basal-plane clusters.

It might be expected that with higher temperatures during irradiation exposure, there would be concurrent annealing, with the residual damage becoming less as the temperature is increased. Measurements of lattice constants tend to confirm this view. The real situation is more complex, however, for single crystals irradiated at $\sim 1000^{\circ}\text{C}$ to 10^{21} nvt (fast) show a very considerable amount of fracturing on both basal and prism planes. Also, a number of the irradiated crystals exhibit crystal structure modifications. These modifications are possibly attributable to impurities, but no definite conclusion can be drawn at present.

Microscopic and electron diffraction studies have provided some evidence that the formation of minute regions of β -BeO during irradiation may account for some damage features. However, these conclusions are still very tenuous.

Mechanical Behavior of BeO

The flow and fracture studies of pure and impure polycrystalline BeO, over a wide temperature range (-196°C to 1800°C), were continued and brought to conclusion. It was shown that not only is

flow (creep) sensitive to impurities, but the fracture strength at temperatures above 1000°C (as well as below) is much higher for pure than for impure BeO. The fracture data appear to fit the Griffith equation and are largely consistent with accepted theories of fracture, but in some respects it was necessary to extend the theory. In the case of so-called "stress corrosion", a new theoretical model was developed to explain increased ease of fracture in the presence of atmospheric moisture. This model proposes that a stationary crack front, under stress, is pinned at various individual barriers of high resistance to crack propagation. Intervening segments of the front are of "normal" (i.e., lesser) propagation energy. Stress-induced corrosion occurring at the high-energy barriers releases the pinned segments of the crack front and transfers the load to the lower-energy segments; whereupon crack extension occurs at a correspondingly lower stress.

The modulus of rupture of single crystal BeO from room temperature to 1800°C was found to be considerably higher than for polycrystalline BeO. The average value of the breaking strength at room temperature and at 500°C was 140×10^3 psi, and at 1800°C was 50×10^3 psi. The crystals were loaded so that fracture occurred by cleavage along basal and prism planes. At and above 1000°C, deformation by basal slip preceded fracture, with the detailed distribution of slip bands dependent upon temperature.

The five elastic constants of single crystal BeO were measured to determine their magnitude relative to other hexagonal materials and to enable a correlation with related properties. The pulse-echo method was used. The stiffness constants are c_{11} : 68.2, c_{12} : 24.0, c_{13} : 17.0, c_{33} : 71.6, and c_{44} : 22.2×10^6 psi. The stiffness constants are similar parallel and perpendicular to the "c" axis, consistent with the nearly ideal c/a ratio of BeO, and are appreciably higher than the constants for the hexagonal metals, Be and Co, indicating the relatively high stiffness of BeO. The Young's and shear moduli of nearly randomly oriented polycrystalline BeO are about the same as those calculated from the single crystal elastic constants. BeO single crystals show a minimum in the Young's modulus in a cone whose semi-apex angle is 53 degrees from the "c" axis. The Debye temperature for BeO, as calculated from room temperature elastic data, is in the range of temperatures found by other methods. The volume compressibility gives an exponent of 11 in the term for the short-range repulsive energy between ions of BeO. This result is nearly double the value of the exponent predicted from general rules developed by Pauling for ionic crystals, but is consistent with the values for Al_2O_3 .

Swelling Resistant Metal Fuel Development

Concurrent theoretical and experimental studies of the parameters that influence swelling of metallic fuels are underway in order to fully stabilize fissile metals. Analogue computer simulation has provided a rapid method for studying irradiation and post-irradiation response as the concentration, size, shape, and distribution of

heterogeneous rare gas atom trapping sites is varied. Behavior during irradiation at temperature and during heating following irradiation has been simulated. The flexibility of the technique is such that the input parameters can be varied to deduce what system properties are needed to duplicate experimental gas mobility test results and, following this, to evaluate the actual in-reactor response. This will permit more detailed evaluation of experimental test results and the limitations imposed by boundary conditions, which are needed to obtain exact mathematical solutions to the diffusion equations, can be circumvented. Past practice by workers in the field has generally been to apply solutions to the diffusion equations, ignoring the fact that the assumed boundary conditions are violated.

Concurrently, improvements in experimental techniques and data evaluation techniques have demonstrated that more than one process is definitely involved in the rare gas atom release from uranium metal. Further clarification of these release mechanisms can lead to the identification of the metallurgical factors that will limit or control gas atom mobility. Swelling control, beyond that achieved by fine dispersion of particles, can then be attempted.

A digital computer code which will permit evaluation of the most probable mechanism for the migration of rare gas atoms in metal fuels has been written. This will provide a means for evaluating how reasonable existing theories concerning rare gas atom diffusion are, and also how to apply theories developed in one class of materials (i.e., metals) to other systems (e.g., ceramics).

Fission Gas Mobility and Release from Zirconium Hydride

ZrH_x alloys irradiated between normal and enriched uranium foils to doses of 1.8×10^{13} to 6×10^{15} nvt have exhibited a non-diffusional release of rare gas atoms during post-irradiation annealing. Sequential annealing to successively higher temperatures produces maximum levels of gas release that are temperature dependent. Hydriding or dehydriding in the single phase region has no influence on gas release. The extent of gas release from the fuel is burnup dependent, even at these low exposure levels. Thus, homogeneous nucleation is important at very low dose levels and the motion of small clusters of gas atoms may be a controlling aspect of gas release.

Coupled with other data being generated, these observations provide further clues to the factors that influence gas mobility and the parameters that will reduce volume swelling during high temperature operation.

BATTELLE MEMORIAL INSTITUTE

Coated-Particle Technology

The objective of this program is to develop coated-particle fuels to provide improved fuel materials primarily for gas-cooled reactors. Improvements being sought include operation at higher temperatures, essentially complete fission-product containment, and the use of low cross-section materials.

- (1) With Al_2O_3 coatings, prevention of rapid cracking during irradiation at low temperatures ($< 500^\circ\text{C}$) has been solved through the use of porous UO_2 particles. The optimum Al_2O_3 -coated particle was determined to be 200-micron, 80 per cent dense UO_2 -coated with 60 microns of dense Al_2O_3 . Specimens of this material were irradiated to 1.5×10^{20} fissions per cm^3 (1 per cent of U^{235} atoms) at 100°C and to 1.9×10^{21} fissions per cm^3 (12 per cent of U^{235} atoms) at 870°C with no coating failure occurring. The fission-gas-release fractions remained in the order of 10^{-6} or less.
- (2) With pyrolytic-carbon coatings, prevention of failure during irradiation has been accomplished with dense UC_2 substrates by using thick (> 100 microns) two- or three-layered coatings containing a very porous inner PyC layer. Recent efforts to reduce the coating-thickness requirements by using porous UO_2 as a substrate have been successful. Specimens of 200-micron, 77 per cent dense UO_2 particles coated with 73 microns of columnar PyC (deposited from acetylene at 1400°C) have been irradiated to 1.6×10^{21} fissions per cm^3 (9 per cent of U^{235} atoms) at 815°C and to 7×10^{20} fissions per cm^3 (4 per cent of U^{235} atoms) at 1200 to 1300°C with only a small fraction of the coatings cracking. The fission-gas-release fractions have remained in the range of 10^{-6} or less.
- (3) Special provisions have been found to be required in the design of pyrolytic-carbon coatings to satisfy the objective of essentially complete fission-product containment. Metallic fission products such as barium, strontium, and silver migrate through intact pyrolytic carbon coatings. Release fractions of over 1000 ppm have been found in 6 hr of heating at 1150°C . To prevent this release, it has been found to be necessary to modify the coatings by addition of another material. Barrier layers of SiC are effective, and SiO_2 -doped PyC coatings are showing some promise.

High-Temperature Fuels

The objective of this program is to evaluate the maximum capabilities of uranium carbide and its structural and alloy modifications as fuels for high-temperature, nuclear devices.

- (1) The compatibility of materials at very high temperatures has been recognized as being dependent upon whether or not materials will exist in equilibrium with one another. The importance of equilibrium diagrams was recognized, and several were developed in detail. For example, the upper temperature limit of compatibility of UC with molybdenum was found to coincide with a peritectic reaction isotherm between 1800 and 1850 C. A similar isotherm was found in the UC-tungsten system between 2100 and 2150 C.
- (2) Liquid formation has been observed in slightly hyperstoichiometric UO_2 -tungsten cermets. This liquid was associated with a ternary eutectic containing 70 a/o oxygen and melting between 1300 and 1325 C. The ternary eutectic forms between UO_2 , tungsten, and UWO_3 . The latter phase contains up to 3 a/o uranium and has a simple cubic structure.

Joint U.S.-Soviet Program - Uranium Mononitride

The objective of this program is to determine the potential of uranium mononitride as a reactor fuel material, particularly with respect to its fabricability, properties, and irradiation resistance.

- (1) The arc melting and casting of high-purity polycrystalline and single-crystal UN bodies was developed to a nearly routine process. Specimens prepared by this technique are being used for basic UN studies by four domestic and three foreign AEC laboratories.
- (2) TiN and ZrN were successfully added to UN by arc-melting techniques. Each alloy type possessed a unique structure representing potential improvement to the properties of UN. U(CN) alloys were melted under less than 1 atm of nitrogen.
- (3) The reaction rates of single-crystal UN with CO_2 , oxygen, water, and moist air were determined at temperatures from 100 to 700 C. A UN specimen in boiling water had a corrosion rate of 0.1 mg per cm^2 during the first 400 hr of exposure, and a rate of 1.3 mg per cm^2 during the second 400 hr of exposure; no further change in weight occurred in the next 200 hr.

- (4) Reaction rates of UN with prospective cladding materials including stainless steel, Zircaloy-2, zirconium, aluminum, chromium, and nickel were determined over the full temperature range of possible cladding application. Particularly significant is the fact that stainless steel shows less than 1 mil of attack at 1000 C after 5000 hr of exposure.
- (5) Twenty uranium mononitride specimens clad with Type 316 stainless steel have been irradiated to burnups of 5 to 6 a/o of the uranium at surface temperatures of about 700 C. The UN was prepared by both powder and arc-casting techniques. Although some of the specimens experienced cladding failures by cracking, the stability of the UN was generally very good. No chemical reactions were observed between the fuel and the cladding; and the cracking is attributed to the limited ability of irradiated stainless steel to deform plastically over a swelling fuel. Fuel swelling at the highest burnups was only about 1 per cent per atom per cent burnup. Fission gas released from cast material was about 3 per cent, whereas powder-metallurgy UN specimens released from 15 to 25 per cent.

Joint U.S.-Euratom Program - Fission-Product
Release from Fuel-Element Claddings

The objective of this research study involves the determination of the rates of migration and the magnitude of release of fission products from cladding materials. Mechanisms of release are being investigated to define the influence of material characteristics, temperature, and radiation on fission-product diffusivity and internal precipitation in the cladding.

- (1) Simple diffusion behavior was observed in iron alloys for all fission products except Te^{132} . A two-component concentration profile was found for this nuclide.
- (2) In zirconium, Zr^{95} and Te^{132} followed volume diffusion behavior, but concentration profiles for Ce^{141} and Ru^{103} did not conform to either a volume diffusion model or simple grain-boundary theory.
- (3) Expressing results in an Arrhenius form $D = D_0 \exp(-Q/RT)$, the results fell into two distinct groups. In an iron-20 w/o chromium alloy (bcc) Te^{132} , Ru^{103} ,

and Mo⁹⁹ diffused with D₀'s and Q's similar to self-diffusion and in the range expected by normal vacancy diffusion process. Ce¹⁴¹, Ba¹⁴⁰, I¹³¹, and Zr⁹⁵ were of considerably lower value. In iron-29 w/o nickel, 13 w/o chromium alloy (fcc) all fission-product nuclide behavior exhibited low values of D₀ and Q.

Plutonium Compound Technology

The objective of this program is to determine the suitability of plutonium compounds as reactor fuels, particularly with respect to preparation and physical and chemical properties.

- (1) Synthesis of PuN using a hydride-nitride cycle was found to be the most suitable preparation technique. Complete hydriding of plutonium metal charges was required to obtain a final powder approaching the theoretical nitrogen content of PuN (5.53 w/o nitrogen).
- (2) Although PuN was disintegrated by sodium and lithium in the 950 to 1000 C temperature range, no attack of PuN by these metals was noted at temperatures up to at least 800 C. PuN was compatible with iron-base alloys, Inconel, and refractory metals at temperatures of 1300 C.

Dense Graphite

The objective of this program is to prepare a fine-grained, isotropic, very dense graphite suitable for long-term use in a nuclear reactor.

- (1) Densities greater than 98 per cent of theoretical density (> 2.22 g/cc) have been achieved by high-temperature, high-pressure isostatic compaction. At 220 C and 23,500 psi, spectrographic-grade graphite has been densified to 99 per cent of theoretical density (2.24 g/cc), pure artificial grade to 98 per cent, and natural grades up to 99 per cent. Neutron-diffraction studies have indicated that some of these high-density materials are nearly isotropic.

BATTELLE-NORTHWEST LABORATORIES

PLUTONIUM CERAMIC FUEL RESEARCH

Introduction

The purpose of this program is to investigate the basic properties of plutonium ceramic materials, with special emphasis on high temperature properties, compatibilities, and performance under neutron irradiation.

Plutonium-Oxygen System

Earlier studies showed that the hexagonal form of plutonium sesquioxide (β -Pu₂O₃) might be a superior high temperature fuel compound. A method for preparing β -Pu₂O₃ by carbon reduction of PuO₂ was developed. β -Pu₂O₃ was shown to be usefully stable, with little or no composition range, and to be compatible with Ta at 1650 C. Thorium, however, reduced the compound at 450-500 C. Small plates of PuO₂ and β -Pu₂O₃ were irradiated to 55×10^{20} f/cm³ and 42×10^{20} f/cm³, respectively. PuO₂ underwent severe structural change as evidenced by x-ray diffraction and became highly porous after 22×10^{20} f/cm³.

PuO₂-62 wt% Nichrome cermet were evaluated as an alternate fuel for air cooled reactors such as the 630-A. They exhibited complete compatibility and resistance to air oxidation during 400 hours at 1093 C, while comparable UO₂-Nichrome cermet swelled, spalled, and blistered badly. This is the first clear demonstration of the superiority of a plutonium base fuel over its uranium counterpart.

Plutonium-Nitrogen System

Carbon reduction of PuO₂ under nitrogen was shown to be a feasible alternate to the Pu-metal/hydride/nitride route. Solid solutions of (Pu, Zr)N were prepared for high temperature stability studies; however, no solubility was detected between PuN and ThN or TiN. PuN was shown to be compatible with PuO_{2-x} in 1500 C nitrogen and with graphite during one hour in 1725 C nitrogen. A PuN-50 vol% W cermet successfully withstood irradiation to 15×10^{20} f/cm³ at a few hundred degrees centigrade. Pure PuN was irradiated to 20×10^{20} f/cm³ with minor cracking and extensive crystal structure damage as shown by x-ray diffraction. Sintered pellets of (U_{0.8}Pu_{0.2})N were irradiated to 9×10^{20} f/cm³ at a rod power of 2 Kw/cm (~ 650 w/cm²). No change in lattice parameter was seen after 5.7×10^{20} f/cm³. Although minor reactions occurred with both the type 304 stainless steel cladding and MgO end insulators, the test illustrated a high potential usefulness of mixed nitride nuclear fuel.

Plutonium-Carbon System

The increase in lattice constants of PuC and Pu₂C₃ due to self α -damage was measured at room temperature. The lattice expansion for PuC appeared to be saturated after 975 days, while for Pu₂C₃ it was still increasing at 500 days.

Plutonium-Boron System

From comparison with rare earth borides, it was hypothesized that plutonium borides have useful thermionic emission properties. A beginning study showed PuB₂ to be the only thermodynamically stable phase below 900 C and showed PuB, PuB₄, and PuB₆ to be stable at high temperatures. A tentative phase diagram was developed.

Fast Fuel Development

Historically, solid solution (U,Pu)O₂ has been thought necessary for fast neutron reactor application. Ball-milled, mechanically-mixed, and impacted UO₂ and PuO₂ powders were shown to possess the small particle sizes and homogeneity of distribution necessary for safe Doppler response in a fast reactor fuel. Plutonium distribution was evaluated by electron microprobe analyses, microautoradiography, and ceramography.

PuO₂-80 vol% type 304 stainless steel cermets made by high energy impaction of powders were shown to be stable during 400 hours at 900 C. The high density compacts were easily coextruded. Irradiation tests of this potentially useful fast reactor fuel were begun (in thermal neutron flux).

URANIUM CERAMIC FUEL RESEARCH

Introduction

The major purposes of this program are to identify factors limiting in-reactor performance of ceramic nuclear fuels, to investigate high temperature irradiation properties of nuclear ceramic materials, and to develop improved techniques for fabricating ceramic fuel elements.

High Temperature Properties

The electrical resistivity of UO₂ at its melting point was measured to be approximately 10⁻³ ohm-cm. This value is less than that obtained from the extrapolation of lower temperature data but corresponds well with the electrical conductivity required to explain the apparent high thermal conductivity of UO₂ near its melting point.

The absorption spectrum of single crystal and polycrystalline UO_2 was measured between 0.6 and 2.5 μ . Much improved resolution revealed several new absorption bands. Optical density of polycrystalline UO_2 below 10 μ was shown to be two or three times that of single crystal UO_2 . These results substantiate theories indicating that there should be an internal radiation contribution to the thermal conductivity of UO_2 .

Irradiation Properties

Solid fission products were transferred from an irradiated sample of UO_2 to an unirradiated sample along a potential gradient of approximately 1 volt/cm at a temperature of 1500 C. These results suggest that an ionic conduction mechanism rather than a thermal diffusion process is operative in the migration of fission products in fuel elements. Electrical resistivity and Seebeck EMF of UO_2 were measured in-reactor to more than 2000 C. The measured electrical potential gradients were sufficient to move fission products in the manner indicated by the laboratory experiments.

Radiochemical data showed an accumulation of Cs and Sr in uranium metal inclusions formed during high temperature irradiation of UO_2 . This increased fission fragment concentration could account for both the greater resistance of the inclusions toward chemical etching at higher UO_2 exposure and the stabilization of uranium in the β phase.

Fuel Development

Stainless steel clad, stainless steel-30 vol% UO_2 cermet pins (0.533 cm diameter x 91 cm long) were fabricated by a combination of pneumatic impaction followed by hot extrusion. Fuel particle stringing was essentially eliminated by this fabrication technique.

A UO_2 fuel rod was successfully irradiated at a surface heat flux of 655 watts/cm² to an exposure of 1.2×10^{20} f/cm. The fuel was initially molten to 84% of the radius. It is significant that molten UO_2 within 0.08 cm of the molybdenum cladding caused no adverse effects on the operation of the fuel rod.

BASIC SWELLING STUDIES

Introduction

The purpose of this program is to establish a comprehensive description and understanding of the behavior of fissionable materials during irradiation. Swelling of uranium irradiated at temperatures below 700 C is not due to fission gas agglomeration, as commonly believed, but rather to tearing and cavity formation as a result of mechanical weakness in the metal. Two approaches for overcoming tearing in uranium fuel under investigation are applying external pressure and strengthening the fuel.

Controlled Temperature-Pressure Irradiations

High-purity uranium irradiated to 0.13 atom% burnup in a NaK capsule at a controlled pressure of 1000 psi and a controlled temperature of 450 C exhibited only 1% swelling, whereas uranium irradiated at the same temperature at a pressure of 15-20 psi exhibited 50-100% swelling. This tremendous inhibiting effect of pressure substantiated the previously reported concept that mechanical processes are responsible for the development of internal tears in uranium rather than the agglomeration of fission gases. The forces giving rise to tears are relatively small and are easily overcome by an external hydrostatic pressure. Data obtained at low pressures over a series of controlled, irradiation temperatures indicated that fission gas porosity becomes the major factor in swelling at irradiation temperatures above 700 C. The matrix structure of specimens irradiated at high pressure at a given temperature was the same as that of specimens irradiated under low pressure except that the large, irregular tears were absent in the former.

Effect of Additives on Irradiation Stability

Specimens of two dilute uranium alloys (U+400 ppm Fe, 640 ppm Al, 85 ppm Si, and 500 ppm C; and U+140 ppm Fe, 25 ppm Al, 95 ppm Si, and 400 ppm C) were irradiated in a series of temperature-controlled capsules in the range 400-600 C. Their swelling behavior was evaluated by postirradiation determination of density and microstructure. Swelling was observed to be greatest at about 500 C, analogous to pure uranium. The magnitude of the swelling-versus-temperature maximum, however, was much lower for the alloys. Of the two alloys, the one high in Fe and Al exhibited substantially less swelling at 500 C. The mechanical processes found to be responsible for swelling in pure uranium are also responsible for swelling in the alloy specimens, but the magnitude of the tearing is much less. Both alloys performed satisfactorily in the 400-500 C range, where grain boundary tearing is the dominant mode of swelling. In the 500-600 C range, where crystallographically aligned microtearing predominates, the alloy high in Fe and Al was far superior to the alloy low in Fe. At this temperature the aligned tears originated at twin-matrix interfaces. Both alloys were improved by metallurgical treatments designed to yield large numbers of second-phase particles which impede recovery processes responsible for tearing. After a heat treatment consisting of quenching from the gamma phase followed by heating for a short time into either the beta or the high alpha phase, the alloy high in Fe was completely resistant to swelling at all temperatures below 600 C during a burnup of 0.16 atom%.

IRRADIATION DAMAGE TO REACTOR METALS

Introduction

The purpose of this program is to determine the effects of irradiation and environment on the engineering properties of structural metals in support of the timely development of advanced reactor concepts. Representative studies include in-reactor property measurements, pre- and postirradiation property measurements, neutron effects on metal-environment reactions, basic damage mechanisms, and very-high-temperature irradiations in gaseous and liquid metal coolants.

In-Reactor Measurements

In order to establish more realistic design methods, the effects of a typical neutron environment on the creep strength of structural alloys are being studied. At normal operating temperatures and stresses, neutron irradiation was found to reduce the creep deformation of cold-worked Zircaloy-2. At higher temperatures and stresses, however, neutron exposure caused marked increases in creep rate. In-reactor creep investigations were extended to annealed 304 stainless steel in the temperature range 500-650 C and at applied stresses ranging from 20,000 to 30,000 lb/sq in. Results have shown that in-reactor second stage creep rates are about the same as those measured ex-reactor. However, creep ductility is markedly affected by irradiation, and elongation at failure in-reactor is about a third of that ex-reactor. Similarly, the time for failure in-reactor is much shorter than ex-reactor. Therefore, design limitations would result from premature failure rather than undesirably large creep rates.

Irradiation Temperature Effects

Zircaloy-2 and austenitic steels irradiated at 50 C and 290 C accumulated damage at a greater rate at the higher irradiation temperature. After exposure to 1.0×10^{21} nvt* or higher, the room temperature tensile elongation of austenitic stainless steel irradiated at 50 C was halved, but was nearly eliminated in specimens irradiated at 290 C. The 0.2% yield strength for annealed austenitic steels underwent a 2.5- to 3-fold increase when irradiated at 50 C compared to a 4.5- to 5-fold increase at 290 C. Changes of a similar magnitude were noted for Zircaloy-2 under equal irradiation conditions. Effects of irradiation temperature were small at neutron exposures below 5×10^{20} nvt but became continuously greater at higher exposures. The ductility of irradiated stainless steel at 600 C and Zircaloy-2 at 300 C was significantly lower than their ductility at room temperature.

*Neutron exposures refer to neutron energies greater than 1 Mev.

Nickel-Alloy Studies

The combination of oxidation resistance and high-temperature strength makes nickel-base alloys prime candidates for advanced reactor applications. Several precipitation- and solution-hardened nickel alloys were irradiated at 50 to 750 C to exposures ranging to 8×10^{20} nvt. Although changes in room-temperature strength and ductility were small, the postirradiation properties were found to be sensitive to pre-irradiation alloy treatments. For example, the mechanical properties of irradiated Hastelloy X-280 were markedly affected by variations in the pre-irradiation aging treatment. Both the yield and tensile strength of several nickel-base alloys were reduced by neutron irradiation at 650 C. These reductions in strength were accompanied with drastic reductions in ductility. In some alloys the total elongation was reduced to less than 5%. Methods to overcome this embrittlement by prior metallurgical conditioning are being studied.

Fracture Studies

A technique was successfully developed and tested which enables multiple determinations of fracture toughness from a single specimen. The new specimen replaces thirty to forty conventional fracture toughness specimens. In addition, data relative to crack arrest are made available. The variation in fracture toughness of A302-B and Zircaloy-2, two reactor structural materials, was determined over a range of temperatures. Although A302-B has a slightly higher toughness than Zircaloy-2 over most of the temperatures investigated, the resistance to crack arrest is lower. Consequently, a crack would propagate farther in a structure composed of A302-B than of Zircaloy-2.

Irradiation Effects on Zirconium Alloy Corrosion

Exposure of Zircaloy-2 specimens to the in-core environment of the ETR G-7 Loop accelerated corrosion rates an order of magnitude over specimens exposed out-of-reactor. At short exposures, the fraction of theoretical corrosion hydrogen fell within the range normally found for specimens exposed out-of-reactor. Specimens exposed to high weight gains ($>100 \text{ mg/dm}^2$) showed a trend toward increased fractional pickup. The loop environment consisted of 280 C, pH 10 (LiOH) water containing about 0.8 ppm oxygen. The neutron flux ranged from 0.17 to 1×10^{14} nv.

Zircaloy-2, Zircaloy-4, nickel-free Zircaloy-2, and Zr-3 wt% Nb-1 wt% Sn exhibited comparable weight gains after exposure to low-oxygen, hydrogenated water at several fast fluxes for 16.5 days. Except for the Zr-3 Nb-1 Sn alloy, weight gains in the low-oxygen water were approximately half those observed in oxygen-bearing water for comparable periods of time. Conversely, the fractional pickup of hydrogen was about twice as great as in high-oxygen water. The Zr-3 Nb-1 Sn alloy showed not only the lowest flux effect on weight gain but also the lowest in-reactor hydrogen pickup compared to the other alloys.

Dosimetry Studies

An exposure unit, defined in terms of neutrons per square centimeter above a specified energy limit, was shown to be independent of reactor spectra for a useful variety of spectra. This unit permits cross correlating data obtained in different test reactors. From published data on irradiation effects on steel from the Naval Research Laboratory, shifts in nil-ductility temperature measured in a graphite-moderated reactor and a light-water-moderated test reactor were reconciled. Results of these studies are described in the March 1965 issue of Nuclear Science and Engineering.

ATR GAS LOOP STUDIES

Introduction

The purpose of this program is to investigate major design and materials problems in support of the 2000 F (1100 C) helium-cooled, gas loop to be installed in the Advanced Test Reactor at the National Reactor Test Station, Idaho. These investigations are being accomplished principally by means of a model loop installed at Battelle-Northwest Laboratories and patterned after the proposed ATR loop.

Loop Component Development

Heating the gas for the ATR gas loop loomed as a major design problem, primarily because of acute space limitations in the ATR subpile room. To solve this problem, a two-stage, re-entrant heater constructed of unique materials and rated at 120 kw per cubic foot was developed for the model loop. In addition to highly increased capacity, this heater design offers greater safety, reliability, gas purity, and ease of maintenance over previous designs. The problem of piping 2100 F (1150 C) helium 30 feet from the heater outlet to the test section inlet was solved by developing a water-cooled, 304 stainless steel pressure pipe insulated from the hot gas by internal metal foil insulation. Safe handling of the hot helium exiting from the in-core test section into the downstream piping and components was solved by attemperation. This involves injecting a small portion of the gas flow from the cold leg of the loop into the hot gas emerging from the core. The seal-welded, gas-bearing circulator employed in the loop has maintained extreme gas purity over a wide range of operating conditions with many starts and stops. The model loop has proven to be invaluable for obtaining operating experience and for proving materials selection and design concepts.

Trace Impurity Analysis

A gas chromatograph was developed to analyze helium for the trace impurities, hydrogen, oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide in the ATR Gas Loop helium coolant with lower detection limits below 1 ppm for each component. These lower detection limits are less by a factor of more than 100 for hydrogen in helium and a factor of 10 for other impurities than the best conventional chromatographs. A continuous total impurity analyzer was developed for the ATR Gas Loop which actuates an alarm when total impurities exceed a predetermined value. This instrument, based on the impurity detection method used in the ATR chromatograph, functions reliably at a 1 ppm total impurity setting. The same detection principle in combination with a palladium tube continuously analyzes hydrogen at 1 ppm or greater concentration.

An oxygen probe is under development which is theoretically capable of detecting 10^{-18} atmospheres of oxygen partial pressure. The probe produces a voltage which is related (by a simple equation) to the difference in oxygen partial pressure in contact with the two sides of a zirconia-calcia solid electrolyte. Since corrosion in the ATR Gas Loop is primarily dependent on oxidizing impurities, this development is potentially of great value to conservative loop operation.

NUCLEAR GRAPHITE

Introduction

The purpose of this program is to develop an understanding of graphite as a nuclear material so that its unique properties can be exploited as moderator material, reactor structural material, matrix material for fuel or poison, and high-temperature material in advanced reactor concepts.

High Exposure Irradiations

Conclusive data were obtained on the net growth of nuclear graphite under irradiation at high temperatures. At an irradiation temperature of 800 C, transverse samples contracting under irradiation reached a maximum contraction, started to expand with continued exposure, and reached a net expansion of one per cent at the highest exposure. Samples irradiated at lower temperatures approached maximum contraction at the highest exposure, but at a sharply decreasing rate. Data were obtained for the first time on nuclear graphite behavior irradiated at temperatures of 800 to 1200 C to significant neutron exposures. Transverse samples irradiated at 1200 C contracted about the same as others irradiated at 400 C as expected; however, parallel samples irradiated at 1200 C contracted nearly twice as much as those at 400 C, presenting potentially serious problems to reactor designers and operators.

Fracture Studies

Tensile fracture studies of graphite during irradiation showed that irradiation increases the strain before fracture for parallel, EGCR-type, AGOT graphite. Strains of 0.37 to 0.42% were sustained without fracture during irradiation at 600 C compared to fracture strains of 0.1 to 0.2% for unirradiated samples. The apparatus used for these studies will be described in a technical note to appear in the journal CARBON.

Effects of Inert Gas on Reactor Gas Radiolysis

Inert gases ionized by high energy radiation were found to effect impurity reactions in nuclear reactor gas atmospheres. Inert gases do not remain inert in excited states but contribute to gas reactions by either charge or energy exchange processes. Such a sensitization process involving helium and argon was demonstrated in the radiolysis of carbon monoxide and water vapor mixtures. Energy absorbed by the inert gas was as effective as energy absorbed directly by the impurity in causing reactions at impurity concentrations as low as 0.5%. Inert gas sensitization of gaseous reactions should be quite general.

NONDESTRUCTIVE TESTING RESEARCH

Introduction

The purpose of this program is to fulfill a need for further research in advanced techniques of nondestructive testing which may be applicable to a wide range of testing problems. New testing techniques are being exploited and investigations of a fundamental nature are being initiated to improve the in-service integrity of materials and components.

Electromagnetic Testing

A tubing cross section display device was developed for use in the inspection of metal tubing. This device, fed with signals from a multi-parameter eddy current tester, displays the cross section of the tubing under test. Of special significance was the simultaneous detection and display of holes positioned radially on the outside and inside tube surface. These holes were independently recorded with their proper magnitude shown, demonstrating the capability of the multi-parameter tester in identifying and separating flaw signals. When fully developed, this test will greatly increase the capabilities of the eddy current tubing test.

A specially designed ultrastable eddy current test circuit was developed to detect minute property changes in metals. This equipment detected the presence of hydride in Zircaloy-2 reactor process tubes at a sensitivity

of 250 ppm hydrogen. This test also detected fatigue induced changes in stainless steel before 10 per cent of the fatigue life was reached.

Ultrasonic Research and Development

A model describing ultrasonic wave propagation for a variety of interfaces between acoustically dissimilar media was developed. The model was successfully tested for pulses propagating in media in which attenuation is a linear function of frequency. Nonlinear attenuation, occurring in most practical materials, was treated by numerical approximations through the help of a digital computer.

Techniques and equipment were developed to detect fatigue in metals by ultrasonic boundary waves. Ultrasonic signal differences were observed in aluminum and copper samples at approximately 20 and 40% of fatigue life, respectively. Although fatigue was also detected in stainless steel, the sensitivity limit was not determined. Signal differences from ultrasound propagating parallel and perpendicular to the fatigue orientation offer prospects of sensing direction as well as magnitude of metal fatigue.

An ultrasonic tubing test capable of detecting flaws of less than one mil in depth and less than eight mils in length was developed and demonstrated at the 1964 Geneva exhibition on "Peaceful Uses of Nuclear Energy." This test detects flaws oriented in either the circumferential or axial direction on the inside or outside tube wall surface. Current applications of this test include quality control of fuel element sheath tubing and inspection of thin-wall, fuel-element butt welds for inclusions and cracks.

A method for employing ultrasound to produce a shadow image of defects and irregularities in metal plates was demonstrated. This technique involves the surface distortion of water by ultrasonic energy transmitted through the plate being examined. A shadow image of the plate is made visible by reflecting a beam of collimated light from the water surface onto a ground glass screen. To demonstrate this test, a wire mesh screen placed beneath a 1/8-inch aluminum plate was accurately imaged. This technique will find many applications as a supplement to x-rays in nondestructive testing and in basic crystallographic studies.

Transducer Development

An electrostatic transducer capable of generating and detecting ultrasound at high temperatures without a coupling medium was developed. Results show that the electrostatic transducer functions efficiently at temperatures over 500 C with a mica dielectric, and temperatures over 1000 C should be obtainable with a ceramic dielectric. Equipment using the electrostatic transducer was fabricated to measure elastic moduli of plutonium metal at elevated temperatures. Another typical application involves using pulse-echo techniques (transmission and detection of ultrasound with the same transducer) to measure wall thickness and wall integrity on thermally-hot, isotope, containment vessels.

METALLIC FUEL ELEMENT DEVELOPMENT STUDIES

Introduction

The purpose of this continuing program is to develop swelling-resistant, metallic fuel materials, to develop fabrication methods for these materials, and to evaluate fuel performance under power reactor irradiation conditions.

Thorium Alloy Fuel Irradiations

Three tubular fuel elements containing Th-2.5 wt% U (93.2% enriched)-1 wt% Zr and clad with Zircaloy-2 attained 14 cycles of irradiation in the P-7 high-temperature, high-pressure water loop in the ETR since charging in April 1963. The highest exposure element, which operated at a specific power of 45 to 69 watts/gram (138-210 kw/ft) and a maximum surface heat flux of approximately 75 cal/sec-cm² (1×10^6 BTU/hr-ft²), reached an exposure of over 1.2 atom% burnup. Measured fuel volume increase was 0.9%; no greater than that expected from buildup of solid fission products. The low swelling rate and excellent visual appearance of the fuel elements indicate that 3 atom% burnup is a realistic goal exposure.

Brookhaven National Laboratory

Liquid Metal Corrosion

Boiling liquid metals are currently of interest as working fluids in high performance nuclear reactor-turbine systems. The corrosion behavior of both Hg and Na are being studied since they represent use in immediate and long range systems.

Mercury Corrosion. The proposed power conversion systems require the corrosion products be kept to a minimum since components in these systems contain small passages which can become easily clogged. Experiments conducted at BNL in which Hg was contained in steels showed inhibitors, such as Zr and Ti, when added to Hg, greatly reduced corrosion and mass transfer, however, both Ti and Zr are soluble in Hg, and could very well behave as corrosion products to cause flow restrictions. Capsule and natural circulation loop tests showed it was feasible to preform TiN or ZrN films, but that these films did not remain protective with continued operation without inhibitors present in the Hg. Rupture of the preformed films was probably due to differential expansion or thermal shock caused by unstable boiling.

Inhibition studies performed on Haynes Alloy 25 (Co-20Cr-15W-10Ni-3Fe) showed only a small reduction of corrosion and only qualitative indications of the presence of inhibiting films.

A second approach to solving the boiling Hg container problem would be to use materials of containment, such as the refractory metals, which have extremely low solubilities in Hg.

The first refractory metal loop, fabricated of Nb-1Zr, failed in a brittle manner in the superheater section after 7697 hours of operation. The condition of the alloy container (cold worked) and the environment (high pressure Hg) suggested failure was due to "stress corrosion". Further capsule and loop testing has been done in an effort to better understand the failure process. Results thus far indicate stress (residual and/or applied), and a relatively soluble constituent (Zr) in the alloy are necessary to obtain such a failure. Recently, a second Nb-1Zr natural circulation loop which was fully annealed prior to operation, failed in exactly the same manner as the first loop after 5712 hours. This loop ran with the boiler and superheater 110°C higher (boiler 760°C, superheater 870°C) than in the first loop. A hoop stress of 2500 psia resulting from the Hg vapor pressure of 1000 psia was present in this loop.

A third loop fabricated of Ta and operating at conditions similar to the first loop (650°C boiler and 760°C superheater) has now operated over 18,000 hours with no indications of failure.

A forced circulation boiling Hg loop fabricated entirely of Nb-1Zr is nearing completion. This loop will be used to study velocity and impingement effects on candidate turbine materials.

Sodium Corrosion. Refractory materials to contain boiling Na at temperatures up to 1250°C are being investigated in refluxing capsule tests and natural circulation loops.

Niobium-1Zr has been tested in hot trapped Na up to 1260°C for as long as 8000 hours. To date no corrosion has been detected in either capsule or natural circulation boiling loops.

Tests to determine the effect of oxygen contaminated Na on Nb-1Zr corrosion resistance have shown general attack of the container occurs at the liquid-vapor interface. This attack has been attributed to the concentration of the O in Na at the liquid vapor interface and subsequent oxidation of the Nb-1Zr alloy.

Carbon (up to 600 ppm) was also added to the Na in these capsule tests (8000 hrs., 1250°C). Post test metallographic examination showed no corrosion occurred but the grain boundaries of the Nb-1Zr were penetrated by the C to a depth of 0.01 mm.

Oxygen getters (Ba, Ca, Mg), when added to the Na in concentrations of 500 ppm, had no effect on the corrosion of Nb-1Zr. Grain boundary penetration to a depth of 0.10 mm was detected in the condenser region of the Nb-1Zr capsule containing a chip of Y. The nature of this penetration suggests interaction of the Y rather than Na with the container.

Results obtained thus far on a series of refractory metal alloys indicates their corrosion resistance to hot trapped Na may be predicted by the composition. Alloys (Nb-1Zr, X-110, X-34)* which are "gettered" i.e. contain a stable oxide forming element such as Zr, are extremely resistant to attack by Na. Those alloys (Ta-10W, Nb-10W-10Ta) not "gettered", are severely attacked at the grain boundaries. Under test conditions where no corrosion was detected on the Nb-1Zr in 8000 hours, complete penetration (0.75 mm wall) of the Ta-10W occurred in less than 150 hours.

The effect of high Na vapor velocities on materials will be studied in a Nb-1Zr forced circulation loop nearing completion.

Thermodynamic Properties of Refractory Compounds

Thermodynamic information on thorium carbides was obtained from measurements on solid electrochemical cells at 800°-950°C. The emf cells were of the type $\text{Th}, \text{ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThC}_x$. The free energies of

*X-110 Nb-10W-1Zr-0.1C
X-34 Nb-5W-3.5Zr-0.1C

formation of thorium monocarbide and thorium dicarbide were determined. The monocarbide phase was found to be stable from a composition of $\text{ThC}_{0.66}$ to $\text{ThC}_{0.96}$ from measurements of the variation of lattice parameter with composition.

Partial molar free energies of thorium and carbon were calculated from the data. A qualitative picture of the bonding in nonstoichiometric thorium carbide was developed in which it is assumed that thorium and carbon form covalent bonds which increase in strength as some of the carbon is removed from the lattice.

Nuclear Fuels Materials and Development

Graphite Compounds. A kinetic study of the decomposition of the cesium-graphite lamellar compounds in vacuo has been carried out over the temperature range 400°C to 650°C .⁽¹⁾ A tracer technique was used in which the concentration of cesium in the compounds was measured by a scintillation scanning probe which continuously monitored the activity of tracer Cs-134. The decomposition of the cesium-graphite compounds was found to proceed in distinct stages. Within each stage, a constant rate of decomposition was observed. Each stage corresponds to the transition of one cesium-graphite compound to a compound containing less cesium. A new phase, C_{10}Cs , was found to exist in the cesium-graphite system.⁽²⁾ The observed rates of decomposition were explained by assuming the rate limiting process to be the evaporation of cesium from the external surface of the solid. The proposed mechanism correlates the kinetic data with the thermodynamic properties of the compounds.

In order to test the validity of the proposed mechanism, the vapor pressures of the cesium-graphite lamellar compounds in the two-phase regions were measured at temperatures of 400° to 750°C .⁽³⁾ The Knudsen effusion method, in conjunction with a tracer technique employing cesium-134, was used. The thermodynamic properties calculated from the data were shown to be related to the structures of the cesium-graphite lamellar compounds. The data confirmed the mechanism of decomposition proposed⁽¹⁾ for the cesium-graphite lamellar compounds.

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- (2)F. J. Salzano and S. Aronson, "Some Observations in the Cesium-Graphite System", J. Inorg. Nucl. Chem., 1964, Vol. 26, pp. 1456.
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Nuclear Fuels and Materials Development

Xenon Diffusion in Uranium Carbide. The measured xenon gas release in the temperature range 150° to 975°C is much higher than that calculated from high-temperature diffusion data. The kinetics of the release agree with a model in which the xenon in the first three or four unit cells is released over a range of activation energies. Most of the xenon is released with an activation energy identified as the activation energy for xenon motion. The model also permits a quantitative estimate of the amount of low-temperature gas release to be made.

Xenon Diffusion in Zirconium Carbide. Xenon release experiments have been completed on zirconium carbide powders ranging in composition from $\text{ZrC}_{.59}$ to $\text{ZrC}_{1.01}$. The release data appear to fit a diffusion model. Diffusion coefficients and activation energies are functions of carbon content. Carbide of composition $\text{ZrC}_{.91}$ had the lowest diffusion coefficients ($1 \times 10^{-16} \text{ cm}^2/\text{sec}$ at 1650°C), and highest activation energy (~180 Kcal/mole). There appears to be a minimum in diffusion coefficient and maximum activation energy around this composition.

Radiation Hardening of Iron, Steels and Other BCC Metals

Radiation hardening of iron, steels and other body centered cubic (BCC) metals by neutron bombardment is being investigated at Brookhaven National Laboratory. The objective of the investigation is to understand the mechanism of radiation hardening and its effect on deformation processes and embrittlement. Such information should prove to be useful in developing steels for reactor vessel fabrication. Mechanical property parameters are being determined over a wide temperature range. Effects on the metal structure produced by radiation, post-irradiation heat treatment and deformation are being studied by electron transmission microscopy.

It has been found that Ferrovac E pure iron containing 30 parts per million of carbon was embrittled at temperatures below 125°K and was hardened after irradiation. The embrittlement was ascribed to inhibition of the twinning process of deformation. Ferrovac E containing about 10 parts per million of carbon was also hardened, but was not embrittled after irradiation to very high exposures. If the iron containing 30 parts per million of carbon was alloyed with a strong carbide former such as chromium, no embrittlement was found after irradiation. Although the radiation defects responsible for the change in properties were too small to be detected by electron-transmission microscopy, post-irradiation heat treatments which tended to restore the properties caused aggregation of at least part of the defects into visible clusters. In highly irradiated Ferrovac E containing 10 and 30 parts per million of carbon, the concentrations of clustered defects were proportional to the carbon concentrations.

These results indicate that a complex defect consisting of carbon atoms combined with the radiation defects resulting from displacement of iron atoms may be responsible for the observed radiation hardening and embrittlement. The nature and the configuration of this combined defect and the mechanism by which it affects the hardness and the twinning process are being studied.

ALBANY METALLURGY RESEARCH CENTER

BUREAU OF MINES Albany, Oregon

The following paragraphs describe significant developments in the continuing cooperative research program at the Albany Metallurgy Research Center, Bureau of Mines, Albany, Oregon. The overall object of this effort is to improve the technology for preparing new fuels or materials which have potential uses in reactor development.

Cold-Mold Induction Melting

Melting equipment has been developed for melting reactive metals utilizing induction heating and a water-cooled copper crucible. On the basis of small scale heats conducted, an invention report describing the equipment was submitted. The equipment has been used to melt 1-inch-diameter zirconium and titanium ingots by drip melting a rod of the metal into a water-cooled copper crucible or by side feeding sponge metal into a molten pool. Ingots produced are relatively sound and sidewalls are fair. Further studies at high power levels are necessary before the process can be considered an unqualified success.

Investigation of the System UC-UN-UO

A study is being conducted of the subliquidous phase relationships in the pseudo-ternary system UC-UN-UO. Single phase solid-solution areas within the system may offer attractive possibilities for high temperature nuclear reactor fuels.

Preliminary data indicate a single-phase area approximately bounded by joins between the compositions UC - $U(C_{.65}O_{.35})$, $U(C_{.65}O_{.35})$ -UN and UN-UC. Compositions external to this area consist of three phases including free UO_2 and free U. Uranium carbide and UN form a continuous series of solid solutions whereas the solubility of UO in UC is limited to about 35 mole percent. The solubility of UO in UN appears to be very small, perhaps as low as 1 or 2 mole percent.

Attempts are being made to establish the solubility limits more exactly and to measure the decomposition pressures of single phase compositions within the system. Composition and pressure of the gaseous phase appear to be critical in the synthesis of these materials.

Tungsten-Rhenium Tubing Development

Contributions to the technology of tungsten-25 rhenium alloys have included the development of powder metallurgy and arc melting and casting processes for the consolidation of tungsten and rhenium into

homogeneous alloys and for the preparation of high quality, hollow cylindrical shapes suitable for extrusion into tubing.

A vacuum arc melting and skull casting furnace was modified to permit production of conventional cold-mold ingots and vertical axis centrifugal skull-castings. A method for preparation of conductive consumable electrodes was evolved. Electrodes were prepared from a carefully blended mixture of tungsten and rhenium powders in stoichiometric 75 W-25 Re proportions. Compacts were formed by pressing isostatically at 15 tsi and were sintered subsequently at 2,200° C by electron-beam heating. Sintered bars were then joined end-to-end by TIG welding to obtain the desired length of electrode. Melting and casting parameters were determined and 8 cold-mold ingots and 3 hollow cylindrical castings were prepared for fabrication into tubing. Two of the cast hollow cylinders were extruded and drawn into tubing by another AEC contractor.

A scheme using powder metallurgy techniques was designed for the production of homogeneous, dimensionally perfect alloy shapes which could be used for subsequent extrusion and drawing into tubing. Tungsten and rhenium powders were sized and carefully blended by tumble mixing and screening through 100-mesh sieves. Green compacts in the shape of hollow cylinders were formed by isostatically pressing the blended powders at 15 tsi.

Preheating of 1,100° C in vacuum for an hour and finally sintering at 2,400° C in hydrogen for 15 hours yielded a sintered tube shell of approximately 90 percent theoretical density and completely free of any second phase material. These homogeneous alloy shells have been distributed to several AEC contractors and national laboratories for fabrication and evaluation tests.

COMBUSTION ENGINEERING, INC.

Thermal Conductivity of UO_2

As part of a Joint U.S. -Euratom Program, the thermal conductivity of UO_2 was determined for temperatures up to 2400°C using a high thermal gradient, radial heat flow technique.

Tests were conducted on elements consisting of a column of UO_2 fuel pellets 1.17 cm diameter, clad in stainless steel and containing a tungsten-rhenium heater rod located on the axis of the pellet stack. The cladding was 1.270 cm OD stainless steel tubing with an 0.051 cm wall. Thirteen stainless steel standpipes were brazed to the cladding to provide radial paths to selected depths within the pellets for optical temperature measurements. Temperatures were measured at three radial locations within the UO_2 fuel as well as at the surface of the heater rod. The thermal conductivity of the UO_2 was then calculated from the geometry of the system and the measured values of temperature as a function of radial position and the power input.

A minimum in the conductivity curve was found at 1400°C with values ranging from 0.025 to 0.033 watts/cm- $^\circ\text{C}$. A distinct increase in thermal conductivity was found for temperatures in excess of 1400°C . The range of values at 2000°C is 0.034 to 0.046 watts/cm- $^\circ\text{C}$, and at 2400°C is 0.048 to 0.059 watts/cm- $^\circ\text{C}$.

Onset of small equiaxed grain growth (with grain diameters greater than 15 microns) was observed at temperatures between 1400 to 1700°C . A difference in radial thermal gradient by a factor of approximately two had little influence on the temperature of onset of small equiaxed grain growth. On the other hand the onset of massive, blocky grain growth occurred at 2030 to 2190°C for the lower radial thermal gradient samples, whereas it occurred at 1940 to 2080°C for the samples with the higher gradient.

Another Joint U.S. -Euratom Program has as its objectives the development of a method of determining the thermal conductance of UO_2 fuel elements while operating in a reactor. Transient response of element surface temperature, following a power change, is the parameter to be utilized. Results of computer programs have indicated that the use of frequency response methods of transient testing might reveal detailed information regarding the separate contributions of pellet conductivity and pellet clad conductance to the overall effective

element conductivity from cladding response alone. However, it has been calculated that the sensitivity of the method to changes in thermal properties is less in-pile than out-of-pile, because of the difference in the manner of heat input in the two cases. It is calculated that, for the in-pile case, input frequencies of as high as 1 radian per second yield no significant information; lower frequencies, in the range of 0.1 radian per second, become of interest. Further, it has been calculated that the change in cladding time lag, for comparable changes in effective conductivity, are significantly less for the in-pile case, at comparable frequencies. The net result is that experimental measurements in-pile may well require lower frequencies than out-of-pile, and the instrumentation system must be capable of detecting small changes in the cladding time lag.

Irradiation Testing of Ceramic Fuels

An irradiation program is in progress to demonstrate the high burnup capability and inherent stability of single phase, face centered cubic solid solution fuels containing 4 and 10.2 m/o UO_2 in CaO stabilized ZrO_2 and 7 and 17.5 m/o UO_2 in CeO_2 . Two instrumented capsules have completed irradiation testing in the ETR and MTR to fission burnups of 40% of the U-235 and at target fuel center temperatures just below melting. Irradiations of the remaining four capsules are continuing to fission burnups of 55 and 70% of the U-235.

Post-irradiation evaluations on samples of the four fuel compositions irradiated in the first two capsules are in progress. Significant data developed to date include the following:

1. Preliminary fission gas release values ranged from 25% for the 7 m/o $\text{UO}_2(\text{CeO}_2)$ to 75% for the 17.7 m/o $\text{UO}_2(\text{CeO}_2)$ fuels with intermediate values of 37% for the 4 m/o $\text{UO}_2(\text{stabilized ZrO}_2)$ and 50% for the 10.2 m/o $\text{UO}_2(\text{stabilized ZrO}_2)$ fuels. The lower gas release for the 7 m/o $\text{UO}_2(\text{CeO}_2)$ is probably the result of lower fuel temperatures than those for the 4 m/o $\text{UO}_2(\text{stabilized ZrO}_2)$ fuels; both fuels were irradiated to approximately the same fission density. The high gas release for the 10.2 m/o (stabilized ZrO_2) and 17.7 m/o $\text{UO}_2(\text{CeO}_2)$ fuels is as yet unexplained. Further analyses and correlations between fission gas release, temperature, burnup and microstructure now being performed will provide additional information.

2. The stabilized-zirconia-base fuels had undergone more extensive microstructural changes than the ceria-base fuels as evidenced by void formation and agglomeration, and the development of large radial grains. A multiphase annular region within all fuels is

believed to be the result of fission product migration and formation of U-Zr-Fs or U-Ce-Fs alloys.

Concurrent out-of-pile evaluations were conducted to provide information which would be useful in the post-irradiation evaluations. Long time phase stability studies indicated the retention of the single phase face-centered cubic structures after 250 to 300 days at 1400 to 1475°C and 1380 to 1425°C for the ZrO₂- and the CeO₂-base fuels. A metallic phase and the duplex structure (believed to be a result of fission product migration) in the irradiated fuels were not detected in the out-of-pile samples, lending support to the contention that these structures were irradiation induced.

Thermal conductivity data for the ZrO₂-base fuels were extended to 2200°C and indicated a gradual decrease in values (from 0.017 to 0.022 watts-cm⁻¹-°C⁻¹) up to 1500°C followed by an increase in conductivity (to 0.027 watts-cm⁻¹-°C⁻¹) at 2200°C.

Burnable Poison Additions to UO₂

Development of methods for adding B₄C to UO₂ is being pursued as part of another Joint U.S. -Euratom Program. The objectives of the program are to develop vibratory compaction methods for producing a uniform distribution of burnable poison in high density UO₂ fuel elements, to investigate the potential for burnable poison redistribution as a result of thermal effects, and to determine the irradiation behavior of burnable poison-UO₂ mixtures in fuel rods.

UO₂ fuel elements containing 0.05 wt% B₄C additions (minus 325 mesh particles) have been fabricated to densities up to 88% of theoretical by a combination of incremental loading and electromechanical compaction. Axial boron distribution was maintained to within ±20% of the nominal value. Similar results were obtained for fuel elements containing larger, self-shielded B₄C (20 to 25 mesh particles) when incremental compaction was introduced in the process in addition to incremental loading.

Fuel rods with UO₂-B₄C mixtures compacted around an axially located tungsten heater were tested for periods up to 30 hours in a flowing helium atmosphere at centerline temperatures in excess of 2400°C. No significant axial or radial boron migration was detected for radial thermal gradients up to 4500°C/cm and axial gradients up to 15°C/cm.

Two vibratory compacted fuel rods containing UO_2 and 500 ppm boron (as B_4C) will be irradiated in the Saxton Reactor at a nominal maximum specific power of 585 watts/cm to burnups of 2000 and 5000 MWD/MTU.

Metallurgy Division
Denver Research Institute
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Introduction

The investigation of the phase equilibria of the niobium-rich region of the Nb-W-Hf and Nb-W-Zr ternary alloy systems was completed as of August 30, 1964 at the Metallurgy Division, Denver Research Institute under Contract AT(11-1)-1092-Task B. The objective of this research was to delineate the phase relationships in these refractory-metal alloy systems, thereby providing basic information necessary for alloy development programs currently of interest for elevated-temperature nuclear structural materials.

The Nb-Rich Region of the Nb-W-Hf and Nb-W-Zr Alloy Systems

Three isotherms at 1600, 1300 and 1100C (2912, 2372 and 2012F) in both alloy systems were constructed. The general features for the two systems are similar. Within the region studied there exist only two phase fields: a narrow solid solution region and an extensive two-phase field which consists of the terminal solid solution and a second phase. The second phases identified in the Nb-W-Hf and Nb-W-Zr systems are W_2Hf and W_2Zr , respectively. The solubility limits of the Nb-rich solid solution phase decrease with decreasing temperatures more sharply in the Nb-W-Zr system than in the Nb-W-Hf system.

Reported by Albert S. Yamamoto

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Introduction

A few years ago Dr. John Farr of the Los Alamos Scientific Laboratory discovered the first of a new class of inorganic compounds called the hydryls. Specifically he found that lithium hydride and rhodium reacted to form a compound of simplest formula, $(\text{LiH})_4\text{Rh}$, and that this compound would react with hydrogen to form a compound of apparent stoichiometry $(\text{LiH})_4\text{RhH}$. The analogy between these compounds and the rhodium carbonyls suggested that there might be as many hydryls of the various transition metals as there are carbonyls. The hydryls are worthy of study for two reasons: they are a new group of compounds, and the type of chemical bonding which they exhibit is of fundamental interest; and they are, because of the relatively large amounts of hydrogen which they contain, of interest as nuclear reactor materials. In June of 1962 a research program was begun to study the synthesis and properties of the cobalt metal (cobalt, rhodium, and iridium) hydryls. This program was sponsored by the Joint U.S./EURATOM Research and Development Board under contract number AT(11-1)-1185. This contract ended on May 31, 1964 and the final report (EURAE 1251) was issued in October 1964. Some of the significant results of this research program are summarized below.

Synthesis of New Compounds

Studies of the binary systems Li-Rh and Li-Ir showed that in both systems single intermediate phases of stoichiometries LiRh and LiIr exist. These phases are hexagonal with one mole per unit cell. It was found that iridium forms hydryls of the same stoichiometries as those of rhodium. Whereas the rhodium hydryl, $(\text{LiH})_4\text{Rh}$, melts at about 575°C , the corresponding iridium hydryl was found not to melt at temperatures below 850°C . Experiments with cobalt indicated that the cobalt hydryls and the intermediate phase LiCo exist. However, a reproducible method of synthesis of the cobalt compounds has yet to be found.

Properties of the Hydryls

At room temperature the compounds $(\text{LiH})_4\text{Rh}$ and $(\text{LiH})_4\text{Ir}$ are black, brittle solids. They react with water and oxygen. The crystal structure of $(\text{LiH})_4\text{Rh}$ is tetragonal with $a_0 = 11.240 \pm 0.054 \text{ \AA}$ and $c_0 = 8.932 \pm 0.036 \text{ \AA}$. The unit cell is large; assuming 16 moles of $(\text{LiH})_4\text{Rh}$ per cell the theoretical density is 3.17 grams/cc. This corresponds to a hydrogen density of 5.8×10^{22} H atoms per cc. The structure of $(\text{LiH})_4\text{Ir}$, because of the similarities of the X-ray diffraction patterns, may be assumed to be the same as that of $(\text{LiH})_4\text{Rh}$. Both of these compounds take on one more gram-atom of hydrogen to form $(\text{LiH})_4\text{RhH}$ and $(\text{LiH})_4\text{IrH}$. Room temperature X-ray

diffraction analyses indicate that these latter compounds are of different crystal structure than the former compounds.

Equilibrium hydrogen pressures as a function of condensed phase composition were determined by adding hydrogen to 4 to 1 molar ratio mixtures of Li and Rh and Li and Ir. Over the temperature range from 600°C to 800°C these experiments did not show the existence of more than one condensed phase in either system. Analysis of the data for the Li-Rh-H system gives an integral heat of solution of hydrogen in Li and Rh to form $(\text{LiH})_4\text{Rh}$ of -12.5 kcal/g-atom hydrogen. These equilibrium pressure studies showed that these hydride compounds are quite stable at relatively high temperatures. For example, the pressure of hydrogen over molten $(\text{LiH})_4\text{Rh}$ at the melting point of 575°C is about 20 mm of Hg.

Much has been learned about the hydrides through this research program, but at the same time many new questions have been raised. Work is continuing in these laboratories with the aim eventually to understand fully these unique compounds.

Reported by Charles B. Magee

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Swelling of Uranium Alloys

The objective of this research is to define the swelling behavior of dilute uranium alloys over ranges of metal temperature and exposure of interest in advanced reactor technology. In particular, the critical metallurgical factors that enable the dilute uranium alloys to resist swelling caused by formation of large internal cavities will be determined.

Previous studies under other programs at the Savannah River Laboratory have defined a series of dilute Fe, Si, Al, Cr, and Mo-containing uranium alloys with progressively increased resistance to cavitation swelling. In this series, compositions with Si at levels of 250-350 ppm appeared to play a key role. Alloys containing 350 ppm Fe-350 ppm Si-800 ppm Al and 350 ppm Si-1000 ppm Mo were most swelling resistant.

Irradiation of certain of these alloys as Zircaloy-clad tubular fuel elements in the Heavy-Water-Components Test Reactor established their capability for reaching relatively high exposure levels (6000 MWD/T or greater) under power reactor conditions, with definite evidence that reactor pressurization contributed to their stability.

To establish the performance limits of the dilute alloys under conditions of low external restraints and to determine the metallurgical factors that enable them to resist cavitation swelling, irradiation tests of specimens in NaK capsules were initiated. Over 300 small cylindrical specimens of the alloys with various compositions, initial microstructures, and mechanical properties were prepared and charged to an SRP reactor for irradiation to over 6000 MWD/T at temperatures ranging from 300 to 650°C. Following irradiation the specimens will be examined to determine the effects of various compositions, microstructures, and properties on the volume swelling and internal structural changes produced by irradiation.

GENERAL ATOMIC
DIVISION OF GENERAL DYNAMICS CORPORATION

ADVANCED, GRAPHITE-MATRIX, DISPERSION-TYPE FUEL SYSTEMS
AND
RESEARCH ON GRAPHITE

I. INTRODUCTION

The purpose of this research program is to obtain substantial improvements in the materials required for use in high-temperature, gas-cooled reactors of advanced design. The approach is based on gaining a more complete understanding of the fundamental properties and behavior of these materials in order to provide effective guidance for their further development. Several publications have resulted from these studies.

II. STUDIES OF PYROLYTIC CARBON COATINGS DEPOSITED IN FLUIDIZED BEDS

Owing to the wide variety of structures of pyrolytic carbons, the physical properties of this fuel particle coating material vary widely and may be expected to be sensitive to such processes as thermal annealing or fast neutron irradiation. In order to provide guidance for the development of fuel particle coatings, the structures of pyrolytic carbons which can be produced in fluidized bed coaters have been categorized and the relationships of various physical properties to these structures have been determined.

A. Effect of Coating Variables on the Structure of Pyrolytic Carbon

Four primary, independent coating variables which determine the reactions that produce pyrolytic carbon have been identified. It has been found that these variables, namely the bed temperature, the bed surface area, the composition of the fluidizing gas, and the total flow rate (contact time), determine the structure of the pyrolytic carbon.

The carbon structures are characterized by measuring their density, apparent crystallite size, and degree of preferred orientation, and by categorizing their microstructural appearance. Techniques were developed for the determination of these structural parameters on the extremely small deposits of pyrolytic carbon produced on particles in the fluidized bed.

Systematic investigation of the effect of the four coating variables on coating structure have shown that the structure of the deposits varies systematically with bed temperature, gas composition, and bed surface area.

B. Effect of Structure on the Mechanical and Thermal Properties of Pyrolytic Carbon

Techniques were developed for measuring the mechanical properties of the small specimens of pyrolytic carbon prepared in the fluidized bed. The fracture stress and strain, and Young's modulus for the various pyrolytic carbons were found to vary systematically with the structures.

Annealing studies have shown that the effect of heat treatment on the mechanical properties also depends on the structure of the pyrolytic carbon. Thermal diffusivity measurements have shown that the thermal properties are also structure-dependent.

C. Uranium Migration in Pyrolytic Carbon Coatings

Work on this program provided evidence that the mechanism of uranium migration through a coating of pyrolytic carbon involved as the initial step the sorption of uranium in the pyrolytic carbon structure. A systematic correlation between coating structure and extent of uranium migration was found.

III. RELATION OF PHYSICAL PROPERTIES OF GRAPHITIC MATERIALS TO MICROSTRUCTURE

Since the physical properties of a graphite single crystal are extremely anisotropic and this anisotropy is reflected in the properties of polycrystalline graphite, the relationship between the preferred orientation, the single crystal properties, and the polycrystalline properties has been studied by integrating the contributions of individual crystallites over the whole range of orientations using preferred orientation functions to give the relative number of crystallites in any orientation.

A. Young's Modulus and Preferred Orientation

Expressions have been derived which relate Young's modulus in polycrystalline graphite or carbon to the preferred orientation and the single-crystal elastic constants. Measurements on a number of pyrolytic carbons with different anisotropies have shown that the assumption that the tensile stress is constant throughout the aggregate represents the behavior of these materials to a good approximation. The "constant stress" model also fits the elastic behavior of polycrystalline nuclear graphite, provided that the modulus measurements refer to material where the dislocations have been pinned by a low-temperature irradiation.

B. Radiation-Induced Dimensional Changes

Formulae have been derived which express the irradiation-induced dimensional changes in polycrystalline graphite in

terms of the preferred orientation. The analysis is being tested in an irradiation experiment.

IV. CHEMICAL AND METALLURGICAL PROCESSES FOR MODIFYING THE MICRO-STRUCTURE OF GRAPHITE

A. Influence of Additives on Hot-Working

Studies of the influence of additives dispersed within a graphite matrix on the hot-working process and on the properties of the hot-worked bodies has resulted in the development of unique carbide-graphite cermets. The bodies are readily hot-worked, and the structure of the graphite matrix after hot-working is very dense with a uniform dispersion of fine carbide particles.

Hot-working of graphite bodies containing MoC or ZrC has resulted in large increases in the compressive strength parallel to the direction of hot-working, and modest increases in the perpendicular direction. Values of the order of 38,000 psi for the parallel orientation have been obtained. This may be compared with ATJ graphite for which the compressive strength is reported to be 8,500 psi. The helium permeability of these carbide-graphite cermets is near the limit of detection with existing apparatus ($< 7 \times 10^{-7}$ cm²/sec).

IRRADIATION EFFECTS ON STEEL

I. INTRODUCTION

This program dealing with the effect of irradiation and combined stress states on the mechanical properties of A-302B reactor grade pressure vessel steel was completed.

- II. The major test results were those obtained from thin walled tubes tested at principal stress ratios of 2 to 1 and 1 to 1 and tests in simple tension serving as base lines. The post irradiation tests covered the temperature range 0° to 149°C. Theoretical analyses were performed and presented which predict ductility under combined stress states. The major findings and conclusions were:

- A. That the ductility for specimens tested under combined stress states was considerably less than that predicted from theoretical considerations, and much less than those observed in simple tension for the same specimen geometry and other conditions.
- B. That at high neutron doses, ($\sim 8 \times 10^{19}$ nvt) the yield point was immediately followed by highly localized deformation. Measurement of the reduction of area indicated good ductility, however this behavior could be catastrophic due to the almost complete lack of work hardening.

DEFORMATION MECHANISMS IN BCC METALS

I. INTRODUCTION

Tungsten single crystals of exceptional purity are being produced by electron beam floating zone melting. Several crystals were rolled to large reductions and several more were deformed in tension. Three single crystal samples are being irradiated for neutron damage studies. The stored energy release in irradiated Mo has been determined to 1000°C.

- II. The development of methods to produce ultra-pure starting material, to be used in irradiation studies, has included zone refining in ultra high vacuums ($\sim 5 \times 10^{-8}$ torr) and the application of an electric field during zone refining. The high vacuums being used improve the properties by distilling off impurities at the metal surface; and the application of large electric fields (up to 850 amperes/cm²) has shown a definite zone refining effect.

Crystals produced by these methods have room temperature to helium residual resistance ratios of 25,000 to 50,000.

These numbers can be translated approximately into an electron scattering impurity content of $\sim 5 \times 10^{-7}$ (atom %).

A number of zone refined tungsten single crystals have been rolled to total reductions as great as 80% with 20% reduction between annealings. Annealing was performed in air at about 1000°C.

Proportional limits have been measured for a number of these crystals and have been found as low as 2 kg/mm². This may be compared with East German results of typically 4 kg/mm² for tungsten single crystals having resistivity ratios of about 100,000. In view of the sample size the East German values of resistivity ratio were probably corrected for surface scattering.

Neutron damage experiments are presently in progress on specimens grown as above. Measurements of the recovery of both mechanical and electrical properties following irradiation are planned; and these results should provide evidence for the mechanisms of neutron damage with little if any influence of interstitial impurities such as oxygen, nitrogen, and carbon.

III. STORED ENERGY RELEASE IN IRRADIATED MOLYBDENUM

A differential calorimeter previously developed in this program to measure the stored energy of cold work has been extended to higher temperatures of operation in order to measure the stored-energy release spectrum of irradiated molybdenum. Specimens irradiated to fast-neutron fluxes of the order of 10^{19} nvt show two major energy releases, at 200°C and 650°C, and some evidence for annealing reactions at intermediate temperatures.

DISLOCATION DYNAMICS RESEARCH

I. INTRODUCTION:

The ductile-brittle transition in the refractory body centered cubic metals is under study using high-stress-amplitude acoustical methods to measure the mobility of dislocations as a function of temperature, impurity concentration, and mechanical state.

- II. The working hypotheses behind these studies are that a moving crack can be arrested if enough plastic flow (dislocation motion) can take place at the crack tip to reduce the stress concentration and dissipate the crack energy. The major discovery of these acoustical studies is that there exists in these metals two separate modes, L and H, of plastic deformation. In very high purity tungsten, for example, the L mode requires relatively low stresses to excite (< 1000 psi at room temperature) but can produce relatively small amounts of plastic strain ($\sim 10^{-4}$ to 10^{-3}). The H mode, on the other hand, requires much larger stresses to operate ($\sim 10,000$ psi at room temperature) and is responsible for gross plastic flow. It appears that impurities do not affect the mobility of dislocations associated with the H mode, whereas the presence of impurities can greatly affect the amount of strain producible by the dislocations associated with the L mode. One important practical result of these studies can be stated as follows:

For small deformations such as may occur during shock loading, the stress relieving possibilities of the L-type dislocations should be investigated in such brittle metals as tungsten.

General Electric Company
Atomic Power Equipment Department

A considerable portion of the research and development program on reactor materials at the Atomic Power Equipment Department of the General Electric Company has been concerned with light water moderated and cooled reactor technology. The fuel effort has been exclusively on uranium dioxide. The cladding materials that have received the greatest attention are the zirconium-base alloys and the stainless steels; the nickel-base alloys are being examined particularly for use in superheat reactors.

Specific programs have been devoted to determining the capabilities and limitations of these materials and to the development of improved materials for the intended reactor service. These programs have also supplied useful data to the reactor designers on the physical, mechanical, and radiation properties of the reactor materials being investigated. Other programs have included the design, fabrication, testing of prototype and full-scale reactor fuel elements to improve the specific power and useful reactor life of the fuel and/or cladding. These programs are integrated with other programs relating to the properties and operating characteristics of the coolant and other components of a reactor core.

A program is also in progress on the reactor materials required for a thermionic, direct conversion system. For this system, attention again is being given primarily to oxide fuels. Refractory cladding materials are being investigated in conjunction with the fuel that will fulfill the operational requirements of the system.

EVESR Nuclear Superheat Fuel Development Program

This program has as its over-all objective the investigation and establishment of superheat fuel element performance limits and the demonstration of satisfactory fuel performance utilizing UO_2 superheat fuel of proposed economic interest for ultimate use in large central station, nuclear superheating, power plants. A research and development program is in progress that includes the design, fabrication, pre- and post-irradiation examination and testing of superheat fuel elements utilizing the ESADA-Vallecitos Experimental Superheat Reactor (EVESR).

The irradiation of superheat fuel elements in EVESR was initiated in 1964, with the first power operation on March 16 and the attainment of full power on May 13. The Mark II core loading was operated, without any fuel failures, to an average burnup of 710 MWD/T of U and a peak burnup of approximately twice this value. The Mark II fuel is an annular two-pass element, having five different cladding materials for test

purposes, viz., Incoloy-800, Inconel-600, SS-310 VM, SS-304 VM, and SS-304 commercial. This fuel is still under test and all that can be said at this time is that all of the clad materials being tested have demonstrated a minimum capability in a superheat steam environment which is typified by good chemistry control and moderate performance levels. In December of 1964, the first bundles of 7-rod cluster, advanced fuel design were inserted in the EVESR core for operation at much higher performance levels and to high burnup. The EVESR operation has demonstrated at this point the reactor maneuverability and good plant availability with the fuel being tested.

Fuel Cycle Program

The Fuel Cycle Program is a research and development program to extend the performance of UO_2 rod fuels in water reactors. Two major phases of the program involve the irradiation testing in the Vallecitos Boiling Water Reactor (VBWR) of 50 basic fuel assemblies fabricated by current commercial methods, and 12 special fuel assemblies which incorporate advanced fuel concepts that have potential for reducing nuclear power costs.

The basic fuel assemblies, half of which are clad with Zircaloy and half with Type-304 stainless steel, have been operated at average specific powers in the range of 20 to 50 KW/kg of uranium and peak surface heat fluxes as great as 160 watts/cm².

The fuel concepts under test in the twelve special fuel assemblies are among those which offer the potential of lower nuclear power costs through:

1. higher thermal performance
2. alternate clad materials and reduced cladding parasitic absorption
3. reduced fabrication costs and higher fuel density
4. extended life.

Some of the special fuel assemblies provide proof tests of fuel concepts which have been developed by other Atomic Energy Commission contractors.

The irradiations were in progress until December 9, 1963, when the operation of VBWR was terminated by mutual agreement between the AEC and APED.

Detailed examinations of selected fuel rods from both the basic and special fuel assemblies have been conducted to provide information with which to project to some degree the expected performance of these fuel designs to longer exposures.

Several failures had occurred in Type-304 stainless steel clad fuel rods at an average exposure of about 2.5×10^{20} fissions/cc. Metallographic examination revealed the cause of failure was intergranular cracking

which is consistent with other recent experience with Type-304 stainless steel as a fuel clad material.

The Zircaloy-2 clad fuel rods had operated satisfactorily to an estimated average exposure as high as 3×10^{20} fissions/cc at the time of VBWR shutdown, with a peak burnup of 4.5×10^{20} fissions/cc. The detailed examinations did not reveal any evidence which appears to be symptomatic of end-of-life failures, and satisfactory service to average exposures in excess of 6×10^{20} fissions/cc seems likely.

Metallographic determination of corrosion film thickness on the Zircaloy clad indicate the average in-pile corrosion at 286°C is about equivalent to that observed in 370°C steam out-of-pile autoclave tests. This corrosion rate is slightly lower than that previously reported on other VBWR tests of lesser duration. Hydrogen pickup by the clad was quite low, less than 10 percent. No radial or axial migration of hydrogen was apparent. It does not appear that corrosion and hydriding would impair the performance of these fuel rods at exposures well beyond 6×10^{20} fissions/cc.

The room temperature and 345°C mechanical properties of the irradiated Zircaloy-2 and Zircaloy-4 clad at integrated fast fluxes ranging from 0.4 to 1.6×10^{21} n_{fv}t showed an increase in strength and reduction in ductility as expected. Although total elongation to fracture was reduced significantly by irradiation, at least 2 percent elongation at room temperature and 1 percent elongation at 345°C remain after an exposure of 1.6×10^{21} n_{fv}t. Considerably greater ductility was evident in burst specimen fractures.

There was a slight random increase in the diameter of the fuel rods which may be associated with the adherent oxide and/or crud film rather than clad strain. The fuel rod lengths increased in the order of 0.06 to 0.15 percent. Diameter profile measurements showed circumferential ridges have formed at pellet interfaces as indicated by local increases in diameter of about 0.025 mm. These strains are well within the ability of the clad to accommodate them without fracture.

Fission gas release did not exceed 5 percent for fuel rods which had average exposures near 3×10^{20} fissions/cc and had operated to peak linear power generation rates as high as 17 kW/ft.

Defected Zircaloy clad fuel rods showed internal corrosion on the Zircaloy surfaces, particularly at the bottom end plug. The increased volume associated with the corrosion products appears to propagate cracking of the clad. The process of propagation is slow, however, as evidenced by a defected rod which operated about 3,000 hours without any apparent cracks developing in the clad although considerable bottom end plug corrosion had occurred inside the rod.

The performance of most of the advanced concepts was encouraging; however, exposures were generally insufficient to be conclusive. Fuel made by

extrusion, coextrusion with clad, and low temperature sintering with cracked ammonia, which are alternate processes developed by other AEC contractors, performed as well as fuel made by the conventional pellet process to the limited exposures achieved. It is not expected that the relative performance of these fuels would change with additional exposure.

Type-304 stainless steel cladding containing 750 ppm natural boron did not undergo irradiation induced property changes significantly different in magnitude from those observed in ordinary Type-304 stainless steel clad at similar exposures. The degree of boron burnup attained was 39 percent of the B^{10} isotope.

Zirconium diboride, as particles mixed with UO_2 fuel, was found to migrate during irradiation. Alternate sections of fuel containing and not containing boron were all found to contain boron after irradiation of the fuel rod. Investigation of the mechanism of transport is in progress.

High Power Density Program

This program is a research and development program to obtain fuel life-time and performance data on UO_2 rod fuels in water reactors. One phase of the program involved the irradiation testing in the Vallecitos Boiling Water Reactor (VBWR) of 24 fuel assemblies fabricated by current, commercial methods, and 12 special fuel assemblies which incorporated various design concepts and fabrication methods that have potential for reducing nuclear power costs.

The fuel rod design variables included:

1. Differences in the wall thickness of Type-304 stainless steel cladding from 0.008 to 0.020 inch.
2. Variation in the metallurgical condition of the cladding. Type-304 stainless steel cladding in the annealed condition as well as cladding with various degrees of cold work was tested.
3. Variation in the initial cold UO_2 fuel to cladding gap.
4. Several fabrication methods utilizing both sintered UO_2 pellets and UO_2 compacted powder fuel.

The fuel assemblies were irradiated in the VBWR at high power densities (80 to 120 Kw/L) to substantial fuel burnups. The peak fuel rod surface heat fluxes ranged from 340,000 to 500,000 Btu/hr-ft². These irradiations were in progress when the operation of VBWR was terminated on December 9, 1963, by mutual agreement between the AEC and APED.

During the irradiation of the Type-304 stainless steel clad fuel rod in the VBWR, in-service failures occurred. Subsequent examination of failed fuel rod cladding has shown that unsensitized Type-304 stainless steel is susceptible to stress-assisted intergranular corrosion attack in a high purity water environment.

Failure of over 40 Type-304 stainless steel clad fuel rods occurred during irradiation of 950 fuel rods of several different types. Failures occurred in virtually every type of fuel assembly after attaining peak fuel rod burnups ranging from 6,000 to 15,000 MWD/TU. The failures occurred at the peak surface heat flux region of the fuel rods and ranged from microscopic penetrations to multiple large cracks which were invariably intergranular. No precipitates could be observed in the austenitic grain boundaries of failed cladding samples by the use of either light or electron microscopy.

A statistical analysis of the intergranular Type-304 stainless steel failure data indicates that:

1. No significant difference exists between the failure rates of fuel rods clad with initially annealed or with cold-worked Type-304 stainless steel.
2. A much higher failure rate exists for both pellet and powder UO_2 fuel rods with thin collapsed cladding than with heavy, freestanding cladding.
3. Fuel rods operating at high surface heat fluxes (over 300,000 Btu/hr-ft²) 500 to 1,000 hours prior to failure showed an increased failure rate over fuel rods operating at lower fuel rod surface heat fluxes.
4. Fuel rods with small initial fuel-to-clad gaps had higher failure rates than fuel rods with larger initial fuel-to-clad gaps.

The operating stress level of the cladding appears to be a major factor in susceptibility to failure.

Investigations into the cause of failure have not been completed; however, evidence of localized plastic cladding deformation at UO_2 pellet interfaces was obtained and may contribute to the nucleation or propagation of the stress-assisted corrosion attack of the Type-304 stainless steel cladding.

A second phase of the High Power Density Program involves the irradiation of a series of developmental fuel assemblies containing large numbers of fuel rods in the Consumers Big Rock Point reactor as part of a program to demonstrate high power density operation of a boiling water reactor.

The fuel rod fabrication techniques used are:

1. Loading UO_2 pellets in heavy-walled (freestanding) cladding (standard fabrication method).
2. Loading UO_2 pellets in thin-walled (nonfreestanding) cladding and subsequently swaging the cladding over the pellets to reduce the initial pellet-to-clad gap.
3. Loading UO_2 powder in thin-walled (nonfreestanding) cladding followed by swage compaction of the UO_2 fuel.

4. Loading UO_2 powder in heavy-walled (freestanding) cladding using vibratory compaction to increase the fuel density.

The UO_2 fuel used in the various assemblies was cold pressed and sintered pellets or compactible powder made by arc-fusion or hot, high energy impact pressing (Dynapak). Over 1,210 fuel rods containing compactible UO_2 powder are included in the program.

The fuel rod cladding includes weld-drawn and seamless tubing of AISI Types-304 and -304L stainless steel, Zircaloy-2, Incoloy-800, and Inconel-600.

Table I summarizes the various combinations of UO_2 fuel type, cladding material and fabrication techniques for the developmental fuel assemblies.

A valuable design feature of the developmental fuel assemblies allows individual fuel rods to be removed from the assembly structure using simple underwater tools in the Consumers spent fuel pool. Fuel rod removal has been successfully demonstrated by removal and replacement of over 100 fuel rods in several irradiated assemblies. In addition, at various intervals (1,000 to 3,000 MWD/TU) during reactor shutdowns, individual fuel rods have been removed for inspection and to obtain fuel rod dimensional measurements.

Extensive fuel surveillance can be performed in the Consumers spent fuel pool on irradiated developmental fuel assemblies. These operations include: removal and replacement of individual fuel rods or substitution of special test fuel rods; visual examination of fuel rods and assemblies with an underwater periscope; gamma scanning of fuel rods; length measurement of individual fuel rods; diameter measurement of individual fuel rods; dimensional profile measurement over the entire length of fuel rods and ultrasonic testing of the fuel rod cladding.

Profile measurements on several types of fuel rods with freestanding cladding have revealed considerable UO_2 pellet fuel to cladding interaction. Circumferential ridges are evident over the peak power regions of fuel rods even though the accumulated fuel burnup is only in the 1,000 to 2,000 MWD/TU range.

TABLE I

Developmental Fuel Assemblies for the Consumers Reactor

Fuel Assembly	No. of Rods	UO ₂ Fuel Type	Cladding			Fuel to Clad Gap (mils)	Fabrication Process	Accumulated Exposure as of December, 1964	
			Material	Wall (inches)	Condition			Assembly Average MWD/TU	Peak Fuel Rod MWD/TU
PE-1, 2	242	Pellet	304	0.010	Annealed	0 to 2	Swage-over-Pellet	3,420	5,050
PE-3, 4	242	Pellet	304L	0.010	Annealed	0 to 2	Swage-over-Pellet	3,840	5,500
PO-1, 2, 3, 4	484	Arc-Fused Powder	304L	0.010	Cold Worked	0	Swage Compaction	3,930	5,950
D-1, 2, 3	363	Pellet	Zr-2	0.030	Cold Worked	7	Standard	1,550	2,280
D-4, 5, 6	363	Pellet	Incoloy-800	0.019	Annealed	6	Standard	1,630	2,360
D-7, 8, 9	363	Pellet	Inconel-600	0.019	Annealed	6	Standard	1,640	2,350
D-10, 11, 12, 13, 14, 15	726	Arc-Fused Powder	Incoloy-800	0.011	Cold Worked	0	Swage Compaction	1,320	1,900
D-16, 17	242	Pellet	Incoloy-800	0.011	Annealed	0 to 1	Swage-over-Pellet	0	0
D-18, 19, 20	363	Dynapak Powder	Zr-2	0.030	Cold Worked	0	Vibratory Compaction	0	0

Each developmental assembly contains 121 fuel rods: 109 fuel rods are 0.425 inch in diameter by 6 feet long; 12 corner rods are 0.320 inch in diameter by 6 feet long.

High Performance UO₂ Program (Euratom)

The primary research and development effort in this program is the conduct of a series of fuel assembly irradiations in the GETR-Pressurized Water Loop to explore the feasibility and limitations in UO₂ fuel rod operation with central melting. The initial series of irradiations during 1962 demonstrated that the basic obstacle to the attainment of UO₂ fuel rod operation with central melting is the UO₂ phase change volume expansion and consequent clad swelling. Subsequent irradiations in late 1962 and 1963 proved that the clad swelling problem could be avoided by proper initial fuel design.^(1, 2) The general design principle was to provide adequate fuel rod internal free volume, accessible to the molten fuel to accommodate the melting volume expansion. The required free volume was obtained by using hollow UO₂ pellets or with reduced initial bulk density in the case of compacted powder fuel.

Based on this increased understanding, further pellet and powder assembly irradiations were undertaken during 1963 and 1964 to determine whether there was any other failure mechanism related to operation with central melting that would prevent the attainment of long life. The irradiations were conducted at the maximum permissible thermal performance (determined by heat transfer limitations) in the loop facility. The operating conditions were sufficient to generate gross central melting with the rod diameters under test. Over 30 percent of the fuel rod volume and greater than 70 percent of the peak axial cross section were molten during operation.

Several unusual fuel rod failures were experienced during the extended burnup irradiations. These failures were completely unrelated to the earlier clad swelling problem; they appeared to be internally generated and suggested a fuel-clad or fission product-clad interaction. Fundamental out-of-pile studies of Zircaloy-2-UO₂ interaction and fission product (notably iodine)-Zircaloy-2 interactions were undertaken to supplement the post-irradiation examination of these pinhole type failures.

During the course of the program, the Euratom observer has performed basic out-of-pile studies regarding the effects of heat treatment on UO₂ grain growth, physical properties, microstructure, and compatibility with container materials.^(3, 4) The heat treatments included both isothermal and temperature gradient tests at temperatures up to the UO₂ melting point and beyond, and annealing times of up to 1,000 hours. These studies supplemented and materially assisted the interpretation of the in-pile results.

Periodic capsule irradiations were performed to supplement the loop tests. Recently a series of capsule irradiations have been undertaken to measure directly the thermal conductivity of UO₂ while under irradiation. These measurements utilize a unique new temperature sensor that shows good promise of being suitable for extended use to the melting temperature of UO₂.

Analysis of the loop test results on fission gas release indicates that the data can be correlated quite accurately by a model that assumes low, diffusion-limited release below 1650°C (~2%); intermediate release (~20%) in the temperature range 1650 to 1900°C; and complete release above 1900°C.⁽⁵⁾ Although the fission gas release data are among the most consistent ever obtained, the data will not define the above temperature relationship more precisely than just stated. A series of capsule irradiations is being performed to determine more accurately the fission gas release variation in the critical temperature range between 1500°C and 2100°C.

PWL Loop Irradiations - The primary program effort was successfully concluded during 1964 with a conclusive demonstration of the performance capability of Zircaloy-2 clad, UO₂ fuel rods. No performance limit was encountered for either powder or pellet fuel rods despite their operation with gross central melting at the highest specific power attainable in the test facility to burnups comparable to commercial power reactor targets.⁽⁶⁾ The terminal four-rod fuel assembly contained two Zircaloy-2 clad, vibratory compacted UO₂ powder fuel rods that reached 20,000 MWD/Te average (30,000 MWD/Te peak) burnup and two Zircaloy-2 clad, cored pellet UO₂ fuel rods that attained 12,000 MWD/Te average (18,000 MWD/Te peak) burnup. These fuel rods operated continuously throughout their irradiation at axial

peak heat fluxes above 1.1×10^6 Btu/hr-ft² ($\int_0^T k dT \geq 150$ W/cm). The following table summarizes the irradiation data for the individual rods.

Fabrication and Irradiation Data

Assembly EX-12A

<u>Fuel Rod No.</u>	<u>Average Burnup MWD/Te</u>	<u>Power Cycles</u>	<u>Full Power Hours</u>	<u>Peak Heat Flux Btu/hr-ft²</u>
12GV (Powder)	19,530	111	5,501	1.2×10^6
12FV (Powder)	20,570	111	5,501	1.3×10^6
12FC (Pellet)	12,800	63	2,839	1.4×10^6
12KCF (Pellet)	11,170	61	2,827	1.2×10^6

The fuel rods are typical in design of those used in present-day commercial power reactors and are clad with 0.565-inch o.d. by 0.030-inch wall, annealed Zircaloy-2. The fuel column is unsegmented and 29-3/4 inches in length with a 7-1/2-inch long fission gas plenum at the upper end for an over-all length of 39 inches. The pellet rods contained 92-93 percent dense sintered UO₂ pellets, centerless ground to a 6-mil initial diametral gap with the cladding and with a 0.140-inch diameter hole in the

pellet center. The powder rods contained arc-fused UO_2 powder, vibratory compacted to an initial density of 83-85 percent.

Post-irradiation dimensional measurements indicate there has been no fuel rod swelling attributable to burnup. Diameter profile traces taken along the rods by means of a sensitive profilometer show a marked difference between powder and pellet rods in localized clad deformations resulting from fuel-clad mechanical interactions. Profilometer traces taken on the powder rods are extremely smooth with no regular discontinuities. The pellet rods show extensive circumferential ridging similar to that observed in solid pellet rods operated at conventional thermal performance levels. However, the maximum ridge height is 3 mils and, thus, no more severe than those observed in the conventional rods from power reactors. (7, 8) This ridge height observation, coupled with additional profilometer traces on some of the hollow pellet rods irradiated earlier in the program, indicates that the use of hollow pellets is beneficial in reducing circumferential ridging.

The nondestructive examination of the fuel rods has shown no significant alteration or deterioration of the rods has occurred that would limit their useful life by continued irradiation to higher burnups.

A complete examination of three of the four rods from the assembly is in progress that includes fission gas release measurement, sectioning and photography, burnup analysis, and metallographic sample preparation. The condition of both the clad and the fuel will be investigated. The objective of the examination is to evaluate, insofar as possible, the remaining capability of these rods for continued irradiation to higher burnup.

Although some, as yet not completely explained, failures did occur in the course of the program, the results from the terminal irradiation assembly indicates there is no intrinsic failure mechanism that will prevent UO_2 fuel rods from attaining long life while operating with central melting.

UO_2 Thermal Conductivity - The very nature of this program - investigation of UO_2 central melting - has inherently generated considerable data regarding UO_2 thermal conductivity. (9) The data are primarily related to the onset of central melting, and thus particularly significant to the conductivity of UO_2 near its melting point. This elevated temperature conductivity has been the area of greatest previous uncertainty. Although the conductivity data are indirect, i.e., based on examination of post-irradiation microstructures and dimensional changes, they are the most accurate, consistent and reliable determination available for the thermal conductivity of UO_2 pellets under irradiation.

The conclusions from all of the data taken in toto are:

1. The value of the UO_2 conductivity integral from 0°C to melting ($2805^\circ\text{C} \pm 15^\circ\text{C}$)⁽⁴⁾ lies in the range from 90 to 96 W/cm

$$(90 < \int_0^{2805^\circ\text{C}} k dT < 96).$$

The most probable value is closer to 90 W/cm than the top of the range. To ensure no central melting and freedom from clad swelling, the maximum thermal performance level for solid pellet, UO_2 fuel rods should not exceed 90 W/cm.

2. Any improvement in thermal conductivity as a result of the formation of large, columnar UO_2 grains is small and not detectable within the experimental accuracy of the measurements, i.e., 3-4 W/cm.

The above values are in substantial agreement with the most recent results from other investigations^(10, 11, 12) which also do not substantiate the large thermal conductivity improvement reported earlier by Bates.⁽¹³⁾ There does not appear to be any significant change in the conductivity integral as a result of melting or the formation of large, nearly single crystal UO_2 grains. The maximum value of any improvement cannot exceed a few W/cm.

A conductivity equation has been derived from the data obtained in this program in combination with all of the previous out-of-pile measurements. For mathematical simplicity and convenience the form of the equation includes a term for radiant heat transfer at elevated temperature, although this may not be the actual mechanism of energy transfer. The equation for 95 percent dense pellets with T in $^\circ\text{K}$ is:

$$K_{\text{UO}_2} = \frac{38.2}{T + 129} + 4.79 \times 10^{-13} T^{-3} \quad \text{W/cm-}^\circ\text{C}$$

Capsule Irradiations for Direct Thermal Conductivity Measurements - The first successful, direct measurement of UO_2 thermal conductivity in-pile to temperatures near the melting point has been performed.⁽¹⁴⁾ Data were obtained to 2750°C , i.e., 50°C below the UO_2 melting point - 2805°C . The UO_2 thermal conductivity integral from 0°C to melting calculated from the results is 90 W/cm. This value is in excellent agreement with the previously published results from this program that were based on both examination of post-irradiation microstructures combined with thermal analysis and on clad swelling measurements.⁽⁷⁾

The starting fuel material in the capsule was stoichiometric, 95 percent dense, sintered UO_2 pellets and no detectable change in conductivity was observed during the first two hours of steady state operation at a nominal 2750°C central temperature.

The central temperature sensor, which is located in a central cavity in the UO_2 pellets, is basically a form of gas bulb thermometer using rhenium metal for the gas bulb. The gas bulb is connected through a rhenium capillary tube to a null-balance pressure transducer for monitoring the bulb pressure. The entire device is suitable for use in a high radiation field.

The temperature sensor device is being developed concurrently with the performance of the thermal conductivity measurements and shows promise of extended life at extremely high temperatures. Further irradiations are planned with the sensor to observe UO_2 thermal conductivity as a function of burnup and also to determine the effect of initial fuel structure, e.g., large equiaxed grains, columnar grains, compacted powder, etc.

Out-Of-Pile UO_2 Annealing Experiments - A definitive determination of the melting point of UO_2 resulted in a value of $2805 \pm 15^\circ\text{C}$.⁽⁴⁾ The measurement used the thermal arrest technique and, thus, was independent of a subjective observation of incipient UO_2 melting as was the case in previous experiments.

The influence of UO_2 grain growth and void migration on post-irradiation microstructures was conclusively demonstrated in out-of-pile annealing experiments. An annular UO_2 specimen was annealed in a steep temperature gradient. The inside surface temperature was held above the melting point, forming a high density, pore free, inside rim as shown in metallographic examination following annealing. The same specimen was then reannealed at an inside surface temperature of 2600°C for two hours. When again examined metallographically, all evidence of the previous melting was removed. The high density rim had become filled with porosity which presumably migrated from the cooler portion of the fuel.

Fuel Rod Failure Mechanism Investigations - Out-of-pile studies have shown that Zircaloy-2 under stress at a temperature of $350\text{-}400^\circ\text{C}$ is subject to cracking in an iodine atmosphere. In the absence of stress, the Zircaloy-2 simply undergoes a general corrosion attack and pitting from the presence of iodine. The Zircaloy-2 oxide film has been shown to play a role in localizing the attack and determining the critical temperature zone.

The iodine induced cracks are transgranular, similar to those seen in the pinhole type of failures observed in-pile. However, the out-of-pile cracks do not show the isotropic phase - believed to be ZrH_2 platelets - adjacent to the crack as observed in-pile. The formation of the isotropic phase may depend on the presence of water vapor and is being investigated.

The preferential migration and deposition of iodine to the upper end of vertically operating fuel rods - first indicated by post-irradiation gamma has been confirmed by radiochemical analyses. Approximately 30 percent of the fuel rod total iodine inventory was found deposited on the inside surface of the clad with the peak concentration just below the top of the fuel column. Both Cs^{137} and the gross activity reading were found to follow the same distribution. Very little, if any, cesium or iodine entered the fission plenum zone. The evidence just given represents the extent to which a correspondence has been established between the in-pile pinhole failures and the hypothesized fission product interaction with Zircaloy-2. Analysis of the in-pile failures has not provided any indication of the specific agent responsible for the attack.

Molten UO_2 Contact with Zircaloy-2 - Several instances of molten UO_2 coming into direct contact with the Zircaloy-2 have been observed during

post-irradiation examination of the program fuel rods. The evidence for the contact is the presence of large grained, high density UO_2 directly in contact with the clad and an apparent beta transformed structure in the cladding adjacent to the contact point. The beta quenched zone usually extends into the clad about 10 mils or one-third its thickness. A one-dimensional analysis of the clad-fuel temperature transient resulting from molten UO_2 reaching the cladding has been performed. This analysis indicates the transient occurs so rapidly - 150 μ -sec - that temporarily increased heat flow would not last long enough to disturb the heat transfer situation. Furthermore, the depth of cladding exposed to temperatures above the beta phase transformation - 875-925°C - is almost exactly that actually observed. Thus, the analysis supports the experimental observation that molten UO_2 contacting the Zr-2 cladding does not of necessity cause a failure when the cladding is being cooled adequately externally.

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NUCLEAR MATERIALS AND PROPULSION OPERATION GENERAL ELECTRIC COMPANY

The objective of the high-temperature research and development program at GE-NMPO is to extend high-temperature reactor technology by developing improved and new materials and components and by developing a better understanding of the physico-chemical properties of these materials. More specifically, the areas being studied are (1) oxidation- and steam-corrosion resistant alloys and fuel elements, (2) physical and mechanical properties of refractory metals to 2800°C, (3) refractory-metal alloy development, (4) effect of radiation on high-temperature metals and alloys, (5) radiation effects in BeO, (6) fission product transport processes in refractory-metal fuel systems, (7) an internal conversion ceramic fuel element, and (8) high-temperature thermometry.

Oxidation- and Steam-Corrosion Resistant Alloys and Fuel Elements

The number of fuel element cladding materials suitable for use in oxidizing environments such as gas-cooled and superheated steam reactors is quite limited. The Fe-Cr-Al-Y-type alloys were initially developed to extend the maximum temperature capabilities beyond the limitations of fuel elements clad with commercially available stainless steel, zirconium, or nickel alloys. The high-temperature (up to 1300°C) oxidation and steam-corrosion resistance of the Fe-Cr-Al-Y alloys are superior to the commercial alloys.

The first Fe-Cr-Al-Y alloy developed, Fe 25Cr - 4Al - 1Y, had shortcomings. It exhibited low strength at elevated temperatures and embrittlement at low temperatures. Recent studies resulted in a better understanding of the contribution of each of the alloying elements to the properties of the alloy. This in turn resulted in alloy modifications which greatly extend the usefulness of this type of alloy as a fuel element cladding material.

Embrittlement at low temperatures is caused by precipitation of a Cr-rich phase. Reducing the Cr content of the alloy effectively eliminates this embrittlement. However, reducing the Cr content lowers the oxidation resistance of the alloy. It was found that the oxidation resistance could be retained by increasing the Al content. The selective oxidation of aluminum to form an Al₂O₃ surface film is the mechanism responsible for the excellent oxidation resistance at elevated temperatures. Aluminum also increases the stability of the alloy at low temperatures.

Steam-corrosion resistance at low temperatures is more dependent on Cr content than is air-oxidation resistance. Pre-oxidation at elevated

temperatures greatly improves resistance of alloys with low Cr content to low-temperature steam corrosion.

The amount of yttrium, necessary to improve adherence of the Al_2O_3 surface film, contained in the initial alloy (nominally 1%) was detrimental to weldability and ductility. Additional studies showed that corrosion resistance could be maintained with an yttrium content of only 0.1 percent to a temperature of about $1100^\circ C$. Lowering the yttrium content to this amount improved weldability and ductility of the alloy.

Increased high-temperature strength is obtained by small additions of niobium and molybdenum; while stronger, these alloys are still not as strong as the austenitic stainless steels.

The effects of compositional and processing variables on long-time oxidation and steam-corrosion resistance and on mechanical properties are being evaluated.

As a cladding for Fe- UO_2 and Cr- UO_2 fuel element cores, the Fe - 25Cr - 4Al - 1Y alloy is compatible with UO_2 . Excellent oxidation resistance was maintained through 5000 hours at $950^\circ C$ and 3000 hours at $1100^\circ C$ in air.

Chromium-Base Alloys

Chromium-base alloys have good potential for fuel element cladding materials because of their inherent oxidation resistance and high-temperature strength. One of the primary problems is lack of ductility at low temperatures. The addition of large amounts of solutes such as rhenium and ruthenium results in improved low-temperature ductility. Determination of the mechanism through which these solutes are effective could result in the development of improved or less-expensive alloys.

As a result of studies carried out on Cr-base alloys containing Group VII and VIII solutes such as Re and Ru, an explanation for the ductilizing effect of these solutes was developed. The essential feature of the theory is the removal of embrittling interstitial elements from the matrix, thus improving dislocation mobility. The mechanism by which the interstitials are removed is termed spinodal decomposition or Re-induced clustering. In the Cr-Ru alloy system, hardness data and shape and distribution of equilibrium precipitates support the postulation. Comparison of other alloy systems on solubility-temperature relationships, elastic constants of the base metals, and crystal structure of the solute also support the postulation.

Properties of Refractory Metals and Alloys

To effectively design high-temperature reactors operating in non-oxidizing atmospheres, the high-temperature properties of refractory metals and their alloys must be known.

A technique, based on an optical extensometer, was developed for accurately measuring strain in refractory-metal specimens at temperatures to 2800°C. This technique was used to make first-stage creep measurements of arc-cast tungsten at 2200° to 2600°C in hydrogen at stresses from 0.28 to 1.4 kg/mm².

At 1600°C in hydrogen, Ta - 10W alloy has greater stress-rupture strength and is more creep-resistant than Re or W - 25Re in the stress range of 3 to 6 kg/mm².

Arc-cast tungsten has lower stress-rupture strength than wrought powder metallurgy tungsten in the temperature range from 2200° to 2600°C. Arc-cast tungsten is also less creep resistant but considerably more ductile, based on total elongation at rupture.

The stress-rupture strength and creep resistance of Mo - 50Re is an order of magnitude greater than molybdenum at 1600°C and 2200°C.

All body-centered cubic materials evaluated to date in the temperature range from 1600° to 2800°C have creep-rupture characteristics that are linear on a log-log plot, consistent with a power stress law. However, the creep-rupture characteristics for rhenium, which is hexagonal close-packed, is concave downward on a similar plot indicating a change in stress dependency at a certain stress level.

The drop technique for making enthalpy measurements was extended to allow data to be obtained to 2400°C. Enthalpy and heat capacity data were obtained for Re, Nb, Cr, Mo - 50Re, and UO₂; this technique was also used to measure the heat of the BeO phase transformation at 2100°C.

Linear thermal expansion measurements were made for many refractory materials to 2400°C. Modification of the test furnace has increased the maximum temperature at which these measurements can be made from 2400°C to 3000°C. A refraction error was identified in optical measurements of linear thermal expansion which is particularly noticeable at about 600°C. The magnitude of this error depends on the furnace atmosphere (there is no error in vacuum), and corrections to the data must be made to obtain the desired accuracy.

Modifications to the radial-heat-flow apparatus used in measuring thermal conductivity extended the range of measurements to 2500°C. Data for UO₂ to 2500°C show that the minimum thermal conductivity occurs at approximately 1600°C. Similar data for W - 60UO₂ (vol %) show the minimum occurs at about 2100°C.

Refractory Metal Alloys Development

A new series of W-Re-Mo alloys has been developed through the trial sheet production run phase. These alloys offer a broad selection of elevated-temperature properties. The melting point of each is above 2760°C. In general, the alloys are resistant to loss of room-temperature bend ductility after prolonged holding in the 600° to 2600°C temperature range. W - 30Re - 30Mo alloy exhibits complete resistance to loss of room-temperature bend ductility after holding at temperatures to 2600°C. This inherently fine-grained alloy has advanced through fabrication development and is undergoing an apparently successful test as a prototype component of a reactor. Many potential applications are recognized for alloys of the W - 30Re and W - 30Re - 10Mo type which may be age-hardened to develop high creep-rupture strength in the 1200° to 1600°C temperature range.

A processing procedure was developed for W - 25Re which produces very-high-purity finished sheet and extends the high-temperature application of this alloy beyond that of the present commercial alloy. This procedure is also adaptable to other tungsten-rhenium base alloys.

Radiation Effects in Metals

Many of the advanced reactor designs proposed for nuclear propulsion application, for space nuclear auxiliary power, and for high-performance compact core portable systems will operate at high temperature where the better strength properties of the refractory metals and certain high temperature alloys will be required. Therefore, the creep and the strength properties of these materials and the influence of neutron irradiation on these time-, temperature-, and stress-dependent properties must be understood sufficiently so that the reactor system may be designed for maximum reliability over prolonged periods of time.

The current work on radiation effects in metals comprises two parts. One concerns studies of refractory metals; the other, studies of high-temperature alloys. The experimental program on the refractory metals is based primarily on measuring the influence of neutron irradiation on the post-irradiation creep-rupture, tensile, hardness, and resistivity properties of W, Mo, W - 25Re, and Mo-TZM with the bulk of the initial program based on tungsten. In addition to the above studies, theoretical calculations of neutron-induced defects and direct-defect observation by the use of transmission electron microscope are also performed. In-reactor creep-rupture studies will be initiated once the mechanisms of the effects of neutron irradiation on the creep properties are sufficiently understood so that the significant

temperature, stress, and dose rate parameters may be selected. These parameters, then, will be used to obtain the maximum amount of information with the minimum number of expensive in-reactor test capsules. The experimental program on the high-temperature alloys is based primarily on the measurement of the post-irradiation creep-rupture properties of Hastelloy-N, Hastelloy-X, and one precipitation-hardening alloy (A-286).

For the case of tungsten, test results indicate that the irradiation tends to affect the creep-rupture properties by increasing the time-to-rupture by factors of greater than 5 for specimens irradiated to a fast neutron dose of approximately 8×10^{19} nvt with a corresponding decrease in the linear creep-rate. Although there were significant increases in the strength, the ductility of the specimens, however, did not change when compared to unirradiated specimens tested at similar temperatures and stresses. Observable changes in the creep-rupture properties occur when the fast neutron dose is greater than 1×10^{19} nvt for those specimens tested at 1100°C ($0.37 T_m^*$) or greater. For a fixed ratio of thermal-to-fast neutron flux, the stress dependency of the strengthening of irradiated tungsten does not appear to change and is similar to that of the unirradiated specimens when testing in the temperature range of 900° to 1700°C .

Irradiated tungsten specimens show further strengthening upon annealing at higher temperatures when creep-rupture tested at a temperature of 900°C ($0.32 T_m$). For example, specimens irradiated to a fast neutron dose of about 1.6×10^{19} nvt and tested at 900°C show a factor of about 4 increase in the time-to-rupture when tested in the as-irradiated condition and a factor of about 10 increase when tested at 900°C but following a 1-hour anneal at 1200°C .

Isochronal recovery studies on the resistivity properties of irradiated tungsten indicate that three resolved recovery peaks occur at 16, 22, and 31 percent of the absolute melting temperature. Similar studies on the hardness properties indicate that only one recovery peak occurs at 35 percent of the absolute melting temperature. It was further demonstrated that other irradiated, body-centered cubic (bcc) metals show recovery peaks at the same fractions of the absolute melting temperature for the respective metals and that the complete recovery of resistivity at $0.31 T_m$ and hardness at $0.35 T_m$ is in contrast to the recovery of these properties in the irradiated, face-centered cubic (fcc) metals where both occur at a temperature of $0.50 T_m$. It was determined that significant changes in flow mechanisms must occur in the regions of $0.31 T_m$ and $0.35 T_m$ of the irradiated bcc metals and that these are reflected in the resulting mechanical property behavior.

* T_m is melting point temperature, $^{\circ}\text{A}$.

Experimental data on the creep-rupture properties of Hastelloy-X and A-286 alloys indicate that thermal neutrons cause significant reductions in the time-to-rupture and also in the ductility of these alloys over and above that caused by the fast neutrons. It was further determined that this embrittlement occurs at fast neutron doses as low as 1×10^{15} nvt. Calculations indicated that boron atoms segregate to the grain boundaries and to dislocation lines where, through the thermal neutron $B^{10}(n,\alpha)Li^7$ reaction, they cause further atom displacements and generate helium atoms in the sensitive regions of the grain, thereby contributing to the severe embrittlement which is observed.

Absolute Method for Computing Irradiation-Damage Production and Annealing

An absolute method for computing damage production and annealing in neutron-irradiated cubic metals was developed. An absolute method is one which describes the distribution of defects at the level of atomic dimensions on the exact crystal lattice of the metal concerned. This method was designed for computing an unsaturated primary damage state, a saturated damage state, and defect annealing as a function of time and temperature. The effect of impurity atoms is included in the annealing calculation. Experiments show that interactions among dislocations, impurity atoms, and irradiation-produced defects (vacancies and interstitials) determine the effects of neutron irradiation on the mechanical properties. The course of these interactions is determined by the structure and deployment of these imperfections at the atomic scale of observation. Hence the deployment of irradiation-produced defects at the level of atomic dimensions must be known in order to properly interpret experimental data on mechanical properties. This deployment cannot be observed experimentally and, at present, must be estimated using absolute damage production calculations.

An extensive study of the unsaturated primary damage state in alpha-iron has been completed. Annealing and saturation studies for iron, and damage studies for tungsten and copper are in progress. Conventional damage calculations begin with the result for a random (structureless) solid and elastic atomic collisions at absolute zero temperature. This result is then amended via various particular schemes, to correct for the influence of crystal structure, inelastic collisions, and a finite irradiation temperature. A widely used random solid model is that of Kinchin and Pease. They assume elastic collisions only at and below an energy E^* and inelastic collisions for all energies above E^* .

Relative to the Kinchin-Pease model, crystal structure effects were found to reduce damage production by about a factor of 1.8. A further reduction which is a factor of 3 or greater is then afforded by

interstitial atom annealing at irradiation temperatures up to 250°C. Displacement spikes in alpha-iron have a vacancy-rich center and an interstitial-rich peripheral envelope. Channeling effects are pronounced in iron but appear to be totally absent in copper. Comparison of these results with the recent work of Thompson and Wright on the effect of inelastic atomic collision on damage production suggests that crystal structure effects alone lead to the observed damage reduction below $E^* = 56$ keV in iron, relative to that predicted by the Kinchin-Pease model.

Radiation Effects in BeO

In studies of radiation effects in BeO, the expansion behavior and property changes were defined further. In previous work, the most detrimental radiation effect was found to be microcracking, i.e. separation of the grains at their boundaries due to anisotropic expansion. The microcracking occurs in materials of 5- to 20-micron grain size when the volume expansion exceeds 0.5 percent in 100°C irradiation and 1 percent in irradiations at 1000°C. Microcracking is responsible for a marked decrease in the strength and elastic constants as well as much of the bulk expansion. Some expansion in materials irradiated at elevated temperature also occurs from grain boundary bubbles which form from the helium produced in beryllium transmutations. The expansion due to bubbles varies with grain size and is negligible in materials of very small grain size (< 5 microns) at dosages of 1 to 1.5×10^{21} nvt (≥ 1 Mev).

A more detailed analysis of the expansion yielded an apparently consistent picture of the defect structure and of the kinetics of the expansion. For irradiation temperatures up to about 600°C, the expansion results from approximately equal concentrations of interstitial and vacancy defects, but at higher temperatures vacancies predominate. Cluster development was found to progress from small unresolvable dots at 100°C to planar clusters up to 1200 Å in length at 1200°C. The occurrence of both interstitial and vacancy clusters was established using dark field electron transmission microscopy techniques.

Kinetic relationships, derived from the expansion data, show that the during-irradiation annealing of both interstitial and vacancy defects follow first-order kinetics. Equations (1) and (2) describe the microscopic expansion, $(\frac{\Delta V}{V})$, i.e. the expansion exclusive of that due to microcracking

$$\left(\frac{\Delta V}{V}\right) = \frac{K}{A} [1 - \exp(-At)] \quad (1)$$

For repetitive irradiations,

$$\left(\frac{\Delta V}{V}\right) = \frac{K}{A} [1 - \exp(-At)] + \left(\frac{\Delta V}{V}\right)_0 \exp(-At) \quad (2)$$

$$\begin{aligned} K &= 3.3 \times 10^{-23} \phi \\ A_i &= 0.113 \exp(-22,400/RT) \\ A_v &= 2.54 \times 10^{-5} \exp(-9750/RT) \end{aligned}$$

where K is the defect production rate per second; ϕ is the neutron flux, nv (≥ 1 Mev); $\left(\frac{\Delta V}{V}\right)_0$ is the defect concentration at the start of any repeated irradiation; A_i and A_v are, respectively, the annealing rate constants for interstitial and vacancy defects; R is the molar gas constant, cal/°K-mole; T is the absolute temperature, °K; and t is the irradiation time, seconds.

These kinetic equations describe the expansion reasonably well over the temperature range from 100° to 1200°C. Saturation of the expansion is predicted in time periods greater than 10^7 seconds at amounts that are directly dependent on the flux. Although not found experimentally, if undue helium effects do not occur, it should be possible to utilize BeO under flux and temperature conditions such that the amount of expansion at saturation would be less than that at which microcracking occurs.

Progress was made in determining the helium behavior. Escape of the helium was found to be dependent on surface area, in particular on microcracking. In bulk specimens, about 25 percent of the helium formed escaped in 100°C irradiations in which the samples were extensively microcracked, while less gas escaped at elevated temperatures at which microcracking did not occur or was minimal. About 75 to 80 percent of the helium retained in specimens irradiated at elevated temperatures remained in the grains; the remainder of the helium appeared as bubbles at the grain boundaries. Preliminary evidence indicated that diffusion of the helium from bulk specimens in the absence of microcracking followed kinetics similar to that ascribed to vacancies; however, there is at present no direct evidence that the helium is associated with the vacancy clusters. Helium bubbles on the grain boundaries were previously found to contribute about 20 percent of the 1 percent expansion in materials of 20-micron grain size irradiated at 1000°C and 10^{21} nvt (≥ 1 Mev). A potential for further expansion without a significant change in strength was demonstrated in post-irradiation annealing experiments in which expansion increased without microcracking. At present, conclusions regarding helium effects are those derivable from general principles. Specifically, the effects should be minimized by the use of materials of fine grain size (< 5 microns) and of either low density or small dimensional cross section.

Property changes continued to appear to depend primarily on microcracking. Similar to the room temperature strength behavior, the

elevated-temperature strength of specimens irradiated at elevated temperatures was essentially the same as that of unirradiated material in the absence of microcracking. Changes in the elastic constants followed the same pattern as the strength changes. In other measurements, no change in the enthalpy of irradiated specimens was observed up to 900°C for specimens irradiated at 1000°C.

Fission Product Transport Processes in Refractory Metals

The refractory metals and alloys, such as Mo, Ta, W, and W-Re, have the highest temperature potential for use as cladding materials in various coolants. Basic mechanisms of fission product transport and the fission product retention capability of these materials at high temperatures were defined.

Although transport work has concentrated initially on rare gas diffusion and permeation in arc-cast tantalum, similar results are expected for rare gas diffusion in other refractory metals. Results from permeation studies at 2400°C indicate that the transport of krypton in or through tantalum is less than 8×10^7 atoms/sec. This indicates that (1) krypton cannot be dissolved to any extent in tantalum by thermal energies alone and (2) transport through the grain boundaries is not significant, although the grain size increased by a factor of 10 during the heat treatment. To determine rare gas diffusion rates, techniques were developed to overcome the problems of dissolving rare gases in metals and in measuring the concentration profile of the gases in the metal. The results indicate that in the 1200° to 1800°C temperature range, krypton has significant (at least 12 microns) short-range mobility in tantalum.

In-pile tests on powder-metallurgy tantalum capsules containing UO₂ were operated at temperatures up to 2200°C. The low values for the fission gas release showed no evidence for volume diffusion of the fission gases, although fission gases were embedded in the cladding by recoil. This indicates that long-range diffusion (greater than 400 microns) does not occur to any significant extent to at least 2200°C.

Internal Conversion Ceramic Fuel Element Research

The potential usefulness of self-moderating BeO-base fuel elements capable of operation in oxidizing and/or He-O₂ atmospheres, could be increased by incorporation of ThO₂ to give internal conversion.

Results of work in progress show that it is feasible to substitute ThO_2 for part of the UO_2 in the basic $\text{UO}_2\text{-Y}_2\text{O}_3\text{-BeO}$ system. Incorporation of this system into all-ceramic fuel elements for gas-cooled reactors promises sustained life at temperatures up to 1400°C and shorter life-times of well above this temperature.

Studies under this program resulted in the development of a method for reacting UO_2 , ThO_2 , and Y_2O_3 to form well-crystallized solid solutions. The X-ray diffraction analyses in the area of interest in the $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3\text{-O}_2$ system (5 to 65 UO_2 , 0 to 95 ThO_2 , and 0 to 40 Y_2O_3 , all in percent) shows a complete series of face-centered cubic (fcc) solid solutions. Partial pressure measurements of UO_3 from $\text{UO}_2\text{-ThO}_2$, $\text{UO}_2\text{-Y}_2\text{O}_3$, and $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ solid solutions in air show that the addition of only 0.55 mole of Y_2O_3 per mole of UO_2 to $\text{UO}_2\text{-ThO}_2$ binary compositions reduced the UO_3 partial pressure by a factor ranging from 3 to 6.

BeO -base fuel elements containing 7 to 25 volume percent of $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ exhibit good physical and mechanical properties and excellent fuel retention properties. The thin-wall, tubular specimens lose a maximum of 1.7 percent UO_2 in 2000 hours at 1400°C in air, a maximum of 0.6 percent UO_2 in 4000 hours at 1200°C in air, and no UO_2 in 2000 hours at 1200°C in helium and helium containing 5 volume percent oxygen. The high-temperature capability of these fuel elements was illustrated in 100-hour tests at 1650°C in air where the majority of the compositions lost from 0.3 to 3.0 percent UO_2 . From additional fuel retention studies, a method of sintering was developed which reduces the amount of UO_2 lost during testing by a factor of about 2 to 5.

Irradiation testing of unclad BeO fuel elements fueled with $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ solid solutions to determine the kinetics of fission product release and physical integrity showed the dominant fission gas release process is recoil at temperatures from 1250° to 1550°C . There is no diffusion contribution. This is contrary to previous experience with other fuel compositions and may prove to be a significant milestone in the development of an all-ceramic fuel element.

High-Temperature Thermocouple and Electrical Materials

The continuing development of long-life, high-temperature nuclear reactors requires thermocouples capable of continuous stable performance in nuclear environments. The commercially available W / W - 25Re thermocouple was demonstrated to be subject to changes in thermoelectric properties due to transmutation reactions in both the W and W - 25Re. Errors of $+90^\circ\text{C}$ or more may result after 1

month in a 10^{14} thermal neutron flux. Pre-alloying with as little as 1 atomic percent osmium, the transmutation product in tungsten and rhenium, has significantly decreased the error.

Gas-tight metal-to-ceramic seals of Nb and Al_2O_3 made by using high-temperature gas-pressure-bonding techniques had good tensile bond strength ($> 8.1 \text{ kg/cm}^2$) and demonstrated excellent stability at 1600°C for 466 hours with two returns to room temperature.

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Yield Phenomena and Fracture of Hydrided Zirconium

An investigation, supported by the Joint U.S.-Euratom Program, for the purpose of obtaining a better understanding of deformation and fracture modes in zirconium has recently been initiated. The principal characteristic of zirconium presently under study is the occurrence of an abrupt yield point; ordinarily, such behavior is not observed, and conditions for which discontinuous yield occurs are being defined. Thus far, in work on polycrystalline zirconium, it appears that some critically fine grain size must be attained for yield point appearance. There is little doubt concerning the accuracy of this observation in that past investigations, not expressly intended for study of yield phenomena, fortuitously observed similar behavior. Yet, recent work has definitely established the existence of yield points in single crystals of zirconium.

The limited past investigations on yield point occurrence failed to account for this seeming paradox or for grain size dependency. Since past investigations devoted little effort toward mechanistic studies, yield occurrence was simply rationalized on the basis of the Cottrell dislocation locking/subsequent unlocking concepts. Not only does this mechanism fail to explain the grain size dependency of yield point appearance, but it probably is of only limited importance because the dislocation-interstitial interaction energy is low in hcp metals. Moreover, the Cottrell theory, per se, is no longer widely accepted as the mechanism for yield point occurrence. In any case, initial experiments have been designed to test the validity of this mechanism for yield phenomena in zirconium.

A report on yield point occurrence in polycrystalline titanium has recently appeared, and a theory for yield was developed on the basis of interaction between regular networks of dislocations. Such a mechanism might be active in zirconium. However, the recent theory of yield point occurrence based upon initial mobile dislocation density, rapid dislocation multiplication, and stress dependency of dislocation velocity is more widely accepted. Recent evidence has been provided showing that this model can account for yield phenomena in certain fcc alloys. Further, data are available showing that the double cross-glide mechanism of rapid dislocation multiplication does occur in zirconium. It has been proposed, and discussed in reports issued on this program, that a relationship exists between (a) the number of dislocations that can occupy a pile-up of a given length at a grain boundary and still remain an effective barrier and (b) the number of initially mobile dislocations present prior to yield point observance. Such a relationship could account for grain size dependency of discontinuous yield occurrence, and experiments have been initiated to show this relationship and thus explain yield phenomena in zirconium within the concepts of current theory. Ultimately, the influence of hydrogen on this mechanism as well as on certain models for fracture will be studied.

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The Fuels and Materials Development Program at Mound Laboratory is directed toward the study of the fundamental chemical, physical and metallurgical properties of plutonium and plutonium-bearing materials. Information on plutonium-bearing materials over a wide temperature range is required for the economical utilization of plutonium in power reactors. Since many properties of plutonium-bearing materials are influenced by the properties of the element, the study of elemental plutonium has become an essential part of the program. The program is being pursued in three areas of research, namely, (a) development of plutonium and plutonium alloy phase diagrams and crystal structures, (b) measurements of the physical and thermal properties of plutonium, plutonium alloys and plutonium compounds in both the solid and liquid states, and (c) the formulation and evaluation of plutonium-bearing ceramic systems.

Phase Transformations in High Purity Plutonium

Plutonium metal displays unusual structural properties since it exhibits six stable allotropic modifications between ambient temperature and its melting point of 640°C. In the past it has been found that the transformations between the various allotropes occurred more sharply as higher purity plutonium was examined. When electrorefined metal became available with less than 90 ppm total impurities, the phase transformations were examined by a sensitive differential thermal analysis apparatus. Several significant points which were not observed with less pure plutonium were revealed by this examination. The first point concerned the appearance of a small thermal effect at 110°C immediately prior to the alpha to beta transformation, which occurred at 125°C. Secondly, for the first time the delta to delta prime transformation at 462°C was completely separated from the delta prime to epsilon transformation at 485°C. Thirdly, less than one degree was observed between the start and completion of melting.

The latent heats of transformation were quantitatively determined by the DTA method. All of the values for the various transformations were in general agreement with previously published data. The precision of the data for the delta to delta prime and the delta prime to epsilon transformations was improved. The values determined for the delta to delta prime and delta prime to epsilon transformations were 20 ± 1 and 383 ± 4 calories/gram-atom, respectively, as compared to literature values of 20 ± 10 and 444 ± 10 calories/gram-atom, for the same transformations. The data indicated also that the heat capacity of the delta prime phase may be as high as 10 calories/gram-atom.

Further study of the small thermal effect which occurred immediately before the alpha to beta transformation indicated that it was associated with a non-equilibrium condition of the sample since it disappeared after the sample had been annealed at 110°C for five days. The effect reappeared whenever the sample was heated into the beta phase region and slowly cooled to room temperature.

Phase Studies of Low Melting Plutonium Alloys

The phase relationships in the plutonium-cerium-nickel and plutonium-cerium-iron ternary systems have been investigated as part of a program designed to define suitable fuel materials for the molten plutonium fast breeder reactor concept. This reactor concept requires fuel materials which contain plutonium over a wide composition range and which are molten at temperatures below 500°C. The phase studies were conducted by metallography, differential thermal analysis and electron microprobe x-ray analysis.

The phase studies revealed that the plutonium-cerium-nickel system is attractive for this molten fuel application. The ternary phase diagram contains a low melting eutectic valley which extends across the diagram at nearly constant nickel concentration, approximately 20 at. % nickel. Plutonium substitutes for cerium along this valley so that ternary compositions containing from 0 to 85 at. % plutonium are obtained which have liquidus temperatures from 440 to 475°C. The primary phase fields of only four solid phases constitute the low melting region of the phase diagram. These solid phases, which exhibit appreciable amounts of solid solubility are: plutonium, cerium, Ce_5Ni_2 , and CeNi-PuNi solid solution. No detrimental corrosive attack of the tantalum containers was noted from the low temperature molten alloys.

For ternary compositions containing more than 50 at. % nickel the liquidus temperatures are above 700°C. Extensive solid solution is indicated between the isostoichiometric pairs, CeNi-PuNi , $\text{CeNi}_2\text{-PuNi}_2$, $\text{CeNi}_3\text{-PuNi}_3$, $\text{CeNi}_4\text{-PuNi}_4$, and $\text{CeNi}_5\text{-PuNi}_5$.

In the plutonium-cerium-iron system a eutectic valley extends across the phase diagram at approximately 10 at. % iron. The temperatures along this valley are generally higher than those in the valley of the plutonium-cerium-nickel system. A large primary phase field for the solid solution phase, $\text{CeFe}_2\text{-PuFe}_2$ covers the majority of the phase diagram. The low melting valley occurs along the boundary between the $\text{CeFe}_2\text{-PuFe}_2$ phase field and the phase fields for cerium solid solution and plutonium solid solution. A maximum point on this boundary near the cerium corner at a temperature of 665°C divides the directions for the solidification paths of compositions along this boundary. Two ternary, peritectic type, invariant points occur toward the plutonium-rich side of this maximum point. At one invariant point, located at a composition of 76 at. %

Pu - 12 at. % Ce - 12 at. % Fe and a temperature of 435°C, cerium solid solution, plutonium solid solution and CeFe₂-PuFe₂ solid solution are in equilibrium. The second invariant point, located at 90 at. % Pu - 1 at. % Ce - 9 at. % Fe and a temperature of 417°C, has CeFe₂-PuFe₂ solid solution, plutonium solid solution, and Pu₆Fe in equilibrium. The compositions of interest as a molten reactor fuel have a very limited range from 76 to 90 at. % plutonium with liquidus temperatures in the range of 435 to 410°C.

All ternary compositions of plutonium, cerium, and iron containing more than 30 at. % iron have liquidus temperatures above 800°C. A ternary, peritectic type, invariant point occurs in the high temperature, iron-rich corner with equilibrium between CeFe₂-PuFe₂ solid solution, Fe, and CeFe₅.

A study was initiated to define the lowest melting compositions containing plutonium, based on previous knowledge of the ternary systems, plutonium-cerium-nickel, plutonium-cerium-cobalt, plutonium-cerium-iron, and plutonium-cerium-copper. Preliminary results indicate that a eutectic as low as 375°C exists in this multicomponent system with an appreciable plutonium concentration. Although the exact eutectic composition has not been located, the low melting region is apparently broad since several compositions have been examined which have liquidus temperatures below 430°C. Additionally, these alloys have a high concentration of copper which is unreactive with the tantalum container material and a low concentration of iron, cobalt, and nickel which seriously corrode tantalum.

Thermal Diffusivity of Uranium-Plutonium Carbides

The thermal diffusivities of a uranium carbide and two uranium-plutonium carbide compositions were determined in an apparatus in which the thermal diffusivity coefficient is calculated from a measurement of the radial temperature difference across a cylindrical specimen being heated at a constant range. The measurement over the temperature range from ambient to 1000°C requires only 1.5 hours. The three carbide samples were prepared from cold-pressed and sintered powders formed by the carbon reduction of oxides. Each sample was sealed in a thin-walled tantalum capsule with liquid tin as a bonding agent.

The thermal diffusivity values of the uranium carbide, which contained 0.1 weight percent nickel as a sintering aid, decreased rapidly from 0.104 cm²/sec at 250°C to 0.050 cm²/sec at 700°C and gradually increased to 0.055 cm²/sec at 1000°C. The thermal conductivity values, calculated from these data and published values for the density and heat capacity of the material, were in general agreement with data from other investigators for sintered uranium carbide samples.

The average thermal diffusivity values for the samples $(U_{0.8}Pu_{0.2})Co_{0.95}$ and $(U_{0.8}Pu_{0.2})Co_{0.95} + 0.1$ weight percent nickel were $0.039 \text{ cm}^2/\text{sec}$ and $0.028 \text{ cm}^2/\text{sec}$, respectively. These values were independent of temperatures over the range of 250 to 1000°C and were approximately 25 to 45 percent below the values for uranium carbide in the temperature range 600 to 900°C .

Properties of the Liquid Alloy Plutonium - 1 Wt % Gallium

The addition of gallium to plutonium stabilizes at room temperature the high temperature delta phase of plutonium, which has a face-centered cubic structure. Since the delta phase exhibits desirable mechanical and physical properties, the solid state properties of gallium-stabilized, delta plutonium have received considerable study. Several physical properties of the liquid alloy and the latent heat of fusion have now been measured.

The addition of one weight percent gallium had a marked effect on the liquid properties. The liquidus temperature for this alloy, 670°C , was determined precisely during the viscosity experiment. The viscosity of the alloy decreased from 8.75 centipoise at 672°C to 6.36 centipoise at 816°C . These values are 50% larger than the values for the viscosity of unalloyed plutonium over the same temperature interval. The density of the alloy which decreased from 16.180 g/cc at 670°C to 16.033 g/cc at 847°C is 2.6% lower than the density of unalloyed liquid plutonium over the same temperature interval. This alloy exhibited approximately a 0.7% expansion as it transformed from the liquid to the solid state.

The latent heat of fusion for this alloy, as determined by quantitative differential thermal analysis, was 3.64 calories/gram of the alloy, which is approximately 18% greater than the energy required to melt a corresponding amount of plutonium and gallium. This fact indicates that a heat of mixing occurs when plutonium and gallium are combined and further indicates, along with the density and viscosity data, that the liquid alloy is not an ideal solution.

Physical Properties of Liquid Plutonium-Cerium-Cobalt Alloys

The physical properties, density and viscosity, of liquid plutonium alloys which melt at low temperatures are being determined because these alloys are being considered as molten fuels for fast breeder power reactors. Since alloys in the plutonium-cerium-cobalt system are likely fuel materials, the viscosities and densities of four alloys in this system were measured over a range of temperatures. These alloys had compositions which placed them in a low melting valley of nearly constant liquidus temperature ($422^\circ - 459^\circ\text{C}$) with nearly constant cobalt composition (22-24 atom % Co) so that plutonium could be substituted for cerium over a composition range

of 0-50 atom % Pu. When the viscosity data at the liquidus temperatures were plotted as a function of plutonium concentrations, the viscosity increased regularly from 5 to 23 centipoise as the composition changed from 0 to 48 atom % Pu. The viscosity value of 23 centipoise is unusually high for liquid metal systems. Parallel curves were generated from the data up to 200°C above the liquidus temperatures. These data represent the first such correlation attempted for a ternary alloy.

The measurement of the liquid densities of these plutonium-cerium-cobalt alloys revealed that the densities could be calculated within 2% of the experimental values from the assumption of ideal mixing behavior of the alloy constituents. This discovery was unusual since the liquid densities for cerium and cobalt had to be extrapolated over a wide temperature range below their respective melting points. All of the ternary alloys exhibited a volume expansion during the transformation from the liquid to the solid states.

Preparation of Microspheres of Ceramic Materials

High density microspheres of plutonium dioxide and plutonium dioxide mixed with other metal oxides have been produced in all size ranges from 10 to 250 microns diameter by use of the induction-coupled plasma torch. Samples of the spheres are being evaluated as potential reactor fuel materials. Since a unique feature of the plutonium oxide microspheres is their freedom from loose radioactive contamination, the health hazards associated with the handling of this material are significantly reduced. Several samples of microspheres have been sent to biological laboratories for evaluation of this safety feature.

Previous difficulties in the preparation of uranium dioxide microspheres larger than 100 microns were overcome when high density spheres up to 250 microns in diameter were prepared in an argon-helium plasma.

When powdered feed material composed of 50 wt % PuO_2 - 50 wt % BeO was passed through the plasma torch, the majority of the particulates were well-formed polyhedra exhibiting flat faces. Although the polyhedra formation suggested single crystals of a new phase, x-ray powder diffraction photographs indicated that the particulates contained only well-formed crystals of PuO_2 and BeO with no indications of a new compound or solid solution formation.

Structural Studies of Boron

The study of the crystal structures of boron polymorphs is of importance in chemical bonding theory and in the application of boron compounds in reactor components. A new technique was developed for the preparation of single crystals. Polycrystalline particles of finely divided boron

of the beta-rhombohedral structure, were passed through the flame of an induction-coupled plasma torch. The majority of the product consisted of imperfectly spheroidized particles with polyhedral faces. X-ray diffraction patterns revealed that they were polycrystalline of the beta-rhombohedral structure.

A small number of well-formed single crystals of four distinctive shapes up to 75 microns in linear dimensions was produced. The four crystalline habits were regular octahedral, square right-prismatic, dodecagonal prismatic, and truncated tetrahedral.

Examinations of the crystals by x-ray diffraction techniques showed the octahedral crystals to have a simple tetragonal lattice with parameters, $a_0 = 10.061$ A, and $c_0 = 14.210$ A. These lattice parameters are close to those for a structurally unelucidated form of polycrystalline boron previously reported and are similar to those for alpha - AlB_{12} .

The square, right prismatic crystals have a cubic structure with a lattice parameter, $a = 23.71$ A. The large volume of such a cell may contain from 1700 to 1800 boron atoms. This structure is likely related to the rare earth heptaboride structures.

No definitive structural determinations have been performed on the remaining two habits. The dodecagonal prisms appear twinned in a complicated fashion. The tetrahedrons are similar in habit to the beta-rhombohedral form of boron.

Nuclear Materials and Equipment Corporation
Apollo, Pennsylvania

NUMEC is carrying out programs covering the development and evaluation of UO_2 - PuO_2 fuels and on the growth of single crystals of plutonium. The fuels fabrication effort covers development of appropriate preparation and characterization procedures as well as determination of certain physical properties. Irradiation experiments are also being carried out to assess the effects of certain materials characteristics. The project on the growth of single crystals of plutonium was recently initiated and covers the growth of alpha and delta phase crystals.

Thermal Expansion Characteristics of Coprecipitated (U,Pu) O_2 Powders

The thermal expansion characteristics of coprecipitated (U,Pu) O_2 powders have been determined covering the entire composition range. High temperature x-ray diffraction techniques were used and data obtained at 100°C intervals from 0 to 1200°C. Powder samples were heat treated in place on a tungsten ribbon stage at 1300°C for one hour in low pressure nitrogen prior to adding thorium for use as an internal temperature standard. Results show good internal consistency and reasonable agreement with data obtained by others for a few compositions using dilatometry. An effect due to oxygen/metal ratio was observed. Specifically, while the thermal expansion coefficient for UO_2 was found to increase with increasing oxygen/metal ratio, the reverse was found for PuO_2 .

Morphological Studies on (U,Pu) O_2 Powders

The morphological characteristics of (U,Pu) O_2 coprecipitated powders have been studied as a function of composition by means of electron microscopic examination of plastic replicas. Results show that the characteristics are transferred from step to step in the production of the oxide powders. This phenomenon has been referred to as the relic effect. However, the size of protuberances or crystallites on the surface of the oxide powders decreases with increasing plutonium content until the 35 w/o PuO_2 concentration level is reached. Above this concentration, the morphological characteristics of the powders are significantly different from those observed for lower plutonium content materials.

Homogeneity of Mechanically Mixed UO_2 - PuO_2 Powders

Mechanical blending of UO_2 and PuO_2 can be used for the preparation of ceramic grade fuel materials. Microscale homogeneity of the blend is sometimes important from a physics standpoint and, in addition, can markedly affect sintering parameters as well as some physical properties. Autoradiography techniques with polished surfaces of sintered pellets have

been utilized to provide qualitative data on the mixing efficiency of various powder blending methods. Results indicate that techniques which depend upon a tumbling action, such as twin-shell cone blending, are inadequate for fine scale blending. While gross blending does take place, rapid agglomeration of the component powders results. Dry ball milling provides a tumbling-crushing-shearing action which gives a homogeneity pattern differing from that of twin-shell blended material only in the size of the high and low concentration areas. Wet ball milling results in homogeneity similar to that of coprecipitated material except that autoradiographs show a more mottled appearance, indicating a zoning effect. Of the dry methods studied, hammermilling has been found to be most effective in producing a homogeneous blend. This method is far more effective than dry ball milling, although it is decidedly inferior to the wet ball milling.

Irradiation Testing of $\text{UO}_2\text{-PuO}_2$ Fuels

A set of five fuel capsules are being fabricated to determine in-pile performance of $\text{UO}_2\text{-PuO}_2$ fuels having compositions of interest for fast breeder reactors and for plutonium recycle in thermal reactors. Irradiations will be carried out for periods ranging from approximately 10,000 to 80,000 MWD/Tonne. Post-irradiation examination is expected to shed light on the following aspects:

1. Relative performance between fuel pellets prepared from coprecipitated $\text{UO}_2\text{-PuO}_2$ and pellets fabricated from feed material prepared by the mechanical mixing of component powders.
2. The effect on performance of relatively gross inhomogeneities that may result from incomplete powder blending.
3. Differences in performance that may arise due to differences in pellet stoichiometry or the presence of Pu_2O_3 .
4. The performance of fuel elements formed by the vapor cementation with tungsten of spherical particles composed of $\text{UO}_2\text{-PuO}_2$.

Growth of Single Crystals of Plutonium

Plutonium is unique among the metallic elements as it exists in six different allotropic modifications which collectively have physical and mechanical properties covering an extremely broad spectrum. Research studies directed towards understanding this metal would be aided if single crystals of the various allotropes could be obtained. Initial attempts to grow single alpha phase crystals utilizing beta to alpha phase transformation have thus far been unsuccessful although some grain growth was obtained. Growth techniques which have been attempted include the following:

1. Progressively transforming plutonium wire samples through the beta to alpha phase transformation,
2. Progressively cycling plutonium wire samples through the beta to alpha phase transformation with and without applied tensile stress, and
3. Long-time beta to alpha isothermal transformations at 100, 105, 100, and 95°C.

Very high pressure equipment has now been installed, and crystal growth experiments by freezing directly into the alpha range will be carried out. In addition, a precision tensile machine has been installed in a glove box, and growth experiments with delta stabilized plutonium by the strain anneal technique are being initiated.

Nuclear Metals Division of Textron Inc.
West Concord, Massachusetts

Three programs have been conducted by Nuclear Metals in CY 1964 for the Fuels and Materials Development Branch. The first program, "Development of Fabrication Methods for Seamless Tungsten and Tungsten-25 Rhenium Tubing," is concerned with developing methods of extrusion, drawing, reeling, and heat treatment to produce relatively small diameter seamless tungsten and W-25Re tubing of high quality. Such tubing is required in certain high temperature reactor applications.

The second program, "Fundamentals of Single Crystal Deformation in Zone-Refined Beryllium," is a continuing study of the deformation and fracture behavior of beryllium single crystals produced by floating zone-refining. The work is leading to a fundamental understanding of the effects of purification and selected realloying on the flow and fracture characteristics of these crystals. The ultimate objective is to apply the findings toward attainment of ductile polycrystalline beryllium.

The objective of the third program, "SLIS Alloys of Uranium and Zirconium," is to improve the high temperature behavior of uranium and zirconium by dispersing throughout the base material a metallurgical phase in the form of submicron particles. Such a dispersion can be accomplished by the very rapid cooling of tiny molten droplets of suitable alloys.

Development of Fabrication Methods for Seamless Tungsten
and Tungsten-25 Rhenium Tubing

Nuclear Metals is continuing to develop techniques for the fabrication of seamless tungsten and tungsten-25 rhenium tubing by combinations of the following operations: primary extrusion, secondary extrusion, and drawing. In the more recent work the emphasis has shifted to the W-25Re alloy.

For unalloyed tungsten the standard extrusion temperature is 1200°C. The extrusion technique has been refined so that a reliable billet design and procedure are available. This technique has been applied primarily to obtain tubing with 3/8-inch OD and 30- to 40-mil wall by reductions of 16:1. The technique has been applied to sleeves as long as 8 inches. The possible use of steel instead of molybdenum for the fillers, in conjunction with extrusion at lower temperature (1020°C), has been explored and appears quite promising.

Tungsten extruded at 1200°C is drawn at 580°C after a one-hour anneal at 1450°C. The principal method for ironing by drawing over a hardened mandrel involves the use of a plug (stationary mandrel). By this technique reductions of about 30 percent have been obtained in a

single pass with cumulative reductions of over 50 percent. The moving-mandrel technique is applicable with greater difficulty because of the problem of subsequently separating the mandrel, a problem that is made particularly difficult by the brittleness of tungsten, which leads to the rapid propagation of any cracks.

For the extrusion of W-25Re, powder metallurgy sleeves of satisfactory quality (essentially free of second phase) have been obtained from several commercial sources and from the Bureau of Mines, Albany, Oregon. An extrusion temperature of 1600°C has been adopted for this alloy. This temperature permits the incorporation of a graphite core, which facilitates subsequent removal of the inner molybdenum filler. The reference extrusion technique involving 16:1 reduction (and also 25:1 reduction) has been applied to several sizes. Initially the principal size of interest was 3/8-inch OD by 40-mil wall as for the tungsten tubing. Recently a size of 0.28-inch OD by 25-mil wall has become of greater interest; it is to be drawn to 0.25-inch OD by 20-mil wall. When available, sleeves 8 inches long are used as stock. The technique has also been applied to arc-melted sleeves.

The re-extrusion of W-25Re to small sizes (below 0.1 inch) requires a filler material that can be removed chemically to provide a pilot hole in the inner molybdenum filler. Calcium carbide has received prime attention in this investigation; whereas successful re-extrusion has been achieved with an inner filler consisting entirely of molybdenum, satisfactory conditions for re-extrusion with a CaC_2 core have yet to be defined. Prior recrystallization of the extruded W-25Re tube appears desirable and may even be mandatory.

In the development of drawing techniques it appears that W-25Re can be drawn at 510°C directly after being extruded at 1600°C. Techniques for pointing and gripping the tube for the drawing have been established. Pointing is accomplished by swaging with chopper dies over a TZM (molybdenum alloy) insert, which is left in the point for the drawing. The W-25Re point can then be gripped directly in the drawing. Cracks initiated by the gripping do not propagate. Plug drawing has been successfully applied down to a size of about 0.310-inch OD by 30-mil wall. With smaller sizes the draw forces are so large as to exceed the strength of the drawn tubing. For the smaller sizes, satisfactory reductions can be achieved in ironing over a moving mandrel. The mandrel can be removed by reeling. Both the drawing and the reeling require tools of sufficient strength to withstand the large forces necessitated by the strength of the W-25Re. Sinking without a mandrel and drawing over a deformable mandrel consisting of the molybdenum extrusion filler have been successfully accomplished with the products of both primary and secondary extrusions, covering sizes from about 0.4-inch to less than 0.1-inch OD. Although it is not yet clear that pre-draw anneals of extruded materials are advisable, it is quite apparent that surface conditioning is necessary to obtain tubing smooth enough to draw properly. It is also apparent that stress-relieving anneals at 1400°C should be performed after each pass.

Various metallurgical evaluations at Nuclear Metals have served primarily to guide the development of the fabrication operation. In addition, samples have been sent to various other sites for evaluation. One such evaluation has been burst testing at NASA Lewis Research Center where it was found that as-extruded tubing failed at 4500°F (2480°C) at a pressure equivalent to a hoop stress at 4140 psi.

Fundamentals of Single Crystal Deformation in Zone-Refined Beryllium

In the work on high purity beryllium, a major achievement was the preparation of a massive beryllium crystal having the highest purity attained to date in these studies. In achieving this goal, double distilled beryllium was subjected to six zone-refining passes. A resistance ratio $R_{298}/R_{4.2} = 3300$ and mass spectrographic analysis both indicate a very low level of metallic impurities. The total impurity content is believed to be <100 weight ppm. The deformation behavior of this material has been evaluated in basal flow, prism flow, and in "c" axis compression tests. In prior studies at lower purity levels, improvements in flow and fracture behavior included increased basal glide capacity, elimination of fracture in single prism slip, and increased resistance to basal cleavage. No new significant changes in deformation behavior have been seen in the six-pass double distilled material. New significant changes still sought include elimination of basal cleavage and activation of deformation modes permitting "c" axis contraction.

Work has also been carried out on the effect of alloy additions on the properties of beryllium single crystals. Beneficial solid solution strengthening had previously been observed in zone-refined beryllium realloyed with about 1000 weight ppm iron. In the recent studies, the addition of 1 w/o nickel has resulted in similar benefits. In both of these alloys, it is significant that plastic anisotropy, $\frac{CRSS(10\bar{1}0)}{CRSS(0001)}$, is reduced to the level of 5/1 of commercial purity from the undesirably high range, 30-40, seen in purified material. The improvement in anisotropy ratio is realized while retaining the other benefits from purification.

Combinations of impurities such as iron + silicon and iron + silicon + aluminum are believed to impair ductility by precipitate formation. Zone-refined crystals realloyed with these combinations have been evaluated for basal glide behavior. Metallographic observation of fracture surfaces and studies of response to heat treatment both suggest that these impurities interact to form precipitates harmful to ductility.

Zone-refining has reduced the metallic impurities to low levels of the order of 1 weight ppm without altering a basic anomaly in deformation behavior, namely, that beryllium with its low c/a ratio should exhibit easy prismatic glide. The interstitial level of zone-refined material has been difficult to define but appears to be in the 10 weight ppm range for carbon and oxygen and 1 weight ppm for nitrogen. The presence of

interstitials, as with other h.c.p. metals, could influence the competition between glide systems. Attempts are currently being made to assess prismatic glide in zone-refined crystals to which "scavenging" additions (Ti and Th) are being made to lower the interstitial level.

SLIS Alloys of Uranium and Zirconium

The term SLIS is applied to alloys in which a dispersion of very small particles of a metallic phase is achieved by splat cooling the liquid alloy. The particles must have a negligibly small solid solubility in the base material to insure that they remain stable in size during subsequent exposure at elevated temperature. Alloys of uranium with small additions of carbon, beryllium, or aluminum and silicon were prepared by splat cooling and then consolidation by extrusion. In each case the product contained particles smaller than 0.1 micron in diameter at concentrations up to 10^{13} per cubic centimeter. The alloy containing 0.4 weight percent beryllium showed the best particle stability and tensile strength at various temperatures up to 600°C. This material appears to be worthy of further evaluation in a reactor to determine its behavior during irradiation to high burnups.

Two SLIS alloys of zirconium were prepared using beryllium as the added element to form fine particles of Be_2Zr . The particles were about 0.1 micron in diameter and were present in concentrations of about 10^{13} per cubic centimeter. One of the alloys contained 0.8 weight percent beryllium in commercial grade zirconium, and the other had 0.68 percent beryllium in Zircaloy-2. The ultimate strengths at room temperature were 122,000 psi and 134,000 psi, respectively, while at 600°C they were respectively two and three times as strong as Zircaloy-2. Preliminary tests showed that corrosion resistance in 650°F water was reasonably good. Further investigation of SLIS alloys of zirconium must be carried out to determine if they will lead to the higher strength alloy which is needed for many reactor applications.

OAK RIDGE NATIONAL LABORATORY

Our part of the Fuels and Materials Program comprises several studies in varied aspects of this area. The program on Zirconium Metallurgy includes fundamental studies that should lead to improved alloys in the future as well as investigation of physical and mechanical properties of existing alloys to improve their usefulness. In Radiation Effects on Structural Metals and Alloys, we are studying theoretically and experimentally the changes in structure that take place on irradiation. In our research on Mechanical Properties, we are also considering radiation effects on structural alloys, and we are devising methods of improving stability to radiation. Solid Reaction Studies emphasize the measurement of diffusion behavior in metals of both practical and theoretical importance. An active program in Nondestructive Test Development studies penetrating radiation, eddy currents, ultrasonics, and other physical phenomena and their application to the testing of reactor materials and components. The Fuel Element Development program emphasizes the use of novel simplified techniques for the fabrication of advanced fuels and other materials. The High-Temperature Materials Program provides new knowledge on the physical and mechanical properties, fabrication, and resistance to environmental conditions of fuels, coolants, and structural materials for the high-temperature reactors that are needed for space programs. In Tungsten Metallurgy, we are seeking ways to improve the usefulness of this high-temperature metal, with emphasis on fabrication by thermochemical deposition. Materials Compatibility Studies concern the interactions between the alkali-metal coolants for high-temperature reactors and the refractory container metals. In the Behavior of High-Temperature Materials Under Irradiation, we study the effects of large neutron doses on ceramic oxides and carbides.

Stress Oriented Precipitation of Hydrides in Zircaloy-2

Hydrogen pickup during corrosion of zirconium alloys in water and steam deters their use as reactor materials, since even modest concentrations of hydrogen can allow precipitation of hydride in alloys cooled from the operating temperature. The decrease in ductility in Zircaloy-2 of low hydrogen content varies from zero when the stress axis is parallel to the hydride platelets to a maximum when the stress axis is perpendicular.

Specimens of Zircaloy-2 having a variety of preferred orientations and hydrogen levels of about 50, 100, and 150 ppm were stressed to 11,000 and 20,000 psi at 400°C, cooled under stress, and studied by a new technique. A three-surface metallographic analysis of the hydride trace angles relative to selected reference directions, a count of the number of hydride particles per square centimeter of surface area, and a determination of the volume fraction of hydrides present permitted construction of "hydride pole figures," which show the concentration of hydride platelet poles on a conventional pole-figure plot. The principal conclusions reached were:

- (1) The preferred orientation of the matrix has little, if any, influence on the orientation of hydride platelets in annealed as-received sheet material; the hydride texture is quite similar to that of slag inclusions in rolled steels.
- (2) The hydride platelets precipitated after plastic deformation tend to align themselves parallel to the tensile strain component and perpendicular to the compressive strain component.
- (3) The number of hydride platelets was independent of the hydrogen concentration in some areas of the hydride pole figures but strongly dependent in other areas. Apparently, preferred sites for precipitation fill up at low hydrogen levels, and higher hydrogen contents force the occupation of less favorable sites.
- (4) An elastic stress in annealed material orients hydride precipitates only when the stress axis is perpendicular to a high concentration of basal planes.
- (5) Increasing the hydrogen content increases the number but decreases the proportion of stress-oriented platelets.
- (6) The stress orientation of hydride platelets increases as the elastic stress increases.
- (7) The average hydride particle size was essentially independent of both the hydrogen content and the stress level under the conditions of testing.
- (8) Stress orientation of precipitated hydride can be controlled by selection of the preferred orientation of the matrix relative to the applied stress directions so that the hydrides are innocuous. For example, if the basal poles of the matrix are concentrated in the radial direction of tubing, hoop tension will not cause the hydrides to be unfavorably oriented to the stress axis.

Determination of the (0001) Pole Figures in Zircaloy-2 by Quantitative Metallography

The same three-surface metallographic analysis used in the determination of the hydride pole figures can be used to determine the (0001) pole figure of Zircaloy-2 by the use of a polarized-light metallurgical microscope equipped with a sensitive tint plate. To determine the trace angle of the basal plane relative to the fabrication directions, we rotate the stage of the microscope clockwise and observe the stage angle at the visual purple point as the color of the grain changes from red to blue. These angles for many grains of the matrix are converted to a pole figure by the approximation method used for construction of inverse pole figures from x-ray data. The microtexture of a small volume of a specimen can be readily determined in 1 to 2 hr, compared

to several days by conventional techniques. Now one can determine the variations of texture from the center to the surface of tubing having walls as thin as 0.020 in.

Anisotropy in Zircaloy-2

Prior work has shown that the mechanical properties of textured Zircaloy-2 are highly anisotropic. Yield strengths in tension are nominally 50,000 psi at room temperature for uniaxial stress along a concentration of prism poles and 70,000 psi along a concentration of basal poles; in compression they are 60,000 and 122,000 psi for the same respective directions. No presently available theory of stress analysis or of anisotropy of mechanical properties can treat the behavior of such a highly anisotropic material in biaxial stress. We believe that the maximum allowable design stress of Zircaloy-2 tubing can be appreciably increased by controlling the texture during fabrication and then taking maximum advantage of the yield anisotropy in the application of the material to structures.

Although the octahedral shear stress theory is derived for isotropic materials, we have tried to apply its results, despite the anisotropy of uniaxial yield strengths observed in Zircaloy-2. We calculated the shapes of the yield ellipses that might be produced in biaxial stress for highly textured Zircaloy-2 of several types of texture relative to the tube axes. The results were used to predict the behavior for several commonly found biaxial stress conditions. The predicted behavior fits extremely well with reported experimental and service failure results.

One case is formation of a bulge or blister in the wall of fuel element tube under internal pressure from either gas or growth of fuel. Before the bulge forms, the circumferential stress (hoop tension) in the wall of the tube is twice the axial stress. In the bulge, the stress condition approaches that of an internally pressurized spherical pressure vessel (balanced biaxial stress). If the basal poles are concentrated tangentially (as is typical of most commercial Zircaloy-2 tubing), the yield stress in the bulge is considerably less than that in the wall and the formation of the bulge is catastrophic, once yielding has begun. However, if the basal poles are concentrated radially, the stress required for yielding in the bulge is much higher than that of the wall away from the bulge, and the formation of the bulge is resisted. Thus, formation of a bulge or blister is favored or resisted depending on the texture, simply due to the biaxial stress conditions and the very strong anisotropy of yielding of highly textured Zircaloy-2.

Also, we can predict that the biaxial yield strength of controlled-texture Zircaloy-2 will increase over that of uniaxial tension at least 50% in the wall of an internally pressurized tube and 100% in the wall of a spherical pressure vessel.

Zone-Refined and Single-Crystal Zirconium

Our technique and equipment for purifying and growing single crystals of zirconium and its alloys have been modified to handle large specimens. Bars as large as 5/8 in. in diameter are routinely zone refined over lengths of 5 to 8 in. As many as ten successive passes of the molten zone have been made without serious distortion of the bar shape. Most of the zone-refined bars are either single or bicrystals of the alpha phase. Seeding with selected alpha-phase single crystals has been demonstrated.

Radiation Effects on the Precipitation of Nitrides in Alpha Iron

We are seeking information concerning the basic causes of the hardening and embrittlement of metals and alloys upon irradiation, chiefly iron and steel and the refractory metals. These are body-centered cubic metals that exhibit low-temperature brittleness. Also, we are studying the effect of radiation on metallurgical reactions, particularly precipitation, since the mechanical properties of alloys are quite sensitive to the state of aggregation of solutes and impurities.

The state of nitrogen in steel has an important bearing on mechanical properties. For example, the creep resistance of steels may be related to the amount of nitrogen in solid solution. To observe changes in the amount of nitrogen in solution in alpha iron during irradiation, we have developed an in-reactor internal friction apparatus. Using it, we have shown that reactor irradiation at low temperatures increases the rate of nitrogen removal upon subsequent heating, possibly due to radiation-enhanced precipitation. The enhancement saturates at quite low radiation doses. Under similar conditions, electron irradiations produce no enhancement. One explanation is that large damage clusters, produced by neutron irradiation but not by electron irradiation, nucleate the precipitation of nitrogen.

Irradiation Effects on Mechanical Properties of Stainless Steels

We are continuing our study of radiation damage to the mechanical properties of fuel cladding materials, particularly austenitic stainless steels. Ductility of these materials is reduced by fast neutrons at 200°C and by thermal neutrons above 500°C.

During the past year we have been concerned with producing metallurgical structures in these steels that should reduce the radiation damage in both temperature ranges. We have found that 5 to 15% cold work and annealing successively at temperatures of 500 and 700°C prior to irradiation prevents the loss of ductility in type 304 stainless steel at 200°C for fast neutron doses up to 7×10^{20} neutrons/cm². The high-temperature ductility problem may be solved by heat treatments and slight compositional modifications that reduce the grain size and concentrate certain impurities at the grain boundaries.

Tracer Diffusion in Body-Centered Cubic Metals

We had previously found that diffusion of ^{95}Zr and ^{95}Nb in beta-zirconium and ^{44}Ti and ^{48}V in beta-titanium do not follow the usual Arrhenius-type relations. Thus, indiscriminate extrapolations of data beyond the temperature range of measurement can cause incorrect conclusions regarding diffusion-controlled reactions in these materials. Aided by a new sensitive sectioning technique, we have now investigated diffusion rates of ^{95}Nb and ^{182}Ta in both mono- and polycrystalline niobium and tantalum. The results, which cover much wider temperature ranges than were previously possible, demonstrate conclusively that volume diffusion in each of these systems can be described by an Arrhenius-type expression $D = D_0 \exp(-Q/RT)$ with D_0 and Q constant. Positive deviations from such expressions at the lower temperatures are explained by short-circuiting diffusion paths, loss of resolution of experimental techniques, or both.

Redistribution of Elements in a Temperature Gradient

Nuclear fuel and cladding materials are subjected to large temperature gradients while at temperatures approaching their melting points. Under these conditions, redistribution of certain elements can result in drastic changes in mechanical, physical, and chemical properties. An understanding of the mechanisms and magnitudes of such redistributions can lead to design criteria that accommodate the effect.

We studied the redistribution of ^{124}Sb in silver under a thermal gradient of about $200^\circ\text{C}/\text{cm}$. The antimony tracer preferentially migrated to the hot portions of the specimens. At steady state, the logarithm of the antimony concentration was linear in the inverse absolute temperature. For a temperature difference of about 40° (890 to 850°C) the concentration at the hot side was about 30% greater than that at the cold side. The particular elements studied (antimony in silver) were chosen because there were enough related data available that the results of this experiment could be interpreted.

Effect of Alpha-Bombardment on the Diffusion of ^{212}Pb in Silver

We made the first successful direct measurement of the effect of fast-particle bombardment on diffusion in solids. Using the Hevesy-Seith alpha-recoil method, we measured diffusion rates of ^{212}Pb in silver over the temperature range of 360 to 480°C , both with and without a flux of 2.2 Mev alpha particles from a partially shielded ^{210}Po source. The normal diffusion coefficient could be described by an Arrhenius-type expression, $D = 600 \exp(-61,700/RT)$ cm^2/sec . The increase in diffusion coefficient caused by an alpha flux of 10^{11} particles $\text{cm}^{-2} \text{sec}^{-1}$ was approximately constant at 6 to 7×10^{-18} cm^2/sec . We extended the theory of radiation-enhanced diffusion to include annihilation of point defects at a free surface and found that its predictions agreed well with experimental results. This study should materially aid interpretation of all kinds of experiments in which atom migration (recovery of damage, creep, migration of fission products) occurs during irradiation.

Nondestructive Determination of Fuel Assay

Determination of the fuel content of fabricated fuel plates is difficult without destruction of the plate for chemical analysis. Plates that contain enriched uranium may be assayed by measurement of the gamma radiation from ^{235}U , but the intensity is so low that the method is slow and inaccurate. Recently we have found that rapid and accurate fuel assays can be obtained by an extension of our system for nondestructively measuring inhomogeneity in fuel plates. In this system, variations in fuel concentration are inferred from the attenuation of a collimated x-ray beam as the plate traverses the beam. By calibrating the beam with chemical analyses of scanned plates and developing a method for integrating the point concentrations, we have now extended the method to obtain total uranium concentrations in the plates. Typical plates are scanned in about 8 min and the total fuel contents found have been accurate to 1%.

Vibrating Eddy-Current Probe

Eddy-current testing is an excellent method for the rapid determination of very small discontinuities in items such as tubing. This is because the use of mechanical systems for moving the tube through or past the eddy-current coil allows electronic discrimination and amplification of the quickly changing signals due to flaws without response to the slower changes due to insignificant variations. However, the more common manual probe systems cannot make this discrimination and thus have low sensitivity to defects and suffer from interpretation difficulties. We have developed a tenfold more sensitive manual eddy-current probe that vibrates rapidly. Thus, its motion past a small defect produces a quickly changing signal, allowing discrimination and amplification previously possible only with automated mechanical systems.

The eddy-current probe is mounted between two electromagnets. Switching current from one coil to the other pulls the spring-loaded probe back and forth to vibrate it. The signals from the probe are fed to an electronic filter, which is tuned to pass only the high-frequency signals from defects.

Radiography of Highly Radioactive Materials

Techniques have been developed that permit radiographic inspections to be performed in the presence of a high x- or gamma-radiation background. By chemically defogging the film, we achieved satisfactory images on films that had received 16 r of constant potential x rays ranging from 50 to 300 kv or 380 r of 1-Mev gamma radiation. This capability enables us to remotely inspect irradiated fuel elements, encapsulated radioisotope sources, and fabricated fuel elements containing aged ^{233}U .

Development of Fuel Elements by Thermochemical Deposition

In a continuing program, we are preparing reactor fuels and other high-temperature materials by thermochemical deposition from reacting vapors. Although the ultimate goal of producing complete fuel elements from vapors has not been achieved, several improved materials and fabricated pieces have emerged from this program. The more recent accomplishments include the one-step production of uranium dioxide in several forms from uranium hexafluoride and the production of tungsten-rhenium alloy tubing from the hexafluorides of these metals.

We have deposited bulk UO_2 , in tubular form, directly from UF_6 by reaction with hydrogen and oxygen in the neighborhood of 1200°C and 5 torr. Deposition efficiency is very high and the deposits have uniform thicknesses, residual fluorine contents less than 10 ppm, densities equal to theoretical, and any oxygen-to-uranium ratios in the range from 2.004 to 2.156. With slight changes in deposition conditions, we can also produce coarse dendritic UO_2 crystals or very fine (60 to 200 Å) active UO_2 powders.

For potential use as cladding material, high-quality tungsten tubing has been routinely deposited from its fluoride; industry is now adopting this process for commercial use. Development work has been extended to produce the extremely difficult-to-fabricate tungsten-rhenium alloys. The feasibility of depositing such alloys directly in tubular form by thermochemical deposition has been demonstrated, but problems still exist in obtaining deposits that are large, homogeneous, and uniformly thick. Alloying occurs at the very low deposition temperatures used (450 to 700°C), and we have identified a phase of the beta-tungsten type, which was not previously known to exist in this system.

Advanced Aluminum-Base Dispersion Fuel Elements

We have developed fabrication procedures for aluminum dispersion fuel elements that should be capable of extending the present temperature and burnup limitations on advanced research reactors. For irradiation testing, we fabricated miniature plates in which the fuel was present as niobium-coated spherical UO_2 particles, and neither the fuel nor coating was degraded during fabrication. This type fuel should resist the usual reactions with aluminum and should also more efficiently contain the fission product gases, which promote blistering.

Fabrication and High-Temperature Properties of Refractory Metals and Alloys

Requisite to the construction of high-temperature compact nuclear reactors for propulsive or auxiliary power in various space missions is a fabrication technology for refractory-metal tubing. The practicability of two novel approaches for producing tube shells, from which high-quality tubing can be subsequently wrought, has been demonstrated

during the past year. One scheme, unique to tungsten and molybdenum systems, capitalizes on the fact that these metals generate volatile oxides when exposed to air at high temperatures. This characteristic has led us to rely on the oxide alone to lubricate the bare billets during extrusion into tube shells. This process achieves superior surfaces with extrusion pressures less than in the more conventional schemes that use lubrication with glass. The second scheme of tube-shell production is amenable to the more ductile niobium and tantalum alloys. We have demonstrated with alloys based on both metals that as-cast billets can be flow turned into tube shells at room temperature. In this process, the material is reduced in thickness by a shearing action, causing it to flow uniformly along a fixed mandrel. Flow turning offers advantages of high material yields, simplified fabrication schemes, and minimal contamination by interstitial elements.

Using our knowledge of phase equilibria and physical metallurgy, we have found two attractive brazing alloy systems for very high-temperature service. Alloys from the Ta-Ti-V and Nb-Ta-V systems melt in the temperature range 1650 to 2000°C to form joints that remelt at temperatures several hundred degrees higher, apparently because titanium and vanadium vaporize during brazing. Unlike many brazing alloys, compositions from these two systems have excellent ductility at room temperature; in fact, they can be rolled into thin sheet. These materials have been used to braze alloys of Nb, Ta, W, and Mo with no instance of significant base metal dissolution.

High vacuum creep tests of Nb-1% Zr, D-43, FS-85, T-111, TZM, and B-66 have established the 1000-hr rupture life and attendant creep properties of these alloys over the temperature range from 980 to 1205°C. We have also demonstrated that appropriate pretest annealing can increase the creep strength of Nb-1% Zr and FS-85 nearly tenfold.

We have systematically studied the factors affecting the contamination of refractory alloys by the residual gases in high vacuums. In spite of the extensive use of high vacuum technology, little such information was available at the outset of this work. We devised several potential solutions to the contamination problem; among the more novel are vapor plating with molybdenum and use of low-pressure additions of methane to the residual atmosphere to minimize oxygen uptake. These could reduce the costs associated with ultrahigh vacuum testing.

In our continuing study of the compatibility of boiling potassium with refractory metals we have demonstrated that certain niobium alloys are amazingly inert to boiling potassium. The conclusion is supported by tests in which mass transfer or penetrating attack was imperceptible in refluxing capsules to 5000 hr at 1200°C, natural-circulation loops to 3000 hr at 1200°C, and forced-circulation loops to 3000 hr at 1100°C.

Improvement of Ductility of Tungsten

One of the principal deterrents to the use of tungsten and its alloys in engineering systems is its lack of ductility at low temperatures. To gain some insight into the deformation mechanisms involved

in this ductility problem, we have successfully employed transmission electron microscopy. Using our observations, we have developed a model based on the inability of grain boundaries, hardened by interstitial elements, to act as dislocation sources and foster plastic flow. The model predicts that particles dispersed within the tungsten grains can provide mobile dislocations if the material is subjected to hydrostatic compression prior to tensile loading. To confirm this hypothesis, we hydrostatically compressed sheet specimens and found that ductile-to-brittle bend transition temperatures were reduced by 25 to 50°C. Further experimental confirmation was obtained by annealing specimens at various temperatures from 1150 to 2500°C, and measuring the ductile-to-brittle transition temperatures. Our model predicted that, when the annealing temperature was sufficiently high to dissolve the interstitials that harden the grain boundaries, ductility should be improved. Indeed, increasing the annealing temperature from 1800 to 2500°C decreased the bend-transition temperature from 420 to 255°C. Although in no case has tungsten with room-temperature ductility been produced, a useful model has been devised that indicates several promising avenues of pursuit. This should lead to significantly more systematic and efficient development of tungsten alloys with improved ductility.

Fabrication of Tungsten by Thermochemical Deposition

Production of tungsten by the hydrogen reduction of WF_6 offers the advantages of simplified one-step fabrication at low temperatures (approx 600°C) and ability to generate complex shapes. We have developed procedures to produce leak-tight theoretically dense tungsten tubing varying from 0.040-in. OD by 0.0015-in. wall to 1.50-in. OD by 0.055-in. wall with less than 20 ppm C, 10 ppm O, and 5 ppm N. By similar techniques, we have also prepared sheet tungsten, coated cermet fuel bodies, produced diffusion barriers on the inside surfaces of tubing, and butt welded wrought tungsten sheet without inducing base-metal recrystallization. The demonstrated versatility of the process foretells growing use for numerous applications.

Behavior of Oxygen in Molten Potassium

A recurrent problem in testing the compatibility of molten potassium with various container alloys has been the inability to accurately measure the oxygen content of the potassium. The universally employed approach has been to adopt for potassium those methods already developed for assaying oxygen in sodium. Typically, this involves either amalgamation or vacuum distillation to remove the alkali metal from an oxide residue. Our studies have conclusively demonstrated that, although they are precise, neither of these methods is accurate for potassium. The recovery of oxygen from intentionally doped samples has varied randomly from 12 to 100%. Consequently, we have developed a method of analysis, called the gettering-vacuum fusion technique, based on the fact that oxygen will partition between zirconium and potassium in a known and reproducible fashion. Thus, the oxygen content of a potassium bath can be deduced by measuring the uptake of oxygen in a

zirconium foil after exposure to potassium. This analysis, which involves conventional platinum-bath vacuum fusion of the zirconium foil, has a demonstrated accuracy of $\pm 10\%$.

We have suspected for some time that the explanation of both this analytical problem and some thermodynamically-anomalous observations on the partitioning of oxygen between potassium and refractory metals must involve complex oxides. Such speculations have been recently confirmed with the positive identification of potassium metaniobate (KNbO_3) as a corrosion product in compatibility tests on the potassium-oxygen-niobium system. Having now established a sound analytical tool and gained important proof of the existence of complexes, studies of the corrosion mechanisms in systems involving alkali metals, refractory metals, and oxygen should proceed with greater celerity.

Irradiation of Refractory Compounds

We are determining the effect of large neutron doses, 10^{21} to 10^{22} neutrons/cm² (> 1 Mev), at 100 to 1500°C on the physical properties of pure high-temperature materials that have possible application as fuel matrices, moderators, or components of thermionic devices. A series of experiments to determine the fast-neutron damage to BeO compacts has been completed. A similar series of experiments with MgO is in progress, and studies of the radiation stability of refractory-metal carbides (Ti, Zr, Nb, Ta, and W) and other refractory oxides (Al_2O_3 and Y_2O_3) have been initiated.

Sintered BeO was exposed to fast-neutron doses up to 8×10^{21} neutrons/cm² at 110, 650, and 1100°C. The results are generally consistent with the hypothesis that grain-boundary separation, the primary mode of damage to BeO compacts at all three temperatures, is caused by anisotropic crystal expansion, which results from the production and agglomeration of point defects in the crystal lattice. At 1100°C, a temperature at which in-reactor annealing substantially reduces crystal expansion, the data indicate that grain boundary separation is promoted by thermal cycling. To minimize damage in nuclear reactor operation, BeO of small grain size and low density should be used, the temperature should be as high as practicable, and thermal cycling should be avoided.

Damage to MgO compacts and BeO compacts apparently occurs through different mechanisms. Gross damage to BeO increases with increasing fast-neutron dose and decreases with increasing temperature. Gross damage to MgO occurs randomly to samples exposed to doses exceeding 0.7×10^{21} neutrons/cm² (> 1 Mev), but increases with increasing temperature, at least above 800°C. The expansion of MgO compacts irradiated at 150°C increased with dose up to 1.1×10^{21} neutrons/cm², then leveled off at 1%. Samples irradiated at 800°C expanded very little.

The isotropic structure of the MgO crystal precludes the breaking of grain boundaries by anisotropic expansion, which accounted for fracturing and powdering of BeO. Magnesium oxide fractures transgranularly; at low temperatures, this probably results from random crack propagation through crystals weakened by irradiation. Radiation damage to MgO is largely annealed at high temperatures, as judged from the very small expansion at 800°C. Consequently, gross damage observed at high temperatures, which increases with increasing temperature, must be caused principally by thermal stress.

PRATT & WHITNEY AIRCRAFT
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Introduction

Materials research at CANEL was directed towards advanced space nuclear powerplant applications. The major work categories were: structural alloys, fuels, coolants and working fluids, and fabrication. The structural alloy task was chiefly concerned with the development of high strength columbium-zirconium-carbon alloys and light weight structural alloys for alkali metal service. High temperature properties of refractory ceramic fuels were studied under the fuels task. Fabrication studies were also conducted under this task. The principal objective of the fuels work was to improve high temperature irradiation performance with minimum sacrifice of reactor weight and volume. Work on space powerplant coolants and working fluids was mainly devoted to solubility studies, properties determinations, and thermal compatibility evaluation. The fabrication task was confined to an investigation of joining and compatibility problems in connection with space radiator design concepts. The work was conducted under AEC contract AT(30-1)-2789 for the Fuels and Materials Development Branch, Division of Reactor Development and Technology. The abstracts below cover only the unclassified part of the program.

I Fuels Research and Development

- A. A finely dispersed precipitate in UN was identified as UO_2 by electron microscopy and diffraction studies. The particle density was in the order of 10^{13} to 10^{15} particles/cm³.

Analysis of the fuel showed 1000-2000 ppm oxygen. This fine dispersion was stable for long periods (3000 hours) at elevated temperatures. Coalescence occurred under irradiation at this temperature, however, and the particle density was reduced to about 10^{12} particles/cm³. It was postulated that this dispersed phase in UN slows down the migration of fission gas to the grain boundaries, thus minimizing fuel swelling and gas release at a given burn-up level. This is consistent with experimental data reported by Kramer, et. al. in this country and Bellamy and Greenwood in England. UC, with a higher swelling rate with burn-up, did not show a dispersed phase.

- B. The heat of sublimation of elemental uranium was 125 kcal/mole as determined by thermodynamic Langmuir UC analysis of vapor pressure data. The generally accepted value is 117 kcal/mole. The vapor pressures of N_2 and uranium over $UN_{(s)}$ were defined through Knudsen experiments in the temperature range 1910K to 2265K by the equations

$$\log_{10} P_U = 6.32 - 2.53 \times 10^4 T^{-1}$$

$$\log_{10} P_{N_2} = 8.49 - 2.92 \times 10^4 T^{-1}$$

The standard heat of formation at 298K was -74.5 kcal/mole by Third Law analysis of the vapor pressure data.

- C. The thermal conductivity of stoichiometric UC varied from .223 watts/cm°C at 1015°C to .184 watts/cm°C at 1550°C. Above 1400°C the thermal conduction was predominately by an electronic mechanism. Contamination with 2600 ppm oxygen and 1400 ppm nitrogen lowered the thermal conductivity 20% at 1100°C. A negative deviation, corresponding to only 10% for 80% dense UC, was found in the simple conductivity-porosity relationship.
- D. The thermal conductivity of UN was significantly higher than UC, ranging from .272 watts/cm°C at 1000°C to .286 watts/cm°C at 1375°C. The electronic contribution to thermal conduction does not appear to be large.
- E. The effect of temperature on the compressive creep rates of UC and UN between 1100°C and 1300°C at 6000 psi were as follows:

<u>Composition</u>	<u>Creep Rate $\ln/\ln/Hr$</u>
UC (4.85% C)	$210 \ell \frac{-22,000}{T}$
UC (4.80% C)	$23,000 \ell \frac{-26,000}{T}$
UN	$242 \times 10^7 \ell \frac{-45,000}{T}$

II Structural Alloy Development

- A. The columbium rich corner of the Cb-Zr-C system showed three phases at room temperature: beta (bcc, columbium-zirconium) solid solution; delta (hcp), Cb_2C with as much as 3% zirconium

in solution; and gamma (fcc), a continuous series of solid solutions between ZrC and CbC. These phases were structurally analogous to those in the respective binary systems. No new ternary phase were observed.

- B. The 1538C (2800F) isotherm of this corner of the phase diagram was characterized by: 1) a beta plus delta two phase field, 2) a beta plus gamma two phase field, and 3) a beta plus delta plus gamma three phase region, which lies between the two phase fields. The columbium rich corner of the three phase was located at about 1.25 weight percent zirconium and less than 400 ppm carbon.
- C. Two models were proposed for the strengthening of alloys in this region: (1) warm worked unrecrystallized material derived its strength from dislocation tangles in a subcell network, approximately one micron square, pinned by fine carbides; and (2) solution heat treated material was strengthened through the precipitation of fine carbide particles along the grain boundaries.

III Space Powerplant Coolants and Working Fluids

- A. The apparent solubility of molybdenum in potassium with 500 ppm oxygen exhibited an Arrhenius-type temperature dependence in the range of 260C to 600C. This relationship is expressed by the following equation:

$$\log_{10} S \begin{matrix} \text{(atom fraction)} \\ \text{of Mo} \end{matrix} = -0.126 - \frac{3270}{T(^{\circ}\text{K})}$$

At temperatures between 600C and 1200C, the apparent solubility of molybdenum was a function of oxygen concentration in the potassium and was independent of temperature. A molybdenum to oxygen atom ratio of one to four found in the potassium samples was in excellent agreement with the separated

reaction product identified as K_2MoO_4 . The solubility of columbium in lithium showed a slight temperature dependence over the range of 760C to 1540C but was independent of oxygen and nitrogen additions. The following equation was derived from averaged data:

$$\log_{10} S \begin{matrix} \text{(atom fraction)} \\ \text{of Cb} \end{matrix} = -4.777 - \frac{1094}{T(^{\circ}K)}$$

- B. The Cb-1 Zr alloy showed negligible weight changes and no noticeable deposits in two 3000 hour natural convection boiling potassium loop tests at 1070°C maximum. The mechanical strength of test specimen inserts of FWC-533 alloy (Cb-5 Mo-3 Zr-3 Ti-0.1 C) in one loop and a modified Cb-Zr alloy in the other was not affected.
- C. A FWC-533 alloy monometallic natural convection boiling potassium loop was not essentially affected by test operation at 1095°C for 3000 hours.

IV Space Radiator Fabrication Development

- A. Beryllium reactions with the following metals at 650°C and 760°C in 800 hours varied from moderate to severe: Cu, Ni, Pd, Pt, Co, Cr, Fe, and Zr. Under the same conditions, reactions were only slight with Ag, Cb, Mo, Ti, V, and W.
- B. Other radiator material combinations, excluding beryllium, were compatible at temperatures to 760°C and times to 800 hours.
- C. Silver brazing was generally unsatisfactory for joining beryllium to stainless steel and columbium alloys.
- D. Brittle phase formation between beryllium and stainless steel was suppressed by diffusion bonding with silver.
- E. Several silver base alloys showed promise for joining of beryllium to other space radiator materials by diffusion bonding.

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The over-all objective of the research was the preliminary development of high-hot-strength dispersion-hardened Fe-Al-Cr base alloys possessing moderate neutron-capture cross-sections and exceptional oxidation resistance for use in the fabrication of core components for gas-cooled reactors. The 1964 program had as its most important goal the correlation of alloy preparation techniques and the resulting dispersion morphologies with high temperature mechanical properties and corrosion resistance to provide data on which to base the design of improved alloys. The materials were made by hot-extruding compacts of surface-oxidized master-alloy powders; finished alloys contained 5 to 10 vol. % oxide in matrices consisting of 7 to 10 wt. % Al and 5 wt. % Cr in Fe. Ideally, the oxide was to be in the form of sub-micron size particles. Among the more significant results of the study were the following:

Microstructure and Mechanical Properties. The size and shape of the second-phase particles were found to be greatly affected by the duration and temperature of the pre-extrusion heating given the compacts. Overlong heating or excessive temperature causes the oxide to coalesce into quasi-spherical particles as large as 2 microns in size. Whereas alloys containing finely divided second phase particles exhibited stress-rupture properties at 870°C. superior to those of Type 316 stainless steel, those bearing coarse dispersions were no better than the oxide-free control alloy. The optimum pre-extrusion heat treatment has been tentatively established as consisting of a seven-hour soak at 1100°C.

Oxidation Resistance. While the presence of a finely-divided alumina second phase was observed to have no measureable effect on the inherent oxidation resistance of Fe-Al-Cr alloys, a coarse dispersion apparently causes heavy localized pitting of specimens tested in air at 870°C.

UNITED NUCLEAR CORPORATION
DEVELOPMENT DIVISION
WHITE PLAINS, N.Y.

CARBIDE FUEL DEVELOPMENT (Contract AT(30-1)-2899)

Introduction

The Carbide Fuel Development Program is concerned with the technology of the UC - PuC fuel cycle, particularly as it applies to fast breeder reactors. During 1964, the planned out of pile property measurements, irradiation tests, and the majority of the post irradiation examinations were completed.

Irradiation Tests

Very encouraging results have been obtained by irradiating $(U_{0.8}Pu_{0.2})C$ to burnups in the range of 10 to 37.6×10^{20} fissions/cm³, at 150 to 330 kw/kg U+Pu and 10 to 23 kw/ft. The microstructure is stable, diameter increase is 0.6% per atom per cent burnup, and fission gas release is less than for mixed oxides. The thermodynamic compatibility of fuel with niobium and stainless steel is excellent.

The good in-pile compatibility is consistent with previous out of pile compatibility results which showed that (UPu)C is compatible with Type 316 stainless steel, Nb, Nb-1Zr, and 2 $\frac{1}{4}$ Cr-1Mo steel.

The fuel was made by cold pressing and sintering, a process developed previously on this program.

The major problem encountered is the brittle fracture of stainless steel caused by the relatively small diametral expansion of the fuel. The embrittlement of the stainless steel is believed to be due to the thermal neutron induced transmutation of boron into helium and lithium. Numerous

ways to cope with this problem have been incorporated into future irradiation experiments of full length carbide rods: irradiation in the fast flux of EBR-II, use of a stainless steel with improved ductility, and provision for fuel expansion.

The post irradiation examination of four clad ($U_{0.8}Pu_{0.2}$)C specimens (Nos. 62T and B, 65T and B) irradiated to the 10.4 to 15.7×10^{20} fissions/cm³ level was completed. The examination of four similar specimens (Nos. 63T and B, 66T and B) irradiated to the 32.0 to 37.6×10^{20} fissions/cm³ level is nearly completed. Irradiation conditions and some of the post irradiation results are summarized in Table 1.

Out of Pile Properties

The vapor pressures of uranium and plutonium over ($U_{0.95}Pu_{0.05}$)C were measured by the Knudsen effusion technique:

°C	Uranium, atm.	Plutonium, atm.
1822	9×10^{-8}	$1 \text{ to } 2 \times 10^{-6}$
1995	3×10^{-6}	$1 \text{ to } 2 \times 10^{-5}$

The uranium vapor pressure over (UPu)C was similar to that of uranium over UC. The plutonium vaporized at a higher rate than the uranium. The difficulty in maintaining constant sample composition at high temperatures for relatively long times was recognized.

The melting (liquidus) temperature of ($U_{0.95}Pu_{0.05}$)C was determined to be $2535 \pm 20^\circ\text{C}$. The solidus temperature was estimated to be $2500 \pm 20^\circ\text{C}$.

Table 1-Summary of the Sintered Uranium-Plutonium Carbide Irradiations*

XXII.3

Specimen No.	Composition	Clad	Burnup, MWD/T	Fission Gas Release, %	Clad Diameter Increase, % %/a/o		Fuel Diame-ter Increase, % %/a/o		Fuel Density Decrease, % %/a/o	
UNC-61T ²¹	(U _{0.8} Pu _{0.2})C+ 0.1 Ni	Nb	21,700	0.37	None		1.5	0.6	2.5	1.0
61B	(U _{0.8} Pu _{0.2})C	Nb	24,200	0.25	None		1.4	0.5	4.3	2.4
UNC-62T ²¹	(U _{0.8} Pu _{0.2})C+ 0.1 Ni	Nb	31,300	1.45	None				1.7	0.4
62B	(U _{0.8} Pu _{0.2})C	Nb	35,100	0.94	None					
UNC-63T†	(U _{0.8} Pu _{0.2})C+ 0.1 Ni	Nb	112,700	47.3	3.2	0.3	7.2	0.6	14.9	1.2
63B†	(U _{0.8} Pu _{0.2})C	Nb	114,000	◁ (sam- ple er- ror)	1.9	0.2			13.6	1.1
UNC-64T ²¹	(U _{0.8} Pu _{0.2})C	316	23,400	0.75	None					
64B	(U _{0.8} Pu _{0.2})C+ 0.1 Ni	316	22,800	12.7	None outside of failure		1.6	0.6	3.8	1.4
UNC-65T ²¹	(U _{0.8} Pu _{0.2})C+ 0.1 Ni	316	37,700	Lost	3.4	0.8			5.0	1.1
65B	(U _{0.8} Pu _{0.2})C	316	49,300		3.4	0.6				
UNC 66T†	(U _{0.8} Pu _{0.2})C+ 0.1 Ni	316	101,000	51.3	6.0	0.6			18.3	1.7
66B†	(U _{0.8} Pu _{0.2})C	316	100,500		5.3	0.5			16.6	1.6

*All specimens had a hyperstoichiometric structure and were helium contact bonded.

†Preliminary.

Table 1-Summary of the Sintered Uranium-Plutonium Carbide Irradiations*- (Continued)

Specimen No.	Specimen Temperature, °C											Condition of Clad
	Power Generation				Heat Flux		Average		Maximum		Hours of Operation	
	kw/ft Avg.	kw/ft Max.	kg U+Pu Avg.	kg U+Pu Max.	w/cm ² Avg.	w/cm ² Max.	Clad Surface	Fuel Center	Clad Surface	Fuel Center		
UNC-61T ²¹	10.9	13.7	157	198	165	210	625	1030	795	1305	3267	Intact
61B	10.7	13.4	160	202	165	205	615	1015	770	1280	3267	Intact
UNC-62T ²¹	10.1	13.6	145	194	155	210	640	1005	755	1190	4879	Intact
62B	10.1	12.4	151	185	155	190	580	935	680	1090	4879	Intact
UNC-63T†	12.7	16.6	216	283	204	267	555	925	670	1120	9198	Intact
63B†	10.0	14.8	178	261	154	227	460	790	630	1115	9198	Intact
UNC-64T ²¹	11.6	14.4	172	214	180	220	655	1125	740	1315	2189	Intact
64B	12.1	15.5	173	222	185	240	690	1175	795	1415	2189	Localized failure
UNC-65T ²¹	14.4	23.2	206	330	220	355	445	1025	575	1270	3723	Longitudinal brittle cracks
65B	16.3	21.2	244	319	250	325	473	1090	560	1345	3723	
UNC-66T†	12.0	18.5	172	264	183	282	575	1030	830	1500	8729	
66B†	12.0	18.0	180	269	184	275	455	885	695	1305	8729	

*All specimens has a hyperstoichiometric structure and were helium contact bonded.

†Preliminary.

UNITED NUCLEAR CORPORATION
DEVELOPMENT DIVISION
WHITE PLAINS, N.Y.

STUDY OF URANIUM-PLUTONIUM MONOXIDES
(Contract AT(30-1)-3305)

Introduction

The goal of the plutonium monoxide and uranium-plutonium monoxide study is to find a fuel for water-cooled thermal reactors which has a heat generation capability better than, and a corrosion resistance equivalent to PuO_2 and $(\text{UPu})\text{O}_2$.

Carbothermic Reduction of Oxides

Mixtures of ~ 50 v/o $\text{Pu}(\text{OC}) + 50$ v/o $\beta \text{Pu}_2\text{O}_3$ have been produced by carbothermic reduction of PuO_2 or $\beta \text{Pu}_2\text{O}_3$. $\text{Pu}(\text{OC})$ with high oxygen to carbon ratios was produced. Single phase, carbon free Pu_2O_3 was produced successfully by this process.

Mixtures of up to 80 v/o $(\text{UPu})\text{OC} + 20$ v/o $(\text{UPu})\text{O}_{2-x}$ were produced by the carbothermic reduction of UO_2 and PuO_2 . The oxygen/carbon ratio in the monoxide phase is estimated to be 1/1. Both the monoxide phase and the hypo-stoichiometric dioxide phase are expected to have better thermal conductivity than stoichiometric dioxides.

Most recently, 90 v/o $(\text{UPu})\text{OC} + 10$ v/o $(\text{UPu})\text{O}_{2-x}$ was produced by a reaction which does not produce CO^x . The presence of CO tends to keep the reaction from completion.

Metal Reduction of Oxides

Preliminary experiments with the reaction of metal hydrides and oxides have not produced significant quantities of monoxide phase, indicating that the monoxides may be difficult to prepare without a stabilizing element such as carbon.

U. S. NAVAL RESEARCH LABORATORY
METALLURGY DIVISION
REACTOR MATERIALS BRANCH

Introduction - "Effects of Neutron Irradiation on the Properties
of Reactor Structural Materials"

The purpose of this research program is to evaluate the effects of nuclear radiation upon the properties of reactor structural materials. General objectives of this program are the development of knowledge of the specific effects of nuclear radiation to representative reactor structural materials, the understanding of mechanisms of radiation embrittlement of reactor steels in order to identify steels in terms of neutron sensitivity and to suggest the key factors for minimizing sensitivity, and the determination of the effects of nuclear environment in order that experimental data might be better applied to the operating reactor condition.

During calendar year 1964, research emphasis was placed upon:
(1) a comprehensive determination of changes in ductility of currently used reactor pressure vessel steels and preliminary evaluation of higher strength steels over a wide range of neutron exposure and irradiation temperature conditions, (2) a systematic comparison of steels exhibiting variations in radiation sensitivity in an effort to relate results in terms of composition and microstructural differences, (3) a continuation of the program to explore the effects of nuclear environment including: (a) operating reactor conditions based upon materials removed from nuclear service and long-term surveillance programs, (b) experimental programs utilizing light water, heavy water, organic, and graphite moderated reactors, and (4) the exploration of the effects of applied stress and cyclic-strain fatigue upon the properties of irradiated steels.

The NRL-High Level Radiation Laboratory

In August 1964, the Naval Research Laboratory's High Level Radiation Laboratory was activated. The laboratory complex features five high level radiation containment cells as well as low level radiation facilities which include a radiochemistry laboratory and a radioisotope counting facility. The radiation cells are equipped for metallography, various types of mechanical and physical testing, postirradiation annealing studies, and remote machine shop operations. The laboratory complex also includes facilities for decontamination, isotope storage, and liquid radioactive waste disposal. This laboratory is designed to provide efficient and versatile facilities for the evaluation of radioactive materials.

Variations in Radiation Embrittlement Sensitivity Among Steels

In the course of previous investigations on notch ductility behavior, variations in the irradiation response of steels were noted. More comprehensive studies encompassing a wide variety of steels have shown that variations in sensitivity are common. Whereas steel chemistry was initially suspected as the primary controlling factor, recent experimental evidence points increasingly to microstructure, reflecting cooling transformation characteristics and prior metallurgical heat treatment as a significant variable as well. For example, in a study of the effects of a fissionable alloying addition (uranium) on irradiation response, a uranium-free laboratory heat of A212-B steel serving as a "control" exhibited only two thirds the transition temperature increase of a reference commercial heat of the same nominal composition. Microstructural examinations of the two plate materials revealed a mixed martensite and fine pearlite structure for the laboratory heat and an equiaxed ferrite and fine pearlite structure for the commercial heat. Similarly, the evaluation of specimens from the Yankee reactor surveillance program indicated a wide difference in sensitivity between the pressure vessel steel and the ASTM A302-B reference steel. On the basis of composition, the two materials were quite similar. However, the tempered bainite microstructure of the former was considerably coarser than that of the latter.

In a very recent experiment, specimens of five heats of A302-B steel were irradiated simultaneously and showed a range of transition temperature increases from 120 to 205°F. These variations could be related to the nature of individual tempered bainite formations but not to plate chemistry.

Comparative evaluations of high strength steels and creep resistant steels also have shown a range of radiation sensitivity which generally falls within the limits established by the NRL trend band for Δ NDT with neutron exposure. Thus, the development of partially radiation resistant steels for reactor pressure vessel applications appear feasible once the most desirable combinations of chemistry and microstructure are determined.

Simulation of Periodic Reactor Pressure Vessel Annealing Operations for the Reduction of Neutron Irradiation Embrittlement

Earlier investigations of the effects of cyclic (240°F) irradiation and annealing on pressure vessel steels, indicated that a significant reduction in accrued embrittlement, as measured by notch ductility tests, could be obtained with some steels. Studies of cyclic irradiation and annealing have been extended with the simulation of periodic annealing of a reactor pressure vessel during service at elevated temperatures.

Consistent with earlier observations, the frequency and duration of annealing and the annealing temperature employed, coupled with the inherent annealing response of the steel, were found to dictate the degree of reduction in total embrittlement. To illustrate, frequent 24-hour, 600°F annealing of an A350-LF1 (Modified) steel during irradiation at 430°F (SM-1A reactor operating temperature) to 3.6×10^{19} n/cm² (>1 Mev) produced a 31 percent lower transition temperature increase than that developed by irradiation without annealing. An equivalent annealing treatment applied at half the frequency of the former, however, did not have a measurable effect (~9% reduction). If a higher annealing temperature is employed, however, the benefits of frequent annealing at lower temperatures are more than offset. For example, cyclic 550°F irradiation and 48-hour, 750°F annealing of A212-B and A302-B steels during exposure to 3.5×10^{19} n/cm² (>1 Mev) respectively achieved a 40 and 53 percent reduction of the expected embrittlement. On the other hand, one 48-hour, 800°F annealing treatment applied after an exposure of approximately 1.6×10^{19} n/cm² had an equivalent, if not more pronounced, effect than the more frequent 750° annealing. Thus, in spite of peculiarities related to the steel and to the annealing conditions, cyclic irradiation and annealing simulating periodic in-service annealing of a reactor pressure vessel has proven effective in reducing the magnitude of embrittlement normally developed by the radiation environment. With proper application, this method may be of great value in lessening the accrued embrittlement of steel components in nuclear service.

In-Reactor Studies of Low Cycle Fatigue Properties of Structural Steels for Nuclear Applications

An experimental irradiation assembly and associated instrumentation has been developed and successfully utilized for the performance of dynamic in-reactor low cycle fatigue tests of reactor pressure vessel steels and other structural materials. The equipment provides for the simultaneous reverse bend testing of as many as fifteen sheet type specimens representing a range of strain amplitudes at a controlled temperature between 300 and 700° F.

Exploratory investigations on the fatigue resistance of ASTM Type A302-B steel during irradiation at 500 and 550°F have not revealed a detrimental irradiation effect for neutron exposures up to 8×10^{18} n/cm² (>1 Mev). However, similar studies of the fatigue behavior of ASTM Type A212-B steel at 500°F gave some indication of an improvement in fatigue resistance at high cycles to failure.

The in-reactor fatigue test program is continuing and will include a number of different structural materials tested under more severe neutron exposure conditions.

Steel Embrittlement in a Simulated Reactor Pressure Vessel Wall

Data generated by accelerated irradiations performed in close proximity to the fuel of test reactors are commonly used for the prediction of the transition temperature increases of power reactor pressure vessels. Since the neutron spectra and dose rates are different in these separate situations, an experiment simulating a reactor vessel wall was performed to determine if a satisfactory correlation could be achieved. In this experiment, a large block of a typical pressure vessel steel containing Charpy V-notch impact specimens, was irradiated at the face of a pool reactor. The specimens, which were located at several depths in the steel block, served to measure the degree of in-depth embrittlement to the simulated vessel wall. The transition temperature increases of the specimens compared very favorably with accelerated experimental data when plotted against neutron exposure (>1 Mev). In both cases a seven-fold decrease in neutron flux was accompanied by a two-fold decrease in the transition temperature rise. Therefore, heavy walled pressure vessels are not subject to as large a lessening of embrittlement across the thickness as might be expected by self-shielding effects.

Comparative Effects of Different Nuclear Environments Upon the Mechanical Properties of Pressure Vessel Steels

Recent results have indicated that the rate of exposure to neutrons has no discernable effect upon the degradation of the ductility of pressure vessel steels. However, the separation of this effect from neutron spectral effects is difficult to achieve experimentally. In order to learn more about these effects, a joint effort between NRL and the Battelle-Northwest Laboratories was undertaken. This study has shown that variations in neutron spectra are likely to effect different changes in steels.

The results of many NRL irradiations on the same steel, using five positions in or near the core of the Low Intensity Test Reactor, a reflector position of the Materials Testing Reactor, a pool side position of the Industrial Reactor Laboratories Reactor, and an in-pile position of the Brookhaven Graphite Reactor, have been normalized by Battelle-Northwest for the particular neutron spectrum involved. The results

which were previously compared in terms of neutron dosage greater than 1 Mev have been compared using a neutron exposure criterion of greater than 0.5 Mev, with the result that the previous somewhat divergent steel embrittlement data now fall within a relatively narrow and concise band. It was noted however that the use of the greater than 1 Mev criterion for the several light water irradiation positions compared provides a valid measure of sustained steel embrittlement. On the other hand, for data comparisons involving different moderating media, such as light water versus graphite, a more appropriate measure of radiation effects maybe attained by calculating the spectrum for a given irradiation position and by lowering the nominal threshold level to 0.5 Mev. By formulating correction factors for the various positions of the test reactors used for radiation effects research, more uniform results may be obtained between the several experimenters who are investigating various aspects of this problem.

HIGH TEMPERATURE ALLOYS BRANCH

High Temperature Properties of Refractory Metals

In consideration of the ease with which niobium at elevated temperature is contaminated by atmospheric gases a study is being made of the influence of these gases on the creep-rupture properties of the metal. Oxygen in solid solution was found to strengthen niobium in creep-rupture at temperatures up to 1430°C. In a recent phase of the study in which nitrogen additions up to 0.5 percent were made, nitrogen, in contrast to oxygen, produced no significant effect on rupture life and creep resistance in the range of 1040° to 1430°C. However, at high nitrogen levels where nitrides form, strengthening did take place. Ductility at the elevated temperatures was high for both the single-phase and two-phase materials and appeared to be unaffected by nitrogen content.

Plans for the Future

The various programs described in this report are, in general, of a continuing nature. Thus, research during calendar year 1965 and beyond will be primarily an extension of present efforts. The emphasis in certain areas has shifted, as will be noted below.

An increased effort will be placed on understanding radiation effects on graphite. Various graphites will be irradiated at increasing levels of temperature and neutron dose to define the contraction as a function of these variables. Additional work will be performed on development of graphites with enhanced radiation stability.

The sintered aluminum powder (SAP) materials will be studied in considerable detail. Attempts will be made to fully characterize them, from raw materials through to finished tubing. The primary objective will be the establishment of specifications for reproducible and reliable SAP materials for use in fuel cladding and pressure tube applications.

Increased emphasis will be placed on nickel base alloys and stainless steels in order to define radiation induced embrittlement and develop methods of preparing materials having increased resistance to embrittlement.

Efforts will be increased on development of cladding materials for use in fast reactor systems. Materials will be sought having resistance to high fast fluxes and resistance to corrosion by liquid metals.

Further work will be performed on development of metal fuel systems having improved resistance to radiation induced swelling. Emphasis will be placed on uranium metal with minor additions and on uranium-thorium alloy systems.

The ceramic fuels programs will concentrate on development of fuels having capability of high burnup in fast reactor systems. Such efforts will be coordinated with the above mentioned cladding development studies in order to develop the optimum fuel-clad combinations.

In all of the research and development programs, continued emphasis will be placed on the use of known, reproducible starting materials and on testing under known environmental conditions by techniques that relate to service requirements.

XXIV. SUMMARY AND PLANS FOR THE FUTURE

Summary

Several of the accomplishments during 1964 are particularly significant. They either advanced the fabrication technology of reactor materials or provided valuable data on their engineering capability. These accomplishments will be listed below, according to the reactor use of the material.

Pressure Vessel Materials

The work at General Atomic (page XII.4) on biaxial testing of irradiated A 302-B steel has emphasized the need for careful interpretation of tensile data. The design engineer must be well aware of the relationship between uniaxial test data and data obtained under conditions of multiaxial stress and how such data relate to engineering applications.

The evaluation performed by Battelle Northwest (page VI.7) of the Naval Research Laboratory's data on Nil Ductility Transition Temperature (page XXIII.4) provided the first known correlation of data obtained from specimens irradiated in different reactor spectra. This was a most valuable reduction to practice of what had previously been unsubstantiated theory.

Moderator Materials

During the year, the Nuclear Materials and Propulsion Operation of the General Electric Company essentially completed the detailed analysis of radiation effects on beryllium oxide (page XIV.7). This work has made available one of the most complete analyses of irradiation stability of a reactor material. For a given set of reactor exposure conditions, one is now able to determine the type of beryllium oxide that would be expected to be most stable for use.

Cladding Materials

Work performed by General Electric-NMPO (page XIV.4) and the Oak Ridge National Laboratory (page XIX.4) has provided important information on neutron embrittlement of the nickel base alloys and stainless steels. Such data are critical to the determination of engineering use limits in fuel cladding applications.

Fabrication of tungsten and tungsten-rhenium alloy tubing was greatly advanced by the work of Nuclear Metals Inc. (page XVIII.1) and the Oak Ridge National Laboratory (XIX.9). The improvement in fabrication

technology greatly advances their availability for use in high temperature reactor systems. The fabrication studies of the tungsten-rhenium-molybdenum alloys performed by General Electric-NMPO (page XIV.4) has provided a similar advance in availability for high temperature use.

The gas loop planned for use in the Advanced Test Reactor has required major advances in high temperature gas technology. One of the more notable developments has been the gas chromatograph assembled by Battelle-Northwest (page VI.8). This will provide the capability of measuring gaseous impurities at levels of one part per million or less, a necessity if the helium coolant is not to be allowed to reach untenable impurity levels.

Fuel Materials

The Battelle-Northwest effort on irradiation of thorium (page VI.11) has extended our knowledge of its technical capability. As of April, 1965, the elements attained a maximum exposure of 11,100 MWD/T. The maximum fuel swelling as determined by interim bulk density measurements is 1.0 v/o, which is the volume change required to accommodate the solid fission product atoms. There is as yet no indication of corrosion. The irradiations are continuing.

The High Performance UO_2 Program of General Electric-APED (page XIII.8) has contributed markedly to our understanding of this fuel's limitations. One accomplishment of merit was the direct measurement of UO_2 thermal conductivity in-reactor to temperatures near the melting point. Also of value is the observation that molten UO_2 contacting Zircaloy-2 cladding does not of necessity cause a failure when the cladding is being cooled adequately externally.

Battelle-Columbus concluded a very successful study of uranium nitride for reactor use (page V.2). This effort provided data on synthesis, fabrication, compatibility, and radiation stability of the fuel. It has provided a good fund of information on use of uranium nitride in reactor systems.

The United Nuclear Corporation's study of $(U_{0.8}Pu_{0.2})C$ fuels was essentially completed during the year (page XXII.1). The excellent appearance and stability of two 3-inch fueled length specimens (Nb clad) irradiated to 112,700 and 114,000 MWD/T respectively is particularly significant to fast reactor fuels technology.

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