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PROGRESS ON DEVELOPMENT OF FUELS AND
TECHNOLOGY FOR ADVANCED REACTORS
DURING JULY, 1969, THROUGH JUNE, 1970
ANNUAL REPORT

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BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Prepared for U. S. Atomic Energy Commission
Under Contract No. W-7405-eng-92

Report Date: July, 1970

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**PROGRESS ON DEVELOPMENT OF FUELS AND
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DURING JULY, 1969, THROUGH JUNE, 1970
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Donald L. Keller

**BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories
505 King Avenue
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REPORTS RELATING TO REACTOR MATERIALS, TECHNOLOGY, AND
SAFETY ISSUED DURING THE PERIOD JULY, 1969, THROUGH JUNE, 1970

- BMI-1865 "Fission-Product Deposition and Its Enhancement Under Reactor Accident Conditions Deposition on Containment-System Surfaces", by Harvey S. Rosenberg, Joseph M. Genco, and David L. Morrison.
- BMI-1866 "Investigation of the Initiation and Extent of Ductile Pipe Rupture. Phase I", by Robert J. Eiber, Willard A. Maxey, Arthur R. Duffy, and Thomas J. Atterbury.
- BMI-1867 "An Evaluation of the Applicability of Existing Data to the Analytical Description of a Nuclear-Reactor Accident. Quarterly Progress Report for April Through June, 1969", by David L. Morrison, Wayne A. Carbiener, and Robert L. Ritzman.
- BMI-1868 "Annual Report - Progress on Development of Materials and Technology for Advanced Reactors During July, 1969, Through June, 1969", by Donald L. Keller.
- BMI-1870 "Progress on High-Temperature Fuels Technology During August, 1968, Through July, 1969. Annual Report", by Donald L. Keller, and Walston Chubb.
- BMI-1871 "An Evaluation of the Applicability of Existing Data to the Analytical Description of a Nuclear-Reactor Accident. Quarterly Progress Report for July Through September, 1969", by Wayne A. Carbiener, and Robert L. Ritzman.
- BMI-1872 "Progress on Development of Materials and Technology for Advanced Reactors During July Through September, 1969", by Donald L. Keller.
- BMI-1873 "Investigation of the Initiation and Extent of Ductile Pipe Rupture. Phase II. Progress Report for May-September, 1969", by Robert J. Eiber, Willard A. Maxey, Arthur R. Duffy, and Thomas J. Atterbury.
- BMI-1874 "Fission-Product Deposition and Its Enhancement Under Reactor Accident Conditions Development of Reactive Coatings", by Harvey S. Rosenberg, George E. Cremeans, Joseph M. Genco, David A. Berry, and David L. Morrison.
- BMI-1875 "Progress on High-Temperature Fuels Technology During August Through October, 1969", by Donald L. Keller, and Walston Chubb.
- BMI-1876 "Investigation of the Initiation and Extent of Ductile Pipe Rupture. Phase II. Progress Report for October-December, 1969", by Robert J. Eiber, Willard A. Maxey, Arthur R. Duffy, and Thomas J. Atterbury.
- BMI-1877 "An Evaluation of the Applicability of Existing Data to the Analytical Description of a Nuclear-Reactor Accident. Quarterly Progress Report for October Through December, 1969", by Wayne A. Carbiener, and Robert L. Ritzman.
- BMI-1878 "Progress on Development of Materials and Technology for Advanced Reactors During October Through December, 1969", by Donald L. Keller.
- BMI-1879 "Progress on High-Temperature Fuels Technology During November, 1969, Through January, 1970", by Donald L. Keller, and Walston Chubb.
- BMI-1880 "Investigation of the Initiation and Extent of Ductile Pipe Rupture. Phase II. Progress Report for January-March, 1970", by Robert J. Eiber, Willard A. Maxey, Arthur R. Duffy, and Thomas J. Atterbury.
- BMI-1881 "An Evaluation of the Applicability of Existing Data to the Analytical Description of a Nuclear-Reactor Accident. Quarterly Progress Report for January Through March, 1970", by Wayne A. Carbiener, and Robert L. Ritzman.
- BMI-1882 "Progress on Development of Materials and Technology for Advanced Reactors During January Through March, 1970", by Donald L. Keller.
- BMI-1883 "Review of Through-Wall Critical Crack Formulations for Piping and Cylindrical Vessels", by Robert J. Eiber, Willard A. Maxey, Arthur R. Duffy, and Thomas J. Atterbury.

HIGHLIGHTS OF RESULTS DURING REPORTING PERIOD

Results of studies at Battelle-Columbus during Fiscal Year 1970 on development of fuels and technology for advanced reactors are summarized in this report. The work is being supported by AEC-DRDT and by ANL. The programs under way are concerned with development of uranium-plutonium nitride fuels for LMFBFR applications, studies of high-temperature fuels for LMFBFR's and advanced fast reactors, and studies of creep of reactor fuel materials. Highlights of the results reported are cited below.

Uranium-Plutonium Nitride Fuels for LMFBFR Applications (Task 7)

The high fissile density, high thermal conductivity as compared with oxide fuels, and high breeding ratio of mixed-nitride fuels make them attractive for LMFBFR applications. To fully define the potential of UN-PuN fuels, a program involving materials preparation studies, property measurements, long-term thermal and fast irradiations, and supporting studies is underway. The use of sodium as a fuel-cladding bond and to accommodate fuel swelling is being evaluated also.

In contrast to specimens with a helium bond, no cladding strain was found in sodium-bonded specimens during postirradiation examination of Capsules BMI-50-5, BMI-50-7, and BMI-50-9 (burnups to 34.5×10^{20} fissions per cm^3 at heat generation rates as high as 29.2 kw per ft). Swelling rates of fuel in all specimens were 0.48 percent per 10^{20} fissions per cm^3 or less. Fission-gas release from the high-density fuels was less than 1 percent. In general, the fuel microstructures were unchanged by irradiation. No nitrogen or fission products entered the cladding. Initial examinations of specimens from Capsule BMI-50-6, which sustained burnups estimated to be from 35.0×10^{20} to 48.6×10^{20} fissions per cm^3 , revealed a cladding failure in one of the two specimens with a 10-mil sodium bond. Both helium-bonded specimens failed. Preliminary examination of specimens from Capsule BMI-50-11, designed to operate at 40 kw per ft and discharged from the reactor after two cycles upon indications of overheating (heat generation rates of up to ~57 kw per ft), revealed cladding strain in all specimens and a circumferential failure in one. Fabrication, machining, and cladding of $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ pellets for Capsule BMI-50-12 were completed. Irradiation of Capsules BMI-50-8 and BMI-50-10 was continued.

In the EBR-II irradiation of mixed-nitride fuels, fabrication of pellets for seven fuel pins was completed for the BMI-3 series experiment and three of the seven capsules were completed. The seven capsules that will make up the BMI-2 series were completed and forwarded to the EBR-II for irradiation. Capsule BMI-1-3, among the four shipped earlier, was inserted into the EBR-II.

In the preparations for transient irradiation evaluations of $(\text{U}, \text{Pu})\text{N}$ fuels, calculations were carried out to establish the adequacy of the capsule conceptual design from the heat-transfer viewpoint as well as to provide a correlation between neutron flux in the capsule and in the TREAT reactor.

The possibility of controlling swelling by incorporating uniformly distributed porosity in nuclear fuels is being studied with a mathematical model as an aid in interpreting experimental results. In the initial work, no influence of density variations in the range of 80 to 95 percent of theoretical on the diametral expansion of clad fuel has been found.

In thermodynamic studies related to development of LMFBFR fuels, experimental work on the behavior of neodymium in NdN revealed no thermal stability, gaseous species, or chemical composition effects which could account for the anomalies encountered when isotopic burnup analyses based upon Nd^{150} are applied to mixed-nitride fuels.

Experiments were conducted to establish the phase limits of PuN and of $(U_{0.8}Pu_{0.2})N$. Under nitrogen at 1 and 0.1 atm, no compositional change in PuN was detected over the temperature range from 1500 to 2140 C. At 1.0×10^{-4} atm of nitrogen, the nitrogen/metal ratio was 0.968 at 1990 C. Similar stability was exhibited by $(U_{0.8}Pu_{0.2})N$. In other experiments it was demonstrated that there is little or no solubility of plutonium in U_2N_3 .

In studies of (U, Pu)N compatibility with reactor claddings and coolants, extrapolation of data from 8000-hr tests involving UN-10 v/o U_2N_3 powder sodium bonded to Type 316 stainless steel indicated that a nitrogen-rich diffusion zone less than 1 mil thick will be formed in the stainless steel in 10,000 hr at 700 C.

In experimental work to develop a reliable method for determination of nitrogen in sodium, a modified micro-Kjekdahl technique was found to give acceptable results with chemically uncombined nitrogen but not with nitrogen compounds.

Development of an electrolytic sectioning technique in an investigation of the self-diffusion behavior of nitride fuels has facilitated determinations of diffusion coefficients of the order of 10^{-4} cm² per sec. Measurements on UN have produced diffusion-coefficient values lower than those reported by other investigators.

In sessile-drop studies of sodium wetting of potential LMFBR fuels and claddings, wetting occurred in all materials between 350 and 500 C. Extrapolation of the data indicated complete wetting would take place at 600 to 650 C. No dewetting occurred on cooling. Wetting of metals and alloys tended to occur at temperatures lower than those for ceramics. Different lots of sodium displayed different wetting characteristics, particularly at lower temperatures. Attack of the surface of mixed-oxide fuel by sodium was observed.

Technology of Nuclear Fuels for Advanced Fast Reactors (Task 6)

Data obtained in this program will provide a unique description of the in-pile behavior of those portions of LMFBR fuels which operate at temperatures from 1300 to 2000 C. Such data will allow determination of the relative contributions of those parts of the fuel operating above 1300 C, of those parts operating below 1300 C, and of the cladding to the overall fuel-element swelling behavior. The data will enhance assessment of the performance of present LMFBR fuel concepts under all credible operating conditions and will tend to validate subsequent use of current fuels at more efficient temperature levels.

In irradiation studies of UO_2 and UO_2 - PuO_2 fuels, external swelling has been found temperature dependent and essentially a linear function of burnup. Swelling rates of 8 v/o per 10^{20} fissions per cm³ were observed at cladding surface temperatures of about 1600 C, while at 1750 C rates were nearly four times as great. Reactor thermal cycles did not influence swelling behavior. In the range from 1300 to 1400 C, where the cladding restraint used in the experiments was comparable to that provided by stainless steel at 650 to 700 C, the swelling was 1 to 5 v/o per 10^{20} fissions per cm³. Fission-gas release also exhibited temperature dependency in these experiments, with release rates at 1840 C being nearly equal to the generation rate. Thus the results show that UO_2 does exert a significant outward stress at high temperatures in spite of high fractional gas release. If the contributions to restraint and swelling provided by the regions of UO_2 below 1300 C and by the stainless steel cladding can be accurately assessed by existing models of the behavior of UO_2 fuel pins, then the data obtained in the experiments can be incorporated into these models to describe the contribution of the hotter regions of the UO_2 . It was concluded that swelling at high temperatures is primarily a consequence of the formation of small, relatively immobile bubbles. A vapor-phase

zone-refining process that restructures the fuel and facilitates gas release was described. Swelling occurs irreversibly in small increments between passages of lenticular voids.

Two tungsten-42 v/o UO_2 cermet incorporating 28 v/o porosity exhibited no external diameter changes at a burnup of 1.65×10^{20} fissions per cm^3 at 1640 C. This performance was attributed mainly to the disengaging effect of the porosity, which also caused rapid release of fission gas (80 percent) through the interconnected porosity.

In an evaluation of irradiated UN and tungsten-UN cermets, variations in swelling behavior and fission-gas release were noted that were ascribed to nitrogen activity and initial porosity effects. Low mobility of fission gas in the materials that showed low swelling rates was noted. Swelling of UN at high temperatures was attributed to the appearance of a small fraction of the fission gas in large bubbles at grain boundaries. Location of interconnected porosity in amounts up to 30 v/o at grain boundaries greatly reduced swelling.

Postirradiation examination of a 60 percent dense UC specimen made up of crushed particles was completed. Burnup was 2×10^{20} fissions per cm^3 at 1530 C. External volume increase was 7 v/o versus the 35 v/o observed earlier in dense UC irradiated at 1680 C. The improved performance was attributed to the low interparticle contact in the material during the initial stages of the irradiation and to the lower irradiation temperature.

Preliminary measurements of fission-gas diffusion suggested that diffusivities in UN and UO_2 are one or two orders of magnitude lower than in UC.

Studies of lightly irradiated UC indicate that fission-gas bubble distribution is sensitive to composition and to postirradiation annealing procedure. Where UC_2 is formed, bubbles will form preferentially at UC_2 platelets. When all the UO_2 is dissolved on heating, large bubbles are seen at grain boundaries and smaller ones are seen homogeneously distributed throughout the grains.

In theoretical analyses of fuel swelling behavior, computer simulations of bubble precipitation in UC and UO_2 were correlated with experimental data. Development and use of a theoretical model of bubble migration in UO_2 delineated the relative importance of such factors as interface kinetics and impurity effects on the formation, configuration, and movement of bubbles. Also, a mathematical model was developed to describe the external dimensional changes of clad UO_2 fuel elements operating in-pile under steady-state conditions.

In three tensile creep tests, UN showed significantly less ductility than that observed earlier in UC. Creep rates were found to depend upon stress to the third power. When increasing-stress tensile creep tests were performed at 1760 C on tungsten and tungsten-26 w/o rhenium, the alloy deformed much more rapidly than tungsten.

In studies of the thermodynamics and kinetics of subliming fuels, experimental work to determine vaporization characteristics in the UC-PuC system showed that plutonium will be preferentially vaporized in metal-rich compositions until the carbon/metal ratio is greater than unity. The initial rate is about half the value that would be expected for pure plutonium. Thermodynamic analyses, using available data, to establish oxygen potential as a function of composition for PuO_{2-x} suggested that at 2000 K a composition near $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_{1.94}$ would vaporize in such a manner that the uranium/plutonium ratio in the solid would be unchanged.

In studies of potential fuel/cladding bonding media, hot-hardness values of 3, 6, and 15 kg per mm^2 were obtained for vanadium, chromium, and niobium, respectively, at 1400 C.

As an aid in the conduct of high-temperature irradiation experiments, an improved pressure transducer was developed to detect, in-pile, changes in gas pressure inside the cladding of fuel specimens. The minimum pressure detectable with the new device is 0.5 psi. Neutron radiography techniques were improved for examination of irradiation capsules.

Creep of Reactor Fuel Materials (Task 6 and ANL)

The differences in creep strength between the cladding, as well as cooler outer regions of the fuel, and the hot inner regions of the fuel are paramount considerations in predicting the swelling behavior of reactor fuels as a consequence of fission-product accumulation. Thus the influence of the fission process on the creep strength of ceramic fuels must be determined if optimum fuel designs are to be achieved. A program to obtain and analyze in-pile creep data on UO_2 and $\text{UO}_2\text{-PuO}_2$, and out-of-pile reference data on these fuels, is under way.

Operation of the second and third capsules in the in-pile creep program was completed successfully. Analysis of the data obtained from the two capsules indicates that, at a fission rate of about 1.2×10^{13} fissions/(cm³)(sec), a stress range of 1500 to 4000 psi, and a nominal temperature range of 1100 to 1200 C, and assuming a stress dependency of only 1 in the plotting of the creep curve, the most conservative case, an enhancement of the creep rate by a factor of 8 to 10 is obtained as a result of the fission process.

In the effort to provide a basis for comparison of in-pile (anisothermal) with out-of-pile (isothermal) creep data, a parametric analysis demonstrated that compensation can be made for the effects of anisothermal conditions in the in-pile tests by subtracting 25 C from the nominal specimen temperature.

Examination of the second creep capsule was conducted after four in-pile tests. Melting of the main heater wire at one location accounted for the temperature-control difficulties encountered with this capsule. The remainder of the components were in good condition. Modifications to reduce the possibility of the introduction of contaminants which could cause heater failure were incorporated into the assembly procedures for the third capsule. This capsule operated successfully until failure of the specimen during the third in-pile test. Postirradiation examination showed capsule components to be in generally excellent condition. Some revisions to capsule heater designs and assembly procedures were made after completion of some laboratory heater mock-up experiments. Operation of the fourth capsule in the series was terminated by specimen failure prior to in-pile testing. A new specimen was incorporated into this capsule. In work on development of a high-flux creep capsule, test-facility evaluations were conducted and specimen and capsule design features appropriate to mixed-oxide and mixed-nitride fuels were evaluated.

Studies were conducted of the compressive creep behavior of $\text{UO}_2\text{-22 w/o PuO}_2$ specimens of varying density and grain structure prepared from mechanically blended and coprecipitated powders sintered under optimum conditions. Fine-grained mechanically blended material exhibited an activation energy for creep of 77 kcal per mole. The stress exponent at 1210 C for stresses from 1500 to 3000 psi was 1.4. Thermal- and stress-induced grain growth produced erratic behavior in this material in long-term tests. Coarser-grained material prepared from mechanically blended powders had a lower creep rate. Tertiary creep was induced at a strain level of less than 1 percent. Specimens prepared from coprecipitated material fractured at strain levels of ~2 percent.

In experimental and analytical studies on the modes and mechanism of creep in UO_2 and $\text{UO}_2\text{-PuO}_2$, creep rates and activation energies for high-temperature creep of single-crystal UO_{2+x} have been found to be strongly dependent upon oxygen/uranium ratio. For power-law stress regimes, this dependence can be expressed as $\dot{\epsilon} \propto x^2$ for values of x above 0.003. At lower stresses, creep rates of UO_{2+x} single crystals appeared to be nearly independent of stoichiometry. Transmission-electron-microscopy studies of nonstoichiometric UO_{2+x} specimens deformed 10 percent in compression revealed features previously attributed to neutron irradiation effects. In studies of polycrystalline UO_2 , at 1100 C creep rates have been found to increase with increasing stress and with increasing oxygen/uranium ratio and to increase with decreasing grain size.

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✕ URANIUM-PLUTONIUM NITRIDE FUELS FOR
LMFBR APPLICATIONS (AEC-DRDT)

W. M. Pardue, A. A. Bauer, P. Cybulskis,
and C. A. Alexander

These studies are being conducted for the AEC Division of Reactor Development and Technology to evaluate the potential of mixed UN-PuN fuels for fast breeder applications. The use of mixed-nitride fuels in liquid-metal fast breeder reactor (LMFBR) applications is considered desirable because of the high fissile density of the materials, the high thermal conductivity as compared to that of oxides, and the high breeding ratio attainable. Several studies of uranium nitride have been undertaken for thermal reactor applications and the UN in these programs has exhibited desirable irradiation-stability behavior, thus implying that the UN-PuN fuels may be satisfactory in this respect.

The program is divided into efforts involving the preparation of materials by gas-solid reactions, property determinations, irradiation studies, and supporting studies. Physical properties of importance for reactor design are being determined, including volatility tendencies, conductivity, expansivity, and chemical stability of the fuels in contact with potential LMFBR cladding materials. The resistance of nitride materials to both thermal and fast flux irradiations will be determined to evaluate the suitability of these fuels for applications involving long-term irradiations.

The evaluation of sodium bonding of the fuel to the cladding is another objective of the program. Nitride fuel grows at a rate of about 0.5 v/o per 10^{20} fissions per cm^3 . To minimize cladding deformation, this fuel growth can probably be accommodated more effectively in the annulus between the fuel and the cladding rather than in the porosity in the fuel. To minimize fuel temperatures, another desirable objective, this annulus must be filled with a good heat-transfer material. Effort is thus devoted to studies of sodium bonding and film formation in contact with nitride fuels and their claddings.

Thermodynamics and Transport Characteristics
of PuN and Alloys of UN-PuN

C. A. Alexander, J. S. Ogden, and W. M. Pardue

Objective of Program

To determine those properties pertaining to plutonium nitride-bearing fuel compositions which allow predictions of fuel stability, transport, and other factors needed to evaluate the behavior of the fuel under possible reactor environmental conditions of both transient and steady-state nature.

Approach being Used

Kinetics and thermodynamics of vaporization processes are being investigated by effusion-thermobalance and mass-spectrometric techniques. The existence of a homogeneity range is being examined under controlled atmosphere conditions. The Oelsen calorimeter is being utilized to experimentally determine heat capacities as a function of temperature and alloy composition.

The experimental apparatus used in the studies consists of a cold-wall furnace constructed of stainless steel which is evacuated through a pipe 10 cm in diameter, a diffusion pump with a capacity of 300 liters per sec, and a mechanical pump with a capacity of 7 liters per sec. The system is equipped with valves so that the furnace

chamber can be isolated from the pumps and backfilled with inert gas or any nonoxidizing gas to the desired pressure. The furnace assembly has a maximum leak rate of 10^{-9} std cm^3 . A Cahn recording microbalance is also incorporated into the vacuum chamber which houses the basic vaporization furnace. The electrobalance is used to continuously monitor the vaporization rates as a function of time and/or temperature.

The double-focusing mass spectrometer used for the surface-ionization studies on neodymium has a focal point about 8 cm on either side of the 25-cm radius of curvature in the electrostatic sector. The magnetic sector is asymmetric, and the distance from the image to the 60-deg, 20-cm sector is shorter than the object distance. The electromagnet incorporates a Rawson field meter in a feedback arrangement to supply short-term stability of about 1 ppm in the magnet power supply. A field sweep is also incorporated in such a manner that the sweep can be made in gaussess rather than in amperes. The design criteria of the machine are such that with 2500 v of accelerating potential, masses up to 1200 are resolvable in the magnetic sector. A resolution of about 2500 at mass 25 was selected as a reasonable compromise between resolution and transmission. The sensitivity is such that the individual events can be monitored. Data output is on a strip-chart recorder using a Cary Model 31 vibrating-reed electrometer and Faraday cage or an electron multiplier tube and appropriate amplifier.

Significant Accomplishments During Fiscal Year 1970

The behavior of neodymium in NdN as a measure of burnup revealed that there was neither a lack of thermal stability, nor the existence of a gaseous species, nor an anomaly in chemistry that can account for any lack of agreement when isotopic analyses of mixed-nitride fuels are compared with those obtained from mixed oxides.

Equations for mass transport and general thermochemical properties were obtained. It was also established that the presence of PuN in solution in UN decreases the uranium activity and thereby prevents the formation of a molten phase at temperatures to at least 2000 K. At both 1 and 0.1 atm of nitrogen no homogeneity range for PuN was detected over the temperature range from 1500 to 2140 C. Pressure-temperature-composition relationships for PuN and (U, Pu)N were also prepared.

The homogeneity ranges for PuN and $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ are very narrow. The nitrogen/metal ratio varies from 1 at 1 atm of nitrogen to 0.968 at 10^{-4} atm of nitrogen.

Summary of Research Carried Out

The usage of the concentration of Nd^{150} as a measure of burnup has been well established for irradiated mixed-oxide fuels; however, when the same technique is applied to mixed-nitride fuels the agreement between the isotopic determination and the burnup calculated from heat-transfer data and fission-gas release is not as close as with oxide fuels. Since little is known concerning the stability and chemistry of NdN, which is the assumed compound formed by the Nd^{150} , it was considered that an understanding of these properties might indicate the reason for the lack of accord when the isotopic technique was applied to burnup measurements of mixed nitrides.

A 3-g right circular cylinder of 99.99 percent pure neodymium metal was electro-discharge machined from a rod and placed within a Knudsen cell suspended from a thermobalance. Hydrogen was admitted to a pressure of 0.9 atm, and the temperature was slowly raised to 420 C. Hydriding was completed in about 30 min at that temperature, and the material reached a composition of $\text{NdH}_{2.70}$. Nitrogen at a pressure of 0.9 atm was introduced to the system and the temperature was slowly raised to 825 C. After about 70 min at that temperature the nitriding ceased; the composition, determined by weight change, was $\text{NdN}_{0.99}$. The apparatus was subsequently evacuated to 10^{-6} torr and a series of effusion experiments begun. At 1500 K the initial rate of weight loss indicated the dissociation pressure of nitrogen to be 1.3×10^{-6} atm; however, it was observed that this initial rate tended to decrease with time. When a composition near

$\text{NdN}_{0.94}$ was reached the evaporation rate was no longer time-dependent, and it appeared that congruent vaporization was occurring. This means the weight loss occurred as a result of the reaction $\text{NdN}_{0.94} = \text{Nd}_{(g)} + 0.47\text{N}_{2(g)}$. At 2000 K the partial pressure of neodymium was 9.8×10^{-5} atm; that of nitrogen was 2.1×10^{-5} atm. These quantities can be compared to the pressure of metal and nitrogen over the mixed fuel at a similar temperature. For $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ at 2000 K: $p_{\text{N}_2} = 1.1 \times 10^{-6}$ atm, $p_{\text{Pu}} = 6.7 \times 10^{-6}$ atm, and $P_{\text{U}} = 4.0 \times 10^{-8}$ atm; hence, pure neodymium nitride is somewhat less stable than the fuel, but these data represent the situation for unit activity. At a concentration of NdN anywhere less than 1 m/o it would be expected to exhibit quite good stability, and this concentration is the case in irradiated fuels.

In an effort to determine whether something in the chemistry of NdN is contributing to the discrepancy, some surface-ionization mass-spectrometric runs were performed. Initially, 1.000 g of Nd_2O_3 was dissolved in 1 liter of 8M HNO_3 . The isotopic distribution of neodymium was run and both Nd^+ and NdO^+ ions were observed. A solution of $\text{Nd}_2^{143}\text{O}_3^{16}$ was then made, and a known quantity of this solution was added to a portion of the oxide solution. On the basis of isotopic intensities and the dilution technique, it was established that about 9×10^{-9} g of neodymium would be sufficient for an isotopic analysis. No attempt was made to optimize the emission; therefore, a considerable improvement over this value may be possible.

The nitride charge was subsequently removed from the Knudsen cell and 0.313 g dissolved in 8M HNO_3 . A spike of the Nd^{143} solution was added and the isotopic analysis run. Within the precision of the mass-spectrometric method the results were identical with those of the oxide experiment; thus, the expected response of neodymium to mass-spectrometric isotopic analysis is the same regardless of its chemical form. It then must be concluded that neither lack of thermal stability, nor existence of gaseous species, nor differences in chemistry can account for any lack of accord when isotopic analyses of mixed-nitride fuel are compared with those obtained from mixed oxides.

Experiments establishing the existence of the phase limits of the PuN phase and the limits of the $\text{U}_{0.8}\text{Pu}_{0.2}\text{N}$ phase were carried out in selected partial pressures of nitrogen. On the basis of effusion and microbalance determinations it was established that the PuN phase exists at all nitrogen pressures greater than those listed in Table A-1 for the corresponding temperatures. If an attempt is made to lower the system pressure to one of these pressure values at its corresponding temperature, say 2×10^{-4} atm at 2400 K, a liquid phase would not be encountered. This is because the partial pressure of plutonium, as determined in previous work, would be 1.5×10^{-3} atm and the plutonium would sublime at this higher system pressure rather than exist as a liquid. Clearly, then, it is necessary to utilize a total system pressure in excess of the nitrogen partial pressure to suppress the volatilization of plutonium. This is a requirement because of the nature of the measurement. If plutonium is lost by vaporization, then it is not possible to determine the change in the plutonium/nitrogen ratio from the balance measurements. Gases containing nitrogen at pressures of 10^{-4} atm, 10^{-3} atm, 10^{-2} atm, 10^{-1} atm, and 1 atm were selected for use in establishing the entire homogeneity range for PuN. All of the above gases except for the last two are gaseous mixtures of nitrogen in argon, while the pressures of 10^{-1} atm and 1 atm are achieved with nitrogen alone.

In these experiments PuN powder contained in an open crucible suspended from the thermobalance was first outgassed at 1200 C. The constant weight in vacuum at 1200 C was selected as the starting point, and if a composition of $\text{PuN}_{1.00}$ is arbitrarily assigned to this composition all changes in composition can be referred to this point.

TABLE A-1. MINIMUM NITROGEN PRESSURE
FOR EXISTENCE OF PuN PHASE

Temperature, K	Nitrogen Pressure, atm
1400	8×10^{-13}
1600	4×10^{-11}
1800	7×10^{-9}
2000	4×10^{-7}
2200	1×10^{-5}
2400	2×10^{-4}

Temperatures from 1500 to 2140 C were investigated at 1 atm and at 0.1 atm, and after buoyancy corrections were made in the microbalance it was established that the charge gained no weight as a result of nitrogen uptake during these runs. Changes in the plutonium/nitrogen ratio in the third decimal place can be observed with this balance arrangement. It is concluded, then, that PuN (referred to $\text{PuN}_{1.00}$ in vacuum at 1200 C) does not exist at compositions richer in nitrogen than $\text{PuN}_{1.00}$. Of course it is possible that the partial molar free energy of nitrogen in the PuN phase rises so steeply that it is not possible to observe compositional changes when the pressure is changed only by one order of magnitude. Considering the sensitivity of the thermobalance, this is unlikely.

Additional experiments that were performed over the temperature range from 1720 to 1990 C indicated that the nitrogen/plutonium ratio varied from 0.991 at 1720 C to 0.968 at 1990 C at a constant nitrogen pressure of 1.0×10^{-4} atm. The experimental values are plotted in Figure A-1. On the basis of two-phase nitrogen pressures given in BMI-1872, it is calculated that the plutonium-PuN phase boundary at 1.0×10^{-4} atm occurs at 2067 C, or 2350 K. At a temperature of 2350 K, then, the PuN phase can exist at compositions to $\text{PuN}_{0.954}$. Some preliminary thermodynamic quantities have been calculated for the solution of nitrogen in PuN. The partial molal enthalpy $\bar{H} = -112,000$ cal per mole, while the partial molar entropy $\bar{S} = -38.5$ cal/(mole)(deg). The above values were calculated over the temperature range from 2000 to 2200 K. The integral enthalpy change across the homogeneity range is about 4 kcal per mole, which is sufficient to account for some of the differences in first-law and second-law thermodynamic investigations of PuN.

The data obtained to date indicate a moderately small homogeneity range for PuN, only slightly larger than that of UN. Similar experiments with $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ have not indicated any evidence for a homogeneity range in the mixed fuel. The very slight weight change that is observed at temperatures above 2000 C shows a constant rate of change with time. This is indicative of a zeroth-order reaction, and it is considered to be caused by volatilization of plutonium in a gaseous environment.

A series of determinations has been performed to determine the decomposition pressure of the sesquinitride when it is in equilibrium with (U, Pu)N fuels. Charges of between 1.5 and 2.0 g of $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ containing approximately 3 m/o U_2N_3 were employed in the determinations. The average particle size of the powder employed was 3μ ; hence, there was adequate surface for maintaining equilibrium conditions within the Knudsen cell. The cell employed was constructed of tungsten and contained a 0.1-cm-diameter orifice with a Clausing factor of 0.92. The cell was suspended from the Cahn electrobalance into the hot zone of a vacuum furnace. Results of the runs are shown in Figure A-2. The phenomenological interpretation of the results is that there is very little or no solubility of plutonium in U_2N_3 . This can be demonstrated thermodynamically in the following manner.

FIGURE A-1. PuN HOMOGENEITY RANGE AT 1.0×10^{-4} ATM OF NITROGEN

FIGURE A-2. DECOMPOSITION PRESSURES OF NITROGEN-RICH NITRIDE FUELS

Consider first that the standard states are defined as pure $UN_{1.5}$, pure UN, and N_2 gas all at the pressure and temperature of the individual measurement. For the decomposition of $UN_{1.5}$:

$$UN_{1.5} = UN + 0.25N_2 \quad (A-1)$$

$$\text{The equilibrium constant, } K = \frac{a(UN) (p^\circ N_2)^{0.25}}{a(UN_{1.5})} \quad (A-2)$$

or since UN and $UN_{1.5}$ are in their standard states, $a = 1$. Then,

$$K = (p^\circ N_2)^{0.25} \quad (A-3)$$

where p° has been used to refer to the pressure for the pure components for the fuel.

$$UN_{1.5} = UN_{\text{soln}} + 0.25N_2 \quad (A-4)$$

$$K = \frac{a(UN) (pN_2)^{0.25}}{a(UN_{1.5})} \quad (A-5)$$

Since we are referring to the same reaction, the K in Equation (A-3) is the same K as in Equation (A-5). Then

$$(p^\circ N_2)^{0.25} = \frac{a(UN) (pN_2)^{0.25}}{a(UN_{1.5})} \quad (A-6)$$

Previous vapor-pressure determinations have established that UN-PuN is essentially an ideal solution; hence, $a(UN_{\text{soln}}) = 0.8$, and if we assume as a first approximation that $a(UN_{1.5}) = 1$, then

$$\left(\frac{p^\circ N_2}{pN_2} \right)^{0.25} = 0.8 \quad (A-7)$$

or

$$\frac{p^\circ N_2}{pN_2} = 0.41 \quad (A-8)$$

This implies that the decomposition pressure over the sesquinitride in equilibrium with $(U_{0.8}Pu_{0.2})N$ would be 2.5 times higher than for the sesquinitride in equilibrium with UN, provided the activity of $UN_{1.5}$ was the same in both cases, i. e., no appreciable plutonium solubility in $UN_{1.5}$. Since this is the value measured, it certainly appears that the initial assumption of no plutonium solubility was warranted, and such is the case.

It is apparent that nitriding conditions are more severe for $UN_{1.5}-(U_{0.8}Pu_{0.2})N$ than for $UN_{1.5}$ -UN, at least based on equilibrium considerations; however, the pressures, although higher, are not of sufficient magnitude to influence any other properties in the system.

Plans for Future Work

Additional studies of the thermochemistry of mixed-nitride fuels will be undertaken.

(U, Pu)N Compatibility With Reactor
Claddings and Coolants

J. M. Fackelmann, D. P. Moak, and W. H. Pfeifer

Objective of Program

To investigate the compatibility of UN-PuN fuels with potential cladding materials under simulated LMFBR conditions.

Approach Being Used

Studies will be primarily directed toward evaluation of the compatibility of $(U_{0.8}Pu_{0.2})N$ with Type 316 stainless steel in both sodium and helium environments. Studies in progress with Type 304 stainless steel claddings will be concluded. The effect of the presence of sesquinitride in hyperstoichiometric nitride fuels on compatibility with Type 316 stainless steel will be studied.

Fuel-cladding compatibility following in-pile irradiation will be evaluated. In addition, limited out-of-pile studies will be planned in support of the irradiation program.

Metallography, hardness measurements, electron-microprobe analyses, X-ray diffraction techniques, and analytical chemistry techniques will be used as required to identify reaction products and their rates of formation. Procedures for the preparation of compatibility specimens are outlined in BMI-1868.

Significant Accomplishments During Fiscal Year 1970

Powder mixtures of UN-10 v/o U_2N_3 , sodium bonded to Type 316 stainless steel, were found to react with the stainless steel to form diffusion zones rich in nitrogen. On the basis of extrapolation of results obtained in tests of up to 8000 hr in duration, the magnitude of this effect at 700 C is such that a diffusion zone of less than 1 mil in thickness will form in 10,000 hr. When dense UN-5 v/o U_2N_3 is substituted for the powder, the rate of cladding nitriding is significantly decreased. Contact bonding, as opposed to sodium bonding, also reduces nitriding effects at 700 and 800 C.

The low strain failure which had been observed in the cladding of mixed-nitride-fueled specimens was traced to the low ductility of the original as-received material rather than to excessive embrittlement during irradiation.

Summary of Research Carried Out

Heat treatment of UN_{1+x} -sodium-Type 316 stainless steel combinations has been performed in order to study compatibility behavior. The fuels and sodium were sealed in stainless steel capsules by Heliarc welding, and then heat treated for 8000 hr at 700 and 800 C under the static helium atmosphere of an outer Inconel capsule, also sealed by Heliarc welding. Two of these double capsules, containing powder mixtures of UN-10 v/o U_2N_3 , were heat treated for 8000 hr at 700 and 800 C, respectively. The U_2N_3 was heated for 1/2 hr at 500 C in vacuum to decrease its nitrogen content to a value near that at which the mononitride and sesquinitride are in equilibrium. A third capsule, containing 95 percent dense UN-5 v/o U_2N_3 as fuel, was heat treated for 8000 hr at 700 C. After heating, the double capsules were disassembled and examined by analytical and metallographic techniques.

The nitrogen profiles of these capsules, as determined by micro-Kjeldahl analyses of layers machined from the capsule wall at 10-mil increments, are presented in Figure A-3. The nitriding effects were also manifested in the microstructure by the

presence of a Cr_2N precipitate in the stainless steel adjacent to the cladding. Nitriding of the cladding proceeded at a higher rate with the powder fuel. The greater surface area of this fuel leads to a greater nitrogen flux, suggesting that the rate-limiting step in the nitriding process is the diffusion of nitrogen through UN.

The rate of cladding nitriding as a function of reciprocal temperature is plotted in Figure A-4 for UN-10 v/o U_2N_3 powder, sodium bonded to Type 316 stainless steel. The reaction rate in this plot is based on the metallographically measured thickness of the cladding zone containing the Cr_2N precipitate. The second curve is from previous studies, and provides a comparison with contact-bonded fuel elements. From Figure A-4, it is evident that the presence of sodium leads to a significant increase in nitriding rate. It should be noted, however, that past studies with dense, hyperstoichiometric fuels have indicated no significant difference in reaction rates for the two bonding conditions. The curves in Figure A-4 give a quantitative expression to the cladding nitriding kinetics for this fuel. Because of the high surface area and U_2N_3 content relative to actual LMFBR fuels, these curves probably represent upper limits of nitriding to be expected under these conditions. From Figure A-4, the calculated maximum nitride depth after 10,000 hr at 700 C is <1 mil.

In BMI-1868 it was suggested that the nitriding reaction,

reversed at low temperatures, which could result in the formation of U_2N_3 on the surface of UN fuels during cooling of compatibility specimens. In support of this belief it was noted that such surface zones were observed on UN particles in UN-10 v/o U_2N_3 powders after cooling from 800 to 1000 C, as shown in Figure A-5. In addition, chemical analysis of layers machined from the Type 316 stainless steel claddings showed decreasing surface nitrogen content with increasing heat-treating temperature. This effect was reversed in the body of the cladding, and the nitrogen content of the cladding in general increased with the heat-treating temperature as expected. It was suspected that the reverse reaction had occurred during cooling to deplete nitrogen from the stainless steel surface and to form U_2N_3 on the fuel. Two additional heat treatments were conducted in an attempt to reverse the reaction under controlled conditions. Previously nitrided pieces of Type 316 stainless steel were heated with UN under sodium for 72 hr at 500 and 600 C. No metallographic evidence of the reverse reaction was observed; neither depletion of Cr_2N from the surface of the nitrided steel nor U_2N_3 formation on the UN were seen. It therefore appears that the reverse of Reaction (A-9) does not occur at a significant rate at 500 or 600 C. At lower temperatures it is improbable that the rate would be sufficient to produce a visible reaction during the times necessary for the cooling of compatibility capsules. It is concluded that the observations noted above are not caused by the reverse of Reaction (A-9) during cooling.

An alternative explanation for the U_2N_3 observed as a surface phase on UN in capsules heated at 800 and 1000 C is that the UN reacts with nitrogen held in the sodium and capsule plenum during cooling. At temperature, the decomposing U_2N_3 establishes an equilibrium nitrogen activity in the capsule atmosphere. As the temperature decreases during cooling, this nitrogen activity is greater than that in equilibrium with $(\text{UN} + \text{U}_2\text{N}_3)$ at the lower temperature. Therefore, U_2N_3 forms to decrease the activity of nitrogen in the sodium. The apparent depletion of nitrogen from the cladding surface is not explainable at present.

In contrast to hyperstoichiometric UN fuels, (U,Pu)N-based fuels that contain sesquinitride and (U,Pu) O_2 as minor phases show no detectable reaction with Type 316 stainless steel. Several specimens containing mixed-nitride fuel but without (U,Pu) O_2 have been fabricated, along with all the necessary capsule components for heat treating.

FIGURE A-3. NITROGEN PENETRATION INTO TYPE 316 STAINLESS STEEL HEATED WITH UN- U_2N_3 FUELS

The base-line nitrogen content of the stainless steel is
0.053 0.001 w/o.

FIGURE A-4. THE RATE OF Cr_2N FORMATION IN TYPE 316 STAINLESS STEEL HEATED WITH UN-10 v/o U_2N_3 POWDER

These are to be tested in order to more fully define the role of the sesquinitride in (U, Pu)N fuels.

An effort in support of the irradiation task was undertaken when the Type 304L stainless steel claddings of specimens from the thermal irradiation capsules were found to have failed at what were considered relatively low strains (i. e. , approximately 0.5 percent). It was uncertain whether the low ductility was characteristic of the particular cladding material, which had been prepared from rod stock by drilling, as contrasted with normally used commercial seamless tubing, or whether the rod had embrittled during irradiation, possibly as a result of contact with the nitride fuel. Consequently, burst tests were performed on tubing produced by drilling and on commercial seamless tubing to compare their ductilities. The test specimens, as illustrated in Figure A-6, were tubes having the following dimensions:

Inside diameter	0.361 in.
Outside diameter, ends	0.501 in.
Outside diameter, reduced section	0.391 in.
Reduced-section length	1-1/8 in.

After the electron-beam welding of end caps on one end, the specimen was connected to a source of argon with stainless steel fittings. Internal argon pressure was then applied at approximately 1500 psi per min by means of oil pressure on a piston, with this isostatic pressure being measured and recorded as a function of time by means of a transducer-recorder apparatus. After the pressure required to burst the tubing was observed, a second test specimen was pressurized to about 90 percent of the burst pressure and the plastic deformation, as manifested by the expansion in diameter, was measured. Although the final diameter of burst specimens could not be measured directly because the specimens were blown apart, a rough measure was obtained by measuring the circumferential length of the pieces. Tests were conducted at room temperature and 650 C, with total time at 650 C usually less than 15 min.

Data obtained from these tests are summarized in Table A-2, and tested specimens are shown in Figures A-7 and A-8. The results show that the commercial tubing was much more ductile and weaker than the drilled rod at both temperatures. The maximum ductility observed for the machined-rod tubing was <0.5 percent at either temperature, whereas the diameter expansion of the commercially fabricated tubing was 11 to 22 percent at room temperature, and 3 to 4 percent at 650 C.

Although the rupture-strength values of the commercial tubing corresponded reasonably well with those expected on the basis of tensile tests for fully annealed tubing⁽¹⁾, the observed ductility values were considerably lower. This was not unexpected in view of the multiaxial stress state encountered in a tube-burst test. In the case of the drilled rod, the rupture strength and microstructure corresponded to those of a slightly cold-worked structure (≈ 10 percent), and ductility was essentially nil, compared to room-temperature tensile elongations of about 40 percent as reported in the literature for tubing in this condition⁽¹⁾.

On the basis of these limited tests, it was concluded that the drilled-rod cladding exhibits an unusually low ductility not characteristic of normal commercial tubing. Consequently, an unusual embrittling effect during irradiation need not be considered in explaining the low-strain failures encountered in the cladding of nitride-fueled specimens.

500X

9D209

FIGURE A-5. UN-10 v/o U_2N_3 POWDERS SODIUM BONDED TO TYPE 316 STAINLESS STEEL FOR 3000 HR AT 800 C

Stained areas are UN while the white areas are U_2N_3 . The secondary U_2N_3 formation on the surface of the particle in the center of the field was not seen after 700 C heat treatments and became a continuous film after heat treatments at 1000 C.

~1X

FIGURE A-6. TUBE-BURST TEST SPECIMEN

~1X

FIGURE A-7. APPEARANCE OF TYPE 304L STAINLESS STEEL DRILLED-ROD SPECIMENS AFTER "BURST TESTING" AT ROOM TEMPERATURE (SPECIMENS 199 AND 200) AND 650 C (SPECIMENS 202 AND 203)

~1X

FIGURE A-8. APPEARANCE OF TYPE 304L STAINLESS STEEL COMMERCIAL TUBE SPECIMENS AFTER "BURST TESTING" AT ROOM TEMPERATURE (SPECIMENS 193 AND 194) AND 650 C (SPECIMENS 196 AND 197)

TABLE A-2. RESULTS OF BURST TESTS ON 15-MIL-WALL, TYPE 304L STAINLESS STEEL TUBE SPECIMENS

Specimen	Test Temperature, C	Maximum Gas Pressure, psi	Maximum Hoop Stress, ksi	Diameter Swelling, percent
<u>Commercial Tubing</u>				
193	Room	5200	62.4 ^(a)	22 ^(b)
194	Room	4500	54.0	11
196	650	2500	30.0 ^(a)	4 ^(b)
197	650	2200	26.4	3
<u>Drilled Rod</u>				
199	Room	8800	105.6 ^(a)	0 ^(b)
200	Room	7800	93.6	0
202	650	4600	55.2 ^(a)	0 ^(b)
203	650	4100	49.2	0.3

(a) Value also represents rupture stress, since tube ruptured.

(b) Value obtained by measuring length of irregular ruptured segment along circumference.

Plans for Future Work

Oxide-free, hyperstoichiometric, mixed-nitride fuel pellets will be assembled in sodium-bonded stainless steel capsules and heat treated for various times at 700 C. In addition, irradiation specimens will be examined as they are received and prepared at the Battelle-Columbus Hot-Cell Facility. Other compatibility studies pertinent to LMFBR's will also be performed as considered necessary.

(1) Metals Handbook, American Society for Metals (1961).

Chemical Analysis of Irradiation-Capsule Sodium Bonds

P. L. Morris, O. L. Kruger, and W. M. Pardue

Objective of Program

To develop a reliable analytical method for the determination of nitrogen in the sodium used to bond (U, Pu)N irradiation specimens.

Approach Being Used

The approach planned for this program included conduct of a literature search to review various methods reported for analysis of nitrogen in sodium. A cursory review had indicated that very few methods have been developed and that the reliability and accuracy of these techniques are not well defined. After completion of the literature search, an evaluation of the various methods was to be made to determine their adaptability to plutonium glove-box and hot-cell operations. If methods in the literature did not appear to be adaptable, attempts were to be made to develop a suitable analytical technique. Once a choice had been made, effort on the program was to be directed to the following:

- (1) Procurement or synthesis of standard sodium samples and their subsequent analysis for nitrogen to determine the accuracy and reliability of the method
- (2) Determination of the total nitrogen level in the high-purity sodium used to bond (U, Pu)N irradiation fuel specimens

- (3) Analysis of a sodium sample for nitrogen content before and after bonding with (U,Pu)N specimens in a fuel pin
- (4) Transfer of the technique to the Battelle-Columbus Hot-Cell Facility to evaluate the effect of irradiation on nitrogen pickup or transfer by the sodium.

Significant Accomplishments During Fiscal Year 1970

During this fiscal year, studies were conducted to evaluate a modified micro-Kjeldahl method for determining nitrogen in sodium. Sodium samples were dissolved quickly and safely in an ethyl alcohol-water mixture. A combined reagent and procedural blank was accurately determined. Standard solutions were analyzed and nearly 100 percent nitrogen recoveries were noted. Analysis of high-purity sodium samples "spiked" with nitrogen in the approximate range of 10 to 1000 ppm indicated that only "nitride" nitrogen could be accurately determined by this method. The simplicity of the method and apparatus indicate that the procedure can be readily adapted to hot-cell operations.

Summary of Research Carried Out

The work conducted during the fiscal year was directed toward development of a reliable analytical method for the determination of nitrogen in the sodium used to bond (U,Pu)N to metallic specimens claddings. Few reliable methods existed for this purpose and development of a good analytical technique was warranted to expand the understanding of possible (U,Pu)N fuel-cladding-sodium chemical reactions. Such an analysis would shed light on possible transfer mechanisms of materials in the system and permit a more complete understanding of fuel behavior during irradiation. Adaptability of the method to plutonium glove boxes and hot-cell operations was a prime consideration.

The initial effort of the program was directed toward a literature search of the reported methods of nitrogen analysis in sodium and a critical review of these methods. A modified Kjeldahl technique was chosen for further evaluation⁽¹⁾. This method is simple, does not require an ultrahigh-purity atmosphere, and reportedly assures 100 percent recovery of the "nitride" nitrogen in a sodium sample. Briefly, a sodium sample is decomposed to NaOH in an ethyl alcohol-water mixture under an argon purge, whereupon the nitrogen present reacts with the NaOH to form ammonia. Subsequently, the ammonia is collected by steam distillation and determined titrimetrically with standard acid. After selection of this method, a modified micro-Kjeldahl apparatus was designed and fabricated. The apparatus was constructed in such a manner as to allow dissolution of sodium samples under an argon purge to prevent any possibility of fire or explosion from the hydrogen evolved.

The initial experimental work was directed toward determining the combined reagent and procedural blank. This was necessary as the blank level establishes the lower limit of detection of the method. Ten blank runs, involving no sodium metal, were made and subsequently analyzed for nitrogen content. The average blank value of the ten determinations was 1.820×10^{-5} g of nitrogen. This value corresponds to 9.1 ± 2.5 ppm nitrogen in a 2-g sodium sample, which is the normal weight of sodium taken for analysis. This indicated that the minimum detection limit of the method is about 10 ppm nitrogen. Subsequently, nine samples of high-purity sodium (99.99 percent) were analyzed for nitrogen to determine the residual nitrogen content. These analyses were performed as a base line because the high-purity samples were used later to establish the accuracy of the method. Data from these analyses indicated an average nitrogen level of 16.3 ± 1.8 ppm. By subtraction, it can be seen that the average residual nitrogen content of the sodium was about 7.2 ± 3.1 ppm.

The next phase of experimental work was concentrated on establishing the reliability of the method. Solution standards containing 0.1 and 1.0 mg of nitrogen, respectively, were analyzed to determine the relative recoveries that could be expected. These data

indicated that at the 0.1-mg level the average nitrogen recovery of three standards was 97 percent and at the 1.0-mg level the average nitrogen recovery of six standards was 97.3 percent, suggesting that nearly 100 percent nitrogen recoveries can be expected employing this method.

At this point, high-purity sodium samples were "spiked" with "nitride" nitrogen in the form of aqueous NH_4Cl . The samples were then analyzed. Data from this experiment, summarized in Table A-3, indicated that "nitride" nitrogen can be completely and accurately recovered from sodium samples in the ranges studied.

TABLE A-3. RECOVERY OF NITROGEN FROM HIGH-PURITY SODIUM SAMPLES

Amount of Nitrogen Added ^(a) , ppm	Amount of Nitrogen Recovered ^(b) , ppm
1213	1202 ± 5
123	126 ± 4
11.3	10.5 ± 3.3

(a) Nitrogen added in form of NH_4Cl solution.

(b) Values corrected for blank and yield and indicating standard deviation.

The studies completed during Fiscal Year 1970 indicated that sodium can be analyzed for nitrogen content with a reasonable degree of confidence. It is emphasized that at this time the method is applicable only to "nitride" nitrogen. Sodium samples were dissolved rapidly without fire or explosions employing a modified micro-Kjeldahl apparatus. The method is sufficiently developed for transferral to the Battelle-Columbus Hot-Cell Facility to evaluate the effect of irradiation on nitrogen pickup or transfer by the sodium.

Plans for Future Work

No future work is planned on this program.

- (1) Ward, E. H., et al., "The Titrimetric Determination of Traces of Nitride Nitrogen in Sodium Metal", LA-2892 (April, 1963).

Diffusion in Nitrides

J. W. Droege and C. A. Alexander

Objective of Program

To investigate the self-diffusion behavior in nitride fuels of interest to LMFBR applications.

Approach Being Used

Initially the self-diffusion behavior of nitrogen in UN will be determined in the temperature range from 1360 to 1800 C and the nitrogen pressure range of 0.5 to 10 torr. An isotopic tracer technique using N^{15} is employed. The sample is sectioned electrolytically and the nitrogen evolved is analyzed with a mass spectrometer. The primary purpose of the program is to develop techniques that will then be usable to determine diffusion characteristics of (U, Pu)N materials.

Significant Accomplishments During Fiscal Year 1970

An electrolytic sectioning technique has been developed to give suitable results on sections as thin as 0.5μ . This makes possible the determination of diffusion coefficients of the order of 10^{-14} cm^2 per sec in reasonable annealing times. Diffusion anneals of UN under several conditions of temperature and pressure have yielded diffusion coefficients considerably lower than those previously obtained by others.

Summary of Research Carried Out

Diffusion anneals were carried out in a small furnace containing a cylindrical tungsten-mesh heater surrounded by molybdenum shields. The specimen was suspended inside the heater by a thermocouple of tungsten-3 w/o rhenium versus tungsten-26 w/o rhenium. The junction was formed by twisting the 5-mil wires together, and was located inside a hole passing through the specimen. Temperatures were controlled manually with an autotransformer. Gas was circulated through the furnace by a Toepler pump. The gas passed from the pump through a cold trap and over a bed of hot CaH_2 . In this way any oxygen leak was converted to hydrogen before passing over the annealing specimen.

The specimens used in this work were arc-melted UN of fairly large grain size. Figure A-9 shows Specimen 69-1 prior to experimentation. The small-grained material along the curved edge was removed and not used in the experiment. Examination showed that slight quantities of uranium and U_2N_3 were present. Each specimen was therefore equilibrated with nitrogen at 1800 C for at least 24 hr before the N_2^{15} was introduced. Each annealing period was preceded by a period at least 2-1/2 times as long using N_2^{14} at the same temperature and pressure.

FIGURE A-9. UN SPECIMEN 69-1 BEFORE EXPERIMENTATION

Note that the large grains are separated by wide cracks.

The range of homogeneity of UN is not well known with respect to concentration, although the equilibrium nitrogen pressures corresponding to the limits of this composition range are known. The effect of composition on the diffusion coefficient may be studied by carrying out the equilibrium and diffusion anneal at a series of pressures. This has been done at one temperature by Holt and Almassy⁽¹⁾. To extend the treatment

to other temperatures requires more information about concentrations than is now available, but one may estimate the pressure-temperature relationship at constant composition (isopleth) and so approximate the condition of constant composition in expressing the effect of temperature on the diffusion coefficient.

After conditions of pressure, temperature, and composition were established by suitable equilibration periods in N_2^{14} , the gas was replaced with N_2^{15} , which was then circulated during the annealing period. The gas was replaced with fresh N_2^{15} at intervals depending on the temperature and pressure, so that the N_2^{15} composition of the gas did not drop too far by exchange at the UN surface. The gas composition did fluctuate somewhat, however, especially at low pressure. At the end of the annealing period the temperature and pressure were dropped quickly, and the specimen was removed and mounted for electrolysis.

Anodic dissolution of UN, with an inert electrode as the cathode, produces a solution of uranium and gaseous nitrogen, requiring about 6 Faradays per gfw of UN. With some electrolytes, and generally at low current densities, electrolytic etching takes place, attacking the specimen preferentially at the grain boundaries. With suitable choice of electrolyte and current density electrolytic polishing, which tends toward a smooth surface, can be achieved. This condition is required for the present application. Even under polishing conditions the grain boundaries are attacked with some slight degree of preference. A suitable polishing solution was found to consist of 8 parts isopropyl alcohol, 5 parts ethylene glycol, and 5 parts H_3PO_4 (86 percent). A current density of about 80 ma per cm^2 was used. The specimen was mounted in a fixture using RTV silicone sealant to hold it in place and to define the area to be exposed to the electrolyte. The thoroughly outgassed electrolyte was admitted to the evacuated cell. The electrolysis was conducted at a constant current for a measured time. The gas produced, including nitrogen from the anode and hydrogen from the cathode, was pumped through a cold trap and into a sample bulb with a Toepler pump. These samples, consisting of about 100 cm^3 torr of gas, were analyzed with a mass spectrometer for mass peaks 28, 29, and 30. The thickness of each "cut" was determined from the exposed area, the density of UN, and the number of coulombs passed in the electrolysis, together with the previously established relationship between coulombs and mass of UN dissolved.

The concentration, C , of N_2^{15} was plotted on probability paper and extrapolated to zero penetration to find the concentration at the surface, C_0 . Since the useful depth of penetration was of the order of 10 μ or less, the surface could be considered planar, even if the specimen had some curved surfaces. The applicable diffusion equation is

$$C/C_0 = \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \quad , \quad (A-10)$$

where x is distance from the surface (cm), t is time (sec), and D is the diffusion coefficient. From tables of the error function, $x/2\sqrt{Dt}$ was evaluated for each value of C . This quantity was plotted as a function of x . Figure A-10 shows an example. D was obtained from the slope. The results follow the straight line well for the first few μ . At greater distances the deviations are larger. At these greater distances from the surface the concentrations of mass 29 and mass 30 remain higher than expected. It is suggested that this is probably due to penetration of the cracks between grains by the electrolyte, releasing N^{15} which had reached far into the specimen through cracks and grain-boundary diffusion.

Some of the results are summarized in Table A-4. By estimating pressure-temperature relationships within the homogeneity range of UN it is presumed that Specimens 69-2 and 66d were at the same composition while Specimens 69-1 and 66c contained less nitrogen. The first two results are somewhat in doubt because of the possibility of evaporation from the surface. Specimen 66c was annealed with an over-pressure of argon to prevent this. Preliminary experiments without this precaution

showed evidence of evaporative loss of UN. There are also some indications of oxygen contamination, including a dull surface appearance in some cases and the release of some oxygen during the electrolysis. Figure A-11 shows a comparison of the results with those obtained by Sturiale and DeCrescente⁽²⁾ and by Holt and Almassy⁽¹⁾. The results lie well below those found previously. No explanation for the discrepancy is offered, especially since the latter authors used a similar technique, though the analytical method was much different. The two results at 1800 C show the effect of nitrogen pressure, and therefore of composition, on the diffusion coefficient. The effect is similar to that reported by Holt and Almassy at higher pressures and temperature.

TABLE A-4. ANNEALING CONDITIONS AND RESULT OF NITROGEN SELF-DIFFUSION IN UN

Specimen	Anneal Temperature, C	Anneal Time, hr	Nitrogen Pressure, torr	Diffusion Coefficient, cm ² per sec
66c	1800	12.4	0.5(a)	7.4×10^{-12}
69-1	1800	2	7	1.0×10^{-11}
69-2	1360	48	0.5	1.1×10^{-13}
66d	1580	48	10	3.7×10^{-12}

(a) Plus 9.5 torr argon.

Plans for Future Work

Modifications required for removal of the apparatus to the Battelle-Columbus Plutonium Laboratory will be made. These include principally some modifications of the techniques for handling and mounting the specimen. Work will then proceed with UN-PuN specimens.

(1) Holt, J. B., and Almassy, M. Y., J. Am. Ceram. Soc., 52, 631-635 (1969).

(2) Sturiale, T. J., and DeCrescente, M. A., "Self Diffusion of Nitrogen in Uranium Mononitride", PWAC-477 (September, 1965).

Bonding of Nitride Fuels and Cladding Materials by Sodium

R. B. Clark, O. L. Kruger, and W. M. Pardue

Objective of Program

To ascertain the influence of temperature, time, and gaseous atmosphere on the ability of liquid sodium to wet nitride fuel materials and various cladding materials of interest to LMFBR applications.

Approach Being Used

Initially, sessile-drop experiments will be performed over the temperature range from 100 to 700 C for sodium on Type 316 stainless steel and vanadium alloys and for sodium on high-density (U, Pu)N and possibly (U, Pu)O₂. These experiments will be performed in a glove box designed to contain an atmosphere of high-purity helium needed for sodium investigations. The atmosphere of the glove box will be monitored continuously for oxygen and water-vapor content. Contact angles between the liquid sodium and the fuel or cladding will be measured at selected temperatures and for various combinations of time at temperature. The wetting of the nitrides and claddings by the sodium will be

FIGURE A-10. N_2^{15} PENETRATION INTO UN SPECIMEN 69-2 ANNEALED AT 1360 C FOR 48 HR

FIGURE A-11. SELF-DIFFUSION COEFFICIENT FOR NITROGEN IN UN

recorded by photographic techniques for each of the various experimental conditions. Measurements are to be made during both heating and cooling cycles.

Significant Accomplishments During Fiscal Year 1970

Initial wetting studies of sodium on various fuel and cladding materials indicated that discrepancies in behavior can be expected when certain conditions are not properly controlled. In subsequent measurements it was found that sodium wets all of the materials studied between 350 and 500 C since it forms contact angles of less than 90 deg in this temperature range. Generally metals and alloys were wetted by sodium at lower temperatures than were ceramics. The contact angle-temperature relationship was non-reversible for all the materials studied since no dewetting was observed under any cooling conditions. No reactions or intergranular attack by the sodium was seen in the materials studied except for the (U,Pu)O₂, where spalling occurred at temperatures near 450 C. This work has shown that disintegration of the mixed-oxide surface by sodium takes place at low temperatures. Further studies on mixed oxides are recommended in support of the fast-reactor fuels program. It was also found that different lots of sodium do not have the same wetting characteristics on solid surfaces, particularly at low temperatures. This behavior has been attributed to the low solubility limits of various impurities such as oxygen in the sodium at the lower temperatures. At higher temperatures the solubility limits of sodium increase in such a manner that larger amounts of impurities are taken into solution, and the resulting data on various lots of sodium tend to fall closer together. Extrapolation of the contact angle-temperature curves, beyond the point where sodium volatilization occurs, to a contact angle of zero indicates that complete wetting would occur between about 600 and 650 C for all of the materials studied. This result, when analyzed in terms of the maximum size of bubble that can be formed at these temperatures, indicates that heat transfer and fission-gas release in sodium-bonded fuels is not a particularly acute problem.

Summary of Research Carried Out

Sodium wetting tests were performed to ascertain the influence of temperature, time, and gaseous atmosphere on the ability of liquid sodium to wet nitride fuel and various cladding materials of interest to the LMFBR program. The technique that seemed to lend itself most readily for measuring the contact angles of sodium on various materials was the sessile-drop method; further, these data are considered to be necessary in order to fully understand the parameters required for optimum bonding of fuel pins.

The fuel and cladding materials that were studied are shown in Table A-5. The wetting of sodium on an oxide, (U,Pu)O₂, was studied to determine the effect of an oxide layer which might exist on (U,Pu)N fuel. Three batches of sodium (designated Sodium 1, 2, and 3 in Table A-5) were investigated since early work showed that the results obtained from the initial experiments using various sources of sodium were slightly different. The same experimental technique was used throughout this work so as not to introduce another variable which would have to be factored into the analysis. Time and total effort considerations prevented a complete chemical analysis of the different lots of sodium; this is needed to obtain a better interpretation of the difference in the data.

Because of the high reactivity of the sodium, all wetting tests were performed in a glove box containing a high-purity helium atmosphere. Figure A-12 is a schematic drawing of the experimental setup. Initial experiments performed in a glove box indicated that the atmosphere contained some impurities which formed a white film on exposed sodium over a period of several minutes at the elevated testing temperatures. Various experimental procedures were employed to reduce the contamination problem, including high gas purge rates, but none were totally effective. To circumvent the contamination problem, a 6-in.-long stainless steel extension was adapted to the sodium extruder to permit direct loading of the sodium onto the substrate which was placed within the quartz tube of the sessile-drop apparatus. This tube was purged rapidly with ultrahigh-purity helium

FIGURE A-12. SCHEMATIC DIAGRAM OF THE SESSILE-DROP APPARATUS

so there was no possibility for the sodium to become contaminated during the transfer. When handled in this manner, the sodium appeared to stay very clean for the entire experimental run.

TABLE A-5. MATERIALS USED IN SODIUM WETTING STUDY

Fuel Materials
UN, hot pressed, 96 percent of theoretical density
$(U_{0.8}Pu_{0.2})N$, hot pressed, 95 percent of theoretical density
$(U_{0.92}Pu_{0.08})O_2$ sintered, 95 percent of theoretical density
Cladding Materials
Type 304 stainless steel
Type 304L stainless steel
Type 316 stainless steel
Vanadium-15 w/o titanium-7.5 w/o chromium
Vanadium-15 w/o chromium-5 w/o titanium
Sodium
Sodium 1, Battelle distilled
Sodium 2, Battelle distilled
Sodium 3, Gallard-Schlesinger Chemical Company

Cleanliness of the apparatus was imperative and all parts of the apparatus that came in contact with sodium were thoroughly cleaned and outgassed before any tests were made. Initial wetting tests showed that the state of the solid substrate surfaces greatly affected the wetting behavior. It was found that thorough cleaning and high-temperature vacuum outgassing gave the best wetting results. Each substrate surface was also polished in the high-purity helium atmosphere of the glove box with 600-grit paper immediately before loading into the sessile-drop apparatus to insure an initial oxide-free surface.

Isothermal tests of contact angle as a function of time at constant temperature were made in a helium atmosphere to determine the time necessary for equilibrium to be achieved. These tests showed that the drop assumed an equilibrium shape within 5 min at constant temperature since no change in contact angle was observed during longer periods of time. The only exception to this was in the very high temperature range, where volatilization of the sodium caused a change in drop size.

The isothermal results suggested that because of the comparatively small effect of time on the contact angle, except at high temperatures, true contact angle-temperature measurements could be made with sufficient accuracy by increasing the furnace temperature and holding the specimen for 5 min at constant temperature before measuring. A series of silhouette photographs was taken to give good contrast for contact-angle determinations.

A total of 33 sodium wetting experiments were performed. As a result of some of the early contamination problems only about 12 of these generated data acceptable for final reporting. Figures A-13 through A-16 are typical silhouette photographs taken for some of the materials studied. The wetting behavior of sodium on $(U, Pu)N$ is shown in Figure A-13. The sodium begins to visibly melt at 114 C but the sessile drop does not form until a temperature of about 210 C is reached. The drop does not change shape appreciably until a temperature of about 400 C is reached, where the contact angle begins

FIGURE A-13. CHANGE IN THE SODIUM/(U, Pu)N CONTACT ANGLE AT VARIOUS TEMPERATURES

FIGURE A-14. CHANGE IN THE SODIUM/UN CONTACT ANGLE AT VARIOUS TEMPERATURES

FIGURE A-15. CHANGE IN THE SODIUM/TYPE 316 STAINLESS STEEL CONTACT ANGLE AT VARIOUS TEMPERATURES

FIGURE A-16. CHANGE IN THE SODIUM/VANADIUM-15 w/o CHROMIUM-5 w/o TITANIUM CONTACT ANGLE AT VARIOUS TEMPERATURES

to sharply decrease. Wetting characteristics of sodium on UN (see Figure A-14) follow the same pattern as on (U, Pu)N; i. e., the sodium begins to wet the UN ($\theta < 90$ deg) at 455 C. Data for a typical run of sodium on Type 316 stainless steel can be seen in Figure A-15. The last photograph in this figure was taken after cooling to room temperature to determine whether dewetting occurred. The observed contact angle had decreased, probably because of an increase in temperature before cooling had started. Under no conditions was dewetting observed for the materials studied. Photographs showing the wetting behavior of sodium on vanadium-15 w/o chromium-5 w/o titanium are given in Figure A-16. The same type of contact angle-temperature relationship as was seen for the other materials is apparent.

The wetting behavior of the three batches of sodium mentioned previously is compared in Figures A-17 and A-18 for the UN and (U, Pu)N materials, respectively. The lower curve in Figure A-17 was generated using Sodium 1, the middle curve with Sodium 2, and the upper curve with the commercially purchased sodium. The curves are similar in shape but the data for the last two batches of sodium are displaced up and to the right. The curve for Sodium 2 in Figure A-18 is also displaced up and to the right, which is consistent with what was seen in Figure A-17. These results indicate that the differences among the curves are the result of actual differences in sodium and not in the experimental technique, since the relative positions of the curves with respect to the three types of sodium were consistent with all other substrate materials studied. Since volatilization was known to be occurring at the higher temperatures, Run 29 in Figure A-18 was purposely held at approximately 530 C for a period of about 30 min, after which the contact angle had decreased to zero. This behavior was obviously not due to equilibrium wetting but to volatilization of the sodium, since spreading was not simultaneously occurring.

Taylor and Ford⁽¹⁾ of Harwell did a study in 1955 of contact-angle relationships for sodium on various solids. Their results for stainless steel are compared to the Battelle data in Figure A-19. The relative position of the curves as a function of sodium is the same as was shown previously for UN and (U, Pu)N. This trend of behavior among different sodium batches appears to be much greater at the lower temperatures, where the curves are displaced the furthest with respect to one another. In the higher temperature regions, the contact angles tend to fall closer together, which suggests that the disparity among various batches of sodium would not cause a great deal of concern under reactor operating temperatures. Taylor and Ford show that the contact angle for sodium on stainless steel does not go below 60 deg, which by analogy with the data presented here can be attributed to contamination of the sodium. This type of behavior is typical of results first obtained at Battelle when the atmosphere was not purified to the extent later found to be required for this work.

Curves showing the wetting characteristics of Sodium 2 on vanadium-15 w/o titanium-7.5 w/o chromium and vanadium-15 w/o chromium-5 w/o titanium are given in Figure A-20. Both alloys appear to be completely wetted by the sodium between 540 and 660 C. There appears to be some indication that titanium would be wetted by sodium at a somewhat lower temperature than chromium; however, further work would be necessary to show this more conclusively. The wetting behavior of Types 304 and 316 stainless steel, UN, and (U, Pu)N is very similar to that of the vanadium alloys, as can be seen in Figure A-21. It appears that Types 304 and 316 stainless steel behave in a nearly identical manner, whereas the UN appears to be wetted more readily by sodium than does the mixed nitride, (U, Pu)N. In general, it was found that the metals are more readily wetted than the ceramic fuel materials.

The wetting of sodium on (U, Pu)O₂ was carried out to determine the effects of an oxide surface layer which might form on (U, Pu)N fuel. Because of the potentially high interfacial tension between sodium and most oxide materials, it was expected that mixed-oxide fuel would not be as readily wetted by the sodium. However, the two curves shown in Figure A-22 do not verify this; an entirely unexpected result was obtained. In both

FIGURE A-17. TEMPERATURE EFFECTS OF VARIOUS BATCHES OF SODIUM ON THE WETTING OF UN

FIGURE A-18. TEMPERATURE EFFECTS OF VARIOUS BATCHES OF SODIUM ON THE WETTING OF (U, Pu)N

FIGURE A-19. TEMPERATURE EFFECTS OF VARIOUS BATCHES OF SODIUM ON THE WETTING OF TYPE 304 STAINLESS STEEL

FIGURE A-20. TEMPERATURE EFFECTS OF SODIUM 2 WETTING ON VANADIUM ALLOYS

FIGURE A-21. TEMPERATURE EFFECTS OF SODIUM 2 WETTING ON VARIOUS FUEL AND CLADDING MATERIALS

FIGURE A-22. TEMPERATURE EFFECTS OF SODIUM 2 WETTING ON $(U,Pu)O_2$

cases an examination of the oxide-sodium interface after cooling indicated that a reaction or disintegration of the oxide surface had occurred. This reaction explains the differences between the two curves. Microstructures showing a typical, as-prepared interface and an interface examined after testing are given in Figure A-23. As can be seen, there is a general erosion and spalling of the surface after contact with sodium at these low temperatures. These results indicate that mixed-oxide fast-reactor fuels which are operated at considerably higher temperatures than investigated here might react spontaneously if they come into contact with the sodium coolant.

In general, for all of the materials studied, the contact angle-temperature curves can be divided into three areas. One occurs below the knee where the spreading of sodium becomes very sensitive to a change in temperature. Another occurs above the knee at lower temperatures where the slope of the curve is much lower. The third area is where the curve again changes slope and the contact angle is approaching the abscissa of the plot. In this region the contact-angle measurement is affected somewhat by volatilization of the sodium.

The following conclusions have been made regarding this work:

- (1) Sodium wets all of the materials studied between 350 and 500 C since it forms contact angles of less than 90 deg between these temperatures.
- (2) Sodium tends to wet metals and alloys at lower corresponding temperatures than ceramics.
- (3) The manner in which the solid surface of a fuel or cladding material is prepared before sodium loading can affect the manner in which sodium will wet its surface.
- (4) The contact angle-temperature relationship is nonreversible, since no dewetting was observed under any cooling conditions.
- (5) No reactions or intergranular attack by the sodium appear to occur in the materials studied except for the mixed oxide. Further studies of the wetting characteristics of mixed-oxide fuels are recommended in support of the fast-reactor fuels program.
- (6) Different lots of sodium do not wet solid surfaces the same particularly at low temperatures. This may be the result of the low solubility limits of various impurities such as oxygen in the sodium at the lower temperatures. At higher temperatures, where the solubility limits of sodium increase, the differences in wetting characteristics of the various batches of sodium were reduced significantly.
- (7) Extrapolation of the contact angle-temperature curves to $\theta = 0$ indicates that complete wetting of all the materials would occur between about 600 and 650 C.

Plans for Future Work

No further work is planned on this program.

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- (1) Taylor, J. W., and Ford, S. D., "Solid Metal-Liquid Metal Interaction Studies, Part II: Contact Angle Relationships for Sodium Angle of Solids", AERE-M/R-1729 (November 19, 1955).

Fabrication and Cladding ($U_{0.8}Pu_{0.2}$)N Thermal Irradiation Specimens

W. T. Langendorfer, M. D. Houston, E. O. Speidel, and O. L. Kruger

Objective of Program

To fabricate ($U_{0.8}Pu_{0.2}$)N pellets by powder metallurgical techniques and to clad them for use in irradiation experiments designed to evaluate fuel performance under thermal flux conditions.

250X

As Polished

PL7843

a. Typical As-Prepared $(U, Pu)O_2$ Substrate

250X

As Polished

PL7844

b. Inner Area of $(U, Pu)O_2$ Substrate That Was in Contact With SodiumFIGURE A-23. MICROSTRUCTURE OF $(U, Pu)O_2$ SUBSTRATE BEFORE AND AFTER REACTION WITH SODIUM

Approach Being Used

Sintering techniques are being used to fabricate ($U_{0.8}Pu_{0.2}$)N pellets of controlled density, size, and microstructure. Design variables in the thermal irradiation capsules include fuel density, bonding medium, and total diametral fuel-cladding gap.

Powders of the nominal fuel composition are ball milled to reduce the particle size, cold pressed in hardened steel dies, and sintered to pellets that are within ± 2.0 percent of the design densities. The final tolerances on diametral measurements for encapsulation are achieved by centerless grinding after sintering, if required. The pellets are right circular cylinders nominally 0.225 in. in diameter and are stacked to provide fuel specimens 0.75 in. long. Control pellets are characterized with respect to density, microstructure, chemistry, and purity.

The fuel pellets are encapsulated in Type 316 stainless steel cladding with sodium or helium as a heat-transfer medium in the annulus between fuel and cladding. The stainless steel cladding is first machined to dimensional specifications and an end plug is welded into one end of each tube prior to the fuel loading operation. All components are introduced into a glove box which contains a high-purity helium atmosphere.

For helium-bonded specimens, the components are assembled in the purified glove-box atmosphere and sealed by Heliarc welding the second end plug into position. Subsequent decontamination and inspection operations are performed as outlined previously in BMI-1809. The procedure for sodium bonding is similar except that the glove-box atmosphere is analyzed for oxygen content before introducing the sodium. The fuel cladding containing the mixed-nitride pellets is then heated to 300 C and a predetermined quantity of sodium is melted to fill the gap around the fuel specimens. An internal spacer is introduced and the second end plug is welded into position. Massive chill blocks are utilized during the welding procedure to prevent sodium boiling. To assure a continuous sodium bond, each fuel pin is heated to a temperature in excess of the melting point of sodium and centrifuged. The fuel pins are inspected by radiographic and eddy-current techniques to determine the weld penetration, the position and condition of the fuel pellets, and the integrity of the sodium bond.

Significant Accomplishments During Fiscal Year 1970

The fabrication, machining, and cladding of ($U_{0.8}Pu_{0.2}$)N pellets for Capsule BMI-50-12 and the characterization of control pellets were completed.

Summary of Research Carried Out

Work was devoted primarily to the fabrication of solid-solution ($U_{0.8}Pu_{0.2}$)N pellets for irradiation testing. Design variables are summarized in Table A-6. Dimensional, density, and encapsulation data for Capsule BMI-50-12 are summarized in Table A-7.

All fuel specimens were fabricated from nominal ($U_{0.8}Pu_{0.2}$)N powders synthesized using a hydride-nitride cycle on arc-cast uranium-20 w/o plutonium buttons. The as-synthesized powders were wet ball milled for 32 hr in a uranium-lined mill containing tungsten carbide-cobalt balls and nanograde hexane as the milling media. The ball-milled powders were vacuum dried to remove the hexane, and then pressed into pellet form in hardened steel dies using a pressure of 10 or 15 tsi with zinc stearate as a die lubricant. Each cold-pressed pellet had a length-to-diameter ratio of approximately 1 and a density approximately 50 percent of theoretical.

Low-density pellets were pressed at 10 tsi and sintered at 1700 C under 1 atm of nitrogen for a total of 6 hr. High-density pellets were pressed at 15 tsi and sintered for a total of 10 hr at 2100 C under 1 atm of nitrogen. Typical microstructures of the low-density and high-density pellets are shown in Figures A-24 and A-25, respectively.

TABLE A-6. DESIGN VARIABLES FOR EACH (U_{0.8}Pu_{0.2})N FUEL CAPSULE BMI-50-12

Fuel Specimen	Density, percent of theoretical	Bonding Medium	Radial Gap Width, mils
1	95 ± 2(a)	Helium	2.5 ^{+1.0} -0.0
2	85 ± 2	Helium	2.5 ^{+1.0} -0.0
3	95 ± 2	Sodium	10.0 ± 0.5
4	85 ± 2	Sodium	10.0 ± 0.5
5	95 ± 2	Sodium	20.0 ± 0.5
6	95 ± 2	Sodium	20.0 ± 0.5

(a) Pellets will contain a 0.060-in. annular void to determine the effect of this type of porosity on accommodating fuel swelling during irradiation.

TABLE A-7. DATA FOR (U_{0.8}Pu_{0.2})N IRRADIATION PELLETS PREPARED FOR CAPSULE BMI-50-12

Specimen	Pellet	Outside Diameter, in.	Pellet Density, percent of theoretical	Bonding Medium	Radial Gap Width, mils
1	A-29-11	0.2250(a)	93.0	Helium	2.5 ^{+1.0} -0.0
	A-29-12	0.2250(a)	94.0		
	A-29-43	0.2250(a)	94.9		
	A-29-44	0.2250(a)	95.4		
2	A-29-53	0.2250	84.4	Helium	2.5 ^{+1.0} -0.0
	A-29-56	0.2250	84.1		
	A-29-64	0.2250	84.4		
	A-29-65	0.2250	84.3		
3	A-29-18	0.2249	94.8	Sodium	10.0 ± 0.5
	A-29-25	0.2249	94.6		
	A-29-26	0.2249	94.2		
	A-29-27	0.2249	94.8		
4	A-29-66	0.2250	84.3	Sodium	10.0 ± 0.5
	A-29-68	0.2250	84.5		
	A-29-69	0.2250	84.4		
	A-29-67	0.2249	84.5		
5	A-29-29	0.2249	94.7	Sodium	20.0 ± 0.5
	A-29-32	0.2249	94.7		
	A-29-36	0.2249	94.1		
	A-29-49	0.2249	93.6		
6	A-29-14	0.2248	94.7	Sodium	20.0 ± 0.5
	A-29-31	0.2248	94.1		
	A-29-42	0.2248	94.5		
	A-29-46	0.2248	95.0		

(a) Pellet contains a 0.060-in. -diameter annular void.

500X

PL7430

a. As Polished

500X

PL7431

b. Etched

FIGURE A-24. MICROSTRUCTURE OF LOW-DENSITY $(U_{0.8}Pu_{0.2})N$ PELLET
Pellet A-29-73 is shown.

500X

PL7408

a. As Polished

500X

PL7414

b. Etched

FIGURE A-25. TYPICAL MICROSTRUCTURES FOR HIGH-DENSITY (U_{0.8}Pu_{0.2})N PELLETS
Pellet A-29-19 is shown.

Characterization of the $(U_{0.8}Pu_{0.2})N$ densified pellets involved density measurements, with representative metallography and chemical analyses performed on control pellets. Analyses for control pellets are shown in Tables A-8 and A-9.

Type 316L stainless steel was selected as the cladding for these specimens and the chemical analysis of this material is shown in Table A-10. The fuel and cladding details for each specimen in Capsule BMI-50-12 are given in Table A-11. The loading and welding operations were carried out according to procedures described above. Subsequent qualifying tests, radiographs, and leak checks, indicated that each fuel specimen was acceptable for irradiation.

Plans for Future Work

Preparation of specimens for one capsule, BMI-50-13, is anticipated for Fiscal Year 1971.

Thermal Irradiation Studies of Nitride Fuels

E. O. Fromm, N. E. Miller, and J. W. Ray

Objective of Program

To irradiate UN-PuN fuels to burnups of 150,000 MWD/T at fission-heat-generation rates and temperatures typical of sodium-cooled fast-reactor operations.

Approach Being Used

A series of irradiation-capsule experiments involving $(U_{0.8}Pu_{0.2})N$ specimens is planned for exposure in the high-flux facilities of the ETR or MTR. The guiding criteria include:

- (1) Specimen temperature levels up to 700 C at the cladding surface
- (2) Fuel diameters of about 0.225 in.
- (3) Fission heat generation up to 40 kw per ft of fuel pin
- (4) Fuel burnup levels of 40,000 to 150,000 MWD/T.

The program includes design, construction, and loading of capsules, monitoring of the irradiation, and interpretation of the conditions of irradiation.

Significant Accomplishments During Fiscal Year 1970

The irradiation of Capsules BMI-50-6, BMI-50-8, and BMI-50-10 was continued. One new capsule, designated BMI-50-11, was assembled and sent to the ETR for irradiation beginning in December, 1969 (Cycle 105). This capsule was designed to operate at fission rates of 40 kw per ft with cladding surface temperatures of nominally 700 C. It was irradiated for two ETR cycles and discharged at the end of May, 1970, along with Capsule BMI-50-6 and returned to Battelle-Columbus for postirradiation examination. All of the components for Capsule BMI-50-12 were fabricated and, with insertion of fuel specimens, assembly was begun. This capsule is of the same design as Capsule BMI-50-11.

Summary of Research Carried Out

Each of the BMI-50-series irradiation capsules has contained six $(U_{0.8}Pu_{0.2})N$ fuel specimens (in pellet form) 0.225 in. in OD by 0.75 in. long contained in 0.015-in.-thick claddings of Type 304L stainless steel and having either a helium bond, a 10-mil sodium bond, or a 20-mil sodium bond between the fuel and cladding. Two clad specimens with the same type of bond are immersed in sodium within a thick-walled can. Three such cans are seal welded end to end to form a three-compartmented specimen container. Holes for six sheathed thermocouples are drilled longitudinally in the thick wall to accommodate thermocouples for monitoring specimen temperatures. One thermocouple junction is located adjacent to the midsection of each fuel specimen. Heat transfer

TABLE A-8. RESULTS OF VARIOUS ANALYSES OF (U_{0.8}Pu_{0.2})N FUEL PELLETS^(a)

Pellet	Nominal Density, percent of theoretical	Vacuum-Fusion Results, ppm		Nitrogen Content, w/o	Carbon Content, ppm	Wet-Chemical Results, w/o	
		Oxygen	Hydrogen			Uranium	Plutonium
A-29-4	95	292 ± 6	1 ± 1	NA	NA	NA	NA
A-29-5	95	90 ± 4	7 ± 1	5.35	NA	NA	NA
A-29-7	95	NA	NA	NA	200	NA	NA
A-29-8	95	NA	NA	NA	200	NA	NA
A-29-34	95	NA	NA	NA	NA	79.8	20.2
A-29-37	95	NA	NA	5.35	NA	79.4	20.6
A-29-51	85	176 ± 6	1 ± 1	5.45	NA	NA	NA
A-29-52	85	41 ± 2	26 ± 1	NA	NA	NA	NA
A-29-54	85	NA	NA	NA	110	NA	NA
A-29-55	85	NA	NA	NA	140	NA	NA
A-29-61	85	NA	NA	NA	NA	79.4	20.6
A-29-62	85	NA	NA	NA	NA	79.5	20.5
A-29-74	85	NA	NA	5.48	NA	NA	NA

(a) NA = not analyzed.

TABLE A-9. RESULTS OF EMISSION SPECTROGRAPHIC ANALYSES ON (U_{0.8}Pu_{0.2})N FUEL PELLETS

Pellet	Nominal Density, percent of theoretical	Impurity Content, ppm																
		Cu	Ag	Na	Mo	Sn	Ni	Mg	Mn	Pb	B	Al	Bi	Ca	Cr	Fe	Zn	W
A-29-37	95	<3	<0.3	<10	<5	<10	<10	<10	5	3	<0.3	30	<3	5	<10	<10	1	3
A-29-61	85	<3	<0.3	5	<1	<10	<5	<10	3	3	<0.3	30	<3	<1	<1	<10	1	3

TABLE A-10. CHEMICAL ANALYSIS OF TYPE 316L STAINLESS STEEL
CLADDING FOR THERMAL FUEL ENCAPSULATION

Element	Chemical Analysis, w/o	AISI Specifications, w/o
Aluminum	0.007	-
Boron	<0.001	-
Carbon	0.02	0.03
Chromium	17.0	17.00
Cobalt	0.04	-
Copper	0.07	-
Magnesium	<0.001	-
Manganese	1.69	2.00
Molybdenum	2.80	2.50
Nickel	13.60	12.00
Phosphorus	0.023	-
Silicon	0.47	1.00
Sulfur	0.012	-
Titanium	<0.001	-
Zirconium	0.001	-

TABLE A-11. SUMMARY OF FUEL AND CLADDING DATA FOR CAPSULE BMI-50-12

Fuel Specimen	Cladding Dimensions, in.			Fuel Average Dimensions ^(a) , in.		Total Fuel Weight, g	Average Density ^(a) , percent of theoretical	Bonding Medium
	OD	ID	Length	Diameter	Length			
D-2	0.260	0.230	1.770	0.225	0.700 ^(b)	5.9222	94.3	Helium
D-4	0.260	0.230	1.748	0.225	0.776	5.8768	84.3	Helium
E-1	0.275	0.245	1.780	0.225	0.752	6.5780	94.6	Sodium
E-2	0.275	0.245	1.770	0.225	0.747	5.8497	84.4	Sodium
H-2	0.295	0.265	1.775	0.225	0.747	6.5029	94.3	Sodium
H-3	0.295	0.265	1.766	0.225	0.751	6.5679	94.6	Sodium

(a) Total of four ($U_{0.8}Pu_{0.2}$)N pellets for each fuel specimen.

(b) Pellets have a 0.060-in. -diameter annular hole.

from the inner specimen container is through, successively, a 25-mil sodium annulus, a Hastelloy-X heater shell, another 25-mil sodium annulus, an "A" Nickel finned shell, and an "A" Nickel outer shell. The circumferential fins, which are only in the region adjacent to each fuel pin, make an interference fit with the outer shell. Since the heat-transfer path to the outer capsule wall is essentially fixed, the fuel temperature is governed by the heating rate of the fuel. In Capsules BMI-50-4 through BMI-50-10, the specimen container was "A" Nickel, which gave a temperature of about 600 C at the surface of the cladding of the helium-bonded specimen for a fuel-pin power rating of 30 kw per ft. In Capsule BMI-50-11, niobium-1 w/o zirconium was utilized for the specimen container to allow the heating rate to be increased to 40 kw per ft with a temperature of about 700 C on the surface of the cladding of the helium-bonded specimen. Electric heaters brazed into grooves in the heater shell keep the sodium molten in the various annuli during reactor startup. In addition, temperature-control capability up to 45 C is provided by the heaters. For added temperature control, the capsule is moved to different flux-level positions.

Capsule BMI-50-6 was the first of the BMI-50 series to be irradiated in the ETR and was inserted into a position (P-12-SW) with a neutron flux less than that required for design conditions in order to check out the operation at full reactor power. Subsequently, this capsule was moved to higher flux positions to obtain higher burnup rates and fuel temperatures, as indicated in Table A-12. The capsule was discharged in April, 1970 (at the end of ETR Cycle 106), with estimated fuel burnups of 102,000 to 157,000 MWD/T as shown in Table A-12. The variations in calculated burnups can be attributed in part to uncertainties introduced in estimates of burnup rates for some of the specimens because of thermocouple failures, which made it necessary to extrapolate temperatures (and burnups) for associated specimens from thermocouple data for adjacent specimens. The capsule was returned to Battelle-Columbus in May, 1970, for postirradiation examination.

Capsule BMI-50-8 was inserted in the aluminum reflector region of the ETR (P-9-SW) in July, 1968 (Cycle 97), where design irradiation conditions were achieved. However, as the irradiation progressed the fission rate continually declined, and the capsule was relocated into a higher flux position (E-5-NE) in July, 1969. Temperatures in the new position reflected the increase in flux level. The thermocouple opposite Specimen A-26 failed during January, 1970 (Cycle 106A), and the surface temperature for this specimen was extrapolated from thermocouple data from the adjacent specimen, A-25. In general, the specimen temperatures were below desired levels during Cycle 106 (January through April, 1970) and it was decided to relocate the capsule to a higher flux position for the next ETR cycle. Consequently, the capsule was moved into a new position (F-4) for Cycle 107. Preliminary temperatures during initial startup for the cycle in the new position indicated heating rates of about 35 kw per ft. Temperature data for Cycles 102 through 106B are given in Table A-13.

Capsule BMI-50-10 began irradiation in the corner of the reactor core (E-5-NW) during May, 1969 (ETR Cycle 102). The performance during the first cycle of irradiation was excellent, with the specimens operating in the range of 660 to 730 C with heating rates from 27 to 31 kw per ft. However, temperatures during the following cycles were much lower than for the first cycle because of the shielding effect of a new experiment in the companion facility, E-5-NE. It was not possible to relocate the capsule to a higher flux facility until April, 1970 (at the end of Cycle 106). At this time the capsule was moved into Position E-5-NE. Preliminary temperature data during startup for Cycle 107 (June, 1970) indicated heating rates of about 35 kw per ft. Specimen temperatures and burnup data for Cycles 102 through 106B are given in Table A-14.

Capsule BMI-50-11 was assembled and sent to the ETR for irradiation in a beryllium-reflector position (M-4) beginning in December, 1969 (Cycle 105). Temperatures during the cycle indicated fuel-pin power ratings of nominally 50 kw per ft with

TABLE A-12. SPECIMEN TEMPERATURES FOR CAPSULE BMI-50-6

ETR Cycle	Starting Date	Type of Temperature Data	Temperatures for Indicated Specimens ^(a) , °C					
			A-4	A-3 ^(b)	B-2 ^(c)	B-1	C-2 ^(d)	C-1 ^(e)
93 ^(f)	November 1967	Average	480	475	470	460	465	385
		Maximum	530	545	530	490	480	415
94 ^(g)	January 1968	Average	465	530	550	550	575	495
		Maximum	505	560	585	570	605	520
95	April	Average	535	605	630	600	670	565
		Maximum	600	630	650	630	680	570
96	May	Average	460	535	530	500	540	440
		Maximum	495	550	570	525	570	465
97	July	Average	465	530	555	510	560	455
		Maximum	485	555	580	535	575	475
98	September	Average	430	495	525	485	520	420
		Maximum	455	525	550	490	545	445
99	October	Average	410	475	490	440	480	390
		Maximum	440	505	505	460	505	405
100	January 1969	Average	440	510	540	475	540	440
		Maximum	470	535	565	495	465	460
101	February	Average	405	475	495	445	485	395
		Maximum	445	510	520	465	515	415
102 ^(h)	May	Average	605	680	670	545	565	460
		Maximum	680	735	720	560	590	485
103 ⁽ⁱ⁾	July	Average	650	725	720	620	650	550
		Maximum	705	790	780	715	675	570
104	September	Average	645	715	715	655	640	535
		Maximum	695	770	770	705	675	575
105	December	Average	600	670	670	625	655	555
		Maximum	630	705	705	650	680	575
106A ^(j)	January 1970	Average	630	705	705	665	700	640
		Maximum	725	800	800	720	750	645
106B ^(j)	March	Average	560	630	630	590	625	520
		Maximum	625	710	710	620	650	545
Total Accumulated Burnup								
10 ²⁰ Fissions per cm ³			39.7	47.7	48.6	43.1	46.3	35.0
10 ³ MWD/T ^(k)			130	132	157	123	131	102

- (a) Temperatures reported are extrapolated from thermocouple data and are on:
 Inner cladding surface for Specimens A-4 and A-3 (helium bond)
 Fuel surface of Specimens B-2 and B-1 (10-mil sodium bond)
 Fuel surface of Specimens C-2 and C-1 (20-mil sodium bond)
- (b) Thermocouple opposite Specimen A-3 failed at the end of Cycle 96. Temperatures for follow-on cycles were estimated using data from adjacent Specimen A-4.
- (c) Thermocouple opposite Specimen B-2 failed at the end of Cycle 98. Temperatures for follow-on cycles were estimated using data from adjacent Specimen B-1.
- (d) The thermocouple for Specimen C-2 failed on startup for Cycle 105. The temperatures for Specimens C-1 and C-2 for Cycles 105 and 106A and B were obtained using data from Specimen B-1.
- (e) Thermocouple opposite Specimen C-1 failed during Cycle 95. Temperatures for Cycles 95 through 104 were estimated using data from adjacent Specimen C-2.
- (f) Capsule initially inserted into Position P-12-SW for ETR Cycle 93.
- (g) Capsule transferred to Position P-10-SW for Cycles 94 through 101.
- (h) Capsule transferred from Position P-10-SW to beryllium-reflector Position 0-5 for Cycle 102.
- (i) Capsule transferred from Position 0-5 to Position 0-6 for Cycle 103.
- (j) Cycle 106A accumulated 5724 MWD, the length of a normal ETR cycle. Cycle 106B was approximately the same length.
- (k) Based on 200 Mev per fission.

TABLE A-13. SPECIMEN TEMPERATURES FOR CAPSULE BMI-50-8 DURING FISCAL YEAR 1970

ETR Cycle	Starting Date	Type of Temperature Data	Temperatures for Indicated Specimens ^(a) , C					
			A-25	A-26 ^(b)	B-25	B-28	C-25	C-26
102	May, 1969	Average	560	590	640	625	640	660
		Maximum	605	630	670	650	665	685
103 ^(c)	July	Average	595	620	780	700	755	880
		Maximum	690	715	825	760	800	940
104	September	Average	595	640	770	700	765	890
		Maximum	685	725	795	750	795	945
105	December	Average	515	560	670	595	665	795
		Maximum	600	635	715	640	685	800
106A ^(d)	January, 1970	Average	515	560	615	550	620	745
		Maximum	615	665	650	595	630	760
106B ^(d)	March	Average	505	550	615	540	605	735
		Maximum	590	630	640	570	620	755
Total Burnup Accumulated to Date:								
10 ²⁰ Fissions per Cm ³			31.5	34.6	42.6	38.4	42.0	47.9
10 ³ MWD/T ^(e)			105	99	139	110	121	136

(a) Temperatures reported are extrapolated from thermocouple data and are on:

Inner cladding surface for Specimens A-25 and A-26 (helium bond).

Fuel surface of Specimens B-25 and B-28 (10-mil sodium bond).

Fuel surface of Specimens C-25 and C-26 (20-mil sodium bond).

(b) Thermocouple opposite Specimen A-26 failed during Cycle 106A. Temperatures for Cycles 106A and 106B were estimated using data from adjacent Specimen A-25.

(c) Capsule transferred from Position P-9-SW to Position E-5-NE.

(d) Cycle 106A accumulated 5724 MWD, the length of a normal ETR cycle. Cycle 106B was approximately the same length.

(e) Based on 200 Mev per fission.

TABLE A-14. SPECIMEN TEMPERATURES FOR CAPSULE BMI-50-10 IN ETR FACILITY E-5-NW

ETR Cycle	Starting Date	Type of Temperature Data	Temperatures for Indicated Specimens ^(a) , C					
			A-41	A-51	B-41	B-42	C-41	C-42
102	May, 1969	Average	675	660	680	720	730	735
		Maximum	740	720	710	735	745	770
103	July	Average	555	545	555	570	605	635
		Maximum	640	595	580	595	625	660
104	September	Average	535	540	550	575	600	680
		Maximum	630	595	580	630	650	725
105	December	Average	470	490	500	525	570	590
		Maximum	520	530	515	540	580	660
106A ^(b)	January, 1970	Average	475	485	480	505	515	625
		Maximum	535	500	510	515	580	650
106B ^(b)	March	Average	475	490	485	510	545	615
		Maximum	525	525	520	520	570	645
Total Burnup Accumulated to Date:								
10 ²⁰ Fissions per Cm ³			15.6	15.7	15.9	16.9	17.8	20.1
10 ³ MWD/T(c)			59.5	53.3	61.6	53.6	60.0	70.4

(a) Temperatures reported are extrapolated from thermocouple data and are on:

Inner cladding surface for Specimens A-41 and A-51 (helium bond).

Fuel surface of Specimens B-41 and B-42 (10-mil sodium bond).

Fuel surface of Specimens C-41 and C-42 (20-mil sodium bond).

(b) Cycle 106A accumulated 5724 MWD, the length of a normal ETR cycle. Cycle 106B was approximately the same length.

(c) Based on 200 Mev per fission.

periodic fluctuating thermocouple output. As a result, the capsule was moved to a lower flux position (F-4) for the next cycle of irradiation. Nominal pin power ratings of 40 to 45 kw per ft were achieved in the new location. The capsule was discharged in May, 1970 (end of Cycle 106), and was returned to Battelle-Columbus for postirradiation examination. The temperature and burnup data for the two cycles of irradiation are given in Table A-15. Temperatures exceeded design goals for the experiment, with the fuel surface temperatures exceeding the atmospheric sodium boiling point in each specimen for the first cycle of irradiation.

The capsule components for Capsule BMI-50-12 were fabricated and assembly, with insertion of fuel specimens, was begun. The design of this capsule is identical to that of Capsule BMI-50-11.

TABLE A-15. TEMPERATURE HISTORY FOR CAPSULE BMI-50-11

ETR Cycle	Starting Date	Type of Temperature Data	Temperatures for Indicated Specimens ^(a) , C					
			A-43	A-44	B-43	B-54	C-43	C-44
105 ^(b)	December, 1969	Average	900	930	930	970	1055	1010
		Maximum	930	970	980	1015	1105	1035
106A ^(c, d)	January, 1970	Average	815	870	845	925	915	860
		Maximum	845	925	875	965	950	880
106B ^(d)	March	Average	780	835	830	875	900	855
		Maximum	850	895	865	955	960	925
Total Accumulated Burnup:								
10 ²⁰ Fissions per Cm ³			17.0	18.2	15.9	19.2	20.1	18.9
10 ³ MWD/T ^(e)			55.7	52.5	58.5	55.0	57.5	54.5

(a) Temperatures reported are extrapolated from thermocouple data and are on:

Inner cladding surface for Specimens A-43 and A-44 (helium bond).

Fuel surface of Specimens B-43 and B-54 (10-mil sodium bond).

Fuel surface of Specimens C-43 and C-44 (20-mil sodium bond).

(b) Capsule was initially inserted into Position M-4 for Cycle 105.

(c) Capsule was transferred from Position M-4 to Position F-4 for Cycle 106A.

(d) Cycle 106A accumulated 5724 MWD, the length of a normal ETR cycle. Cycle 106B was approximately the same length.

(e) Based on 200 Mev per fission.

Plans for Future Work

The irradiation of Capsules BMI-50-8 and BMI-50-10 will be continued to the end of Cycle 109, tentatively scheduled for August, 1970, at which time they will be discharged from the reactor and returned to Battelle-Columbus for postirradiation examination. Capsule BMI-50-12 will be assembled and sent to the ETR for irradiation. The irradiation of this capsule is tentatively scheduled to begin in September, 1970. It is anticipated that the target burnup of 100,000 MWD/T will be reached in approximately one calendar year.

Postirradiation Evaluation of (U_{0.8}Pu_{0.2})N Thermal
Irradiation Specimens

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Objective of Program

To evaluate the stability of mixed-nitride fuels irradiated in a thermal-neutron flux at cladding temperatures up to 700 C, heat generation rates up to 40 kw per ft, and burnups up to 100,000 MWD/T.

Approach Being Used

Specimens consisting of helium-bonded and sodium-bonded (U_{0.8}Pu_{0.2})N pellets clad in 15-mil-thick Type 304L stainless steel will be examined following irradiation in the ETR or MTR. The postirradiation examination planned involves (1) measurement of fission-gas release from clad specimens to the capsule and from fuel to the cladding, (2) visual inspection of the cladding for defects or evidence of chemical reaction, (3) measurement of the dimensions and density of the specimens, and (4) metallographic examination of the cladding and fuel to determine cladding-fuel compatibility and changes in the microstructures of cladding and fuel. When appropriate, additional investigation techniques such as gamma scanning, autoradiography, X-ray diffraction analyses, electron-microprobe analyses, and fuel-burnup analyses will be used.

Significant Accomplishments During Fiscal Year 1970

During the year, the examination of fuel specimens from Capsules BMI-50-5, BMI-50-7, and BMI-50-9, plus some detailed examinations of claddings from Capsule BMI-50-4 were completed. Capsules BMI-50-6 and BMI-50-11 were discharged from the ETR late in the year and examinations were initiated.

In Capsules BMI-50-5, BMI-50-7, and BMI-50-9, burnups ranged from 11.0×10^{20} to 34.5×10^{20} fissions per cm³, and heat generation rates ranged from 13.5 to 29.2 kw per ft. Fuel swelling rates in these capsules were uniformly low at less than 0.5 percent per 10^{20} fissions per cm³. None of the sodium-bonded specimens exhibited any cladding strain and the remaining sodium-filled annuli were large enough to accommodate considerably more fuel swelling. All the helium-bonded specimens experienced cladding strain and several had failed claddings. Fission-gas release from the high-density fuel was very low, being on the order expected from recoil from the free surfaces. The somewhat higher gas release from low-density specimens was attributed to the greater exposed surface area associated with the high degree of surface-connected porosity.

Consistent with the low swelling and low gas release was the absence of optically resolvable fission-gas bubbles in the fuel.

No evidence of interaction between the cladding and fuel or fission products was found by metallographic examination or electron-microprobe analysis. Electron-microprobe analysis also showed that no segregation of uranium and plutonium had occurred. Micro-Kjeldahl analysis indicated that the cladding did not pick up significant quantities of nitrogen during irradiation.

In Capsules BMI-50-6 and BMI-50-11, the irradiation conditions were more severe in terms of burnup (35×10^{20} to 48.6×10^{20} fissions per cm³ in Capsule BMI-50-6) or heat generation rates (41.6 to 49.0 kw per ft in Capsule BMI-50-11).

Preliminary results of the examination of fuel specimens from Capsule BMI-50-6 indicated large cladding strain in the helium-bonded specimens, a slight amount of cladding strain in the 10-mil sodium-bonded specimens, and no cladding strain in the 20-mil sodium-bonded specimens. Claddings on both helium-bonded specimens and one 10-mil sodium-bonded specimen were ruptured.

In Capsule BMI-50-11, all specimens experienced some cladding strain. However, only one 10-mil sodium-bonded specimen had a visibly failed cladding. This failure was oriented in a circumferential direction and did not appear to be caused by the hoop stresses generally associated with swelling fuel.

Summary of Research Carried Out

During the year, the postirradiation examinations of fuel specimens in Capsules BMI-50-5, BMI-50-7, and BMI-50-9 were completed and the examinations of fuel specimens from Capsules BMI-50-6 and BMI-50-11 were initiated. In addition, some detailed studies of claddings from specimens irradiated in Capsule BMI-50-4 were conducted.

The specimens in Capsule BMI-50-5 were irradiated to burnups of 23.8×10^{20} to 34.5×10^{20} fissions per cm^3 (69,000 to 105,000 MWD/T) at average linear heat generation rates of 13.5 to 19.6 kw per ft. In Capsule BMI-50-7, the fuel attained burnups of 28.5×10^{20} to 32.1×10^{20} fissions per cm^3 (85,000 to 97,000 MWD/T) at heat generation rates of 25.7 to 29.2 kw per ft. Capsule BMI-50-9 was discharged from the MTR when it shut down. Because of the low fission burnup, 11×10^{20} to 12.5×10^{20} fissions per cm^3 (34,000 to 41,000 MWD/T) the examination of specimens from Capsule BMI-50-9 was not extensive.

Specimen descriptions, irradiation conditions, and the results of postirradiation examinations for these capsules are summarized in Tables A-16 through A-18.

Macrophotographs and neutron radiographs of the as-recovered specimens from Capsule BMI-50-9 are shown in Figures A-26 and A-27. Macrophotographs and neutron radiographs of specimens from Capsules BMI-50-5 and BMI-50-7 were presented in BMI-1868.

Note from the tables that all of the sodium-bonded specimens from the capsules were recovered intact with no cladding strain. Four out of the six helium-bonded specimens from these capsules, on the other hand, had visibly failed claddings. These cladding failures were more common at the higher burnups and occurred at cladding strains as low as 0.5 percent. At the lower burnups experienced in Capsule BMI-50-9, the cladding strain in the helium-bonded specimens was low and no cladding failures were noted.

Volumetric and diametral swelling data obtained from specimens irradiated in Capsules BMI-50-4, BMI-50-5, BMI-50-7, and BMI-50-9 are plotted as a function of burnup in Figures A-28 and A-29. Note that volumetric swelling is uniformly low at less than 0.5 percent per 10^{20} fissions per cm^3 . Diametral swelling is likewise low. At burnups of $\sim 30 \times 10^{20}$ fissions per cm^3 , the remaining annular gaps in the 10-mil sodium-bonded specimens are sufficiently large to accommodate considerably more burnup before the fuel would contact the cladding. The swelling data give no consistent indication that swelling behavior is improved by decreasing fuel density. Evidently under the conditions of the irradiations, the fuel, even at the centerline, is sufficiently strong relative to the cladding or cooler outer regions of fuel to preclude fuel swelling into preexisting porosity.

Fission-gas release in all the specimens was low. Release from the high-density fuel was generally on the order expected from recoil at free surfaces. Somewhat higher gas release was measured when the fuel was extensively cracked, as with Specimen C-7 from Capsule BMI-50-5. This specimen also showed evidence of contamination. Release from low-density specimens was consistently higher. The low-density specimens presumably have a high degree of surface-connected porosity which accounts for their higher release rates.

Consistent with the low swelling rates and low gas release was the absence of optically resolvable fission-gas bubbles in the fuel. As shown in Figure A-30, the microstructures of irradiated and unirradiated fuel from Capsule BMI-50-7 are virtually identical.

4X

P1946-7

Specimen A-31

4X

P1944-5

Specimen A-32

4X

P1942-3

Specimen B-31

FIGURE A-26. IRRADIATED SPECIMENS FROM CAPSULE BMI-50-9

4X

P1940-1

Specimen B-32

4X

P1938-9

Specimen C-27

4X

P1936-7

Specimen C-31

FIGURE A-26. (CONTINUED)

Specimen
A-31
(helium bond)

Specimen
A-32
(helium bond)

Specimen
B-31
(sodium bond)

Specimen
B-32
(sodium bond)

Specimen
C-27
(sodium bond)

Specimen
C-31
(sodium bond)

0 Deg

120 Deg

240 Deg

FIGURE A-27. NEUTRON RADIOGRAPHS OF SPECIMENS FROM CAPSULE BMI-50-9

TABLE A-16. IRRADIATION CONDITIONS AND SWELLING DATA FOR FUEL SPECIMENS IN CAPSULE BMI-50-5

	Specimen Designation					
	A-6	A-7	B-5	B-6	C-7	C-8
Bond						
Type	Helium	Helium	Sodium	Sodium	Sodium	Sodium
Cold Gap, mils	<1	<1	10	10	20	20
Density, percent of theoretical						
Pellet	95.1	80.8	80.2	95.6	97.2	92.3
Smear	~95.1 ^(a)	~80.8 ^(a)	67.7	80.7	70.1	66.6
Burnup						
10^{20} Fissions per Cm^3	23.8	24.8	30.9	28.9	34.5	31.9
10^3 MWD/T	69	84	105	82	97	95
Fuel-Surface Temperature ^(b) , C						
Average	395	405	470	445	500	475
Maximum	465	460	535	505	630	630
Average Linear Heat Rating, kw per ft	13.5	14.1	17.6	16.3	19.6	18.1
Cladding Diameter Increase ^(c) , percent	2.2	0.5	0	0	0	0
Fuel Diameter Increase ^(d) , percent	2.5	0.6	1.2	2.6	5.7	2.9
Fuel Length Increase ^(e) , percent	3.4	3.5	4.4	5.4	5.2	2.9
Fuel Volume Increase						
Percent	8.4	4.7	6.8	10.6	16.6	8.7
Percent per 10^{20} Fissions per Cm^3	0.37	0.17	0.22	0.37	0.48	0.27
Fission-Gas Release, percent	--	--	13.5	0.8	4.8	--
Cladding Condition	Failed	Failed	Sound	Sound	Sound	Sound

(a) Sweat fit of cladding to fuel.

(b) Fuel temperature for helium-bonded specimens calculated assuming zero gap during irradiation. Average temperature is time average based on entire irradiation. Maximum value is that occurring during last half of irradiation.

(c) Micrometer measurements.

(d) Fuel diameter changes for helium-bonded specimens calculated assuming fuel-cladding contact; remaining diameter changes measured from neutron radiographs.

(e) Measured from neutron radiographs.

TABLE A-17. IRRADIATION CONDITIONS AND SWELLING DATA FOR FUEL SPECIMENS IN CAPSULE BMI-50-7

	Specimen Designation					
	A-22	A-24	B-22	B-24	C-21	C-22
Bond						
Type	Helium	Helium	Sodium	Sodium	Sodium	Sodium
Cold Gap, mils	<1	<1	10	10	20	20
Density, percent of theoretical						
Pellet	93.8	82.6	95.5	82.5	97.5	96.0
Smear	~93.8 ^(a)	~82.6 ^(a)	80.4	70.2	69.2	70.2
Burnup						
10^{20} Fissions per Cm^3	29.2	28.5	30.7	29.1	30.1	32.1
10^3 MWD/T	85	94	89	97	86	91
Fuel-Surface Temperature ^(b) , C						
Average	605	595	635	610	625	660
Maximum	650	660	650	650	735	765
Average Linear Heat Rating, kw per ft	26.3	25.7	28.0	26.3	27.3	29.2
Cladding Diameter Increase ^(c) , percent	1.6	1.1	0	0	0	0
Fuel Diameter Increase ^(d) , percent	1.8	1.3	2.3	3.9	3.3	2.9
Fuel Length Increase ^(e) , percent	3.2	4.1	4.2	3.7	5.6	2.1
Fuel Volume Increase						
Percent	6.8	6.7	8.8	11.5	12.2	7.9
Percent per 10^{20} Fissions per Cm^3	0.23	0.24	0.29	0.40	0.41	0.25
Fission-Gas Release, percent	--	--	0.4	9.2	--	0.4
Cladding Condition	Failed	Failed	Sound	Sound	Sound	Sound

(a) Sweat fit of cladding to fuel.

(b) Fuel temperature for helium-bonded specimens calculated assuming zero gap during irradiation. Average temperature is time average based on entire irradiation. Maximum value is that occurring during last half of irradiation.

(c) Micrometer measurements.

(d) Fuel diameter changes for helium-bonded specimens calculated assuming fuel-cladding contact; remaining diameter changes measured from neutron radiographs.

(e) Measured from neutron radiographs.

TABLE A-18. SWELLING DATA FOR FUEL SPECIMENS IRRADIATED IN CAPSULE BMI-50-9

	Specimen Designation					
	A-31	A-32	B-31	B-32	C-27	C-31
Bond						
Type	Helium	Helium	Sodium	Sodium	Sodium	Sodium
Cold Gap, mils	<1	<1	10	10	20	20
Pellet Density, percent of theoretical	82.6	94.2	94.6	82.4	94.2	94.4
Burnup ^(a)						
10^{20} Fissions per Cm^3	11.0	11.8	12.5	12.4	12.0	11.4
10^3 MWD/T	36.0	34.2	37.8	41.0	34.5	34.0
Cladding Diameter Increase, percent	0.24	0.55	0	0	0	0
Fuel Diameter Increase, percent	0.27 ^(b)	0.63 ^(b)	0.49 ^(c)	0.49 ^(c)	0.13 ^(c)	2.0 ^(c)
Fuel Length Increase ^(c) , percent	0.0	0.0	2.0	1.9	1.4	1.1
Fuel Volume Increase						
Percent	0.54	1.3	3.0	2.9	1.7	5.1
Percent per 10^{20} Fissions per Cm^3	0.05	0.11	0.24	0.23	0.14	0.44
Cladding Condition	Sound	Sound	Sound	Sound	Sound	Sound

(a) Estimated from irradiation temperatures.

(b) Estimated from cladding diameter changes, assuming initial cladding-fuel contact.

(c) Measured from neutron radiographs.

FIGURE A-28. VOLUME CHANGE OF (U, Pu)N AS A FUNCTION OF BURNUP

FIGURE A-29. DIAMETER INCREASE OF (U, Pu)N AS A FUNCTION OF BURNUP

500X

Etched

PL4039

a. Preirradiation

500X

Etched

HC22714

b. Postirradiation

FIGURE A-30. MICROSTRUCTURES OF SPECIMEN B-22 FROM CAPSULE BMI-50-7 BEFORE AND AFTER IRRADIATION

Note the absence of fission-gas porosity in the irradiated structure.

An apparent second-phase material was noted in the fuel of several specimens from Capsule BMI-50-5, Figure A-31. This structure was only observed after etching. X-ray diffraction analysis of a sample with a large quantity (about 20 v/o) of this apparent phase yielded only characteristic (U,Pu)N peaks and a lattice parameter of 4.89 Å. The lattice parameter of unirradiated UN-20 w/o PuN is 4.90 Å. Thus, the phase is essentially (U,Pu)N in structure. It appears likely that the structure observed metallographically is a solid solution of (U,Pu)N with oxygen [(U,Pu)ON] or carbon [(U,Pu)CN] with somewhat different etching characteristics than the (U,Pu)N. Uranium-plutonium carbonitrides are known to exist, while uranium-plutonium oxynitrides would be analogous to uranium-plutonium oxycarbides.

To check the possibility of uranium-plutonium segregation during irradiation, the radial distribution of uranium and plutonium in two specimens, A-22 and A-24 (irradiated to burnups of about 29×10^{20} fissions per cm^3 at linear heat ratings of about 26 kw per ft), was determined by electron-microprobe analysis. The results for both specimens are typified by the X-ray intensity data for Specimen A-24 shown in Figure A-32. Note that no attempt was made to standardize the X-ray data to obtain absolute quantitative data. These data indicate that the distribution of uranium was fairly uniform across the radius while the plutonium concentration was low near the fuel perimeter and increased upon approaching the fuel center. The relative depletion of plutonium near the fuel surface is expected and is the result of the higher plutonium burnup near the fuel surface as compared to the fuel center because of the self-shielding of thermal neutrons by the fuel. Alpha and beta-gamma autoradiographs also indicated high burnup and plutonium depletion toward the fuel surface. On the basis of these results, it is concluded that no segregation of uranium and plutonium occurred during irradiation.

The claddings from several specimens have been subjected to additional study to check the possibilities of degradation by reaction with fuel or fission products or embrittlement by pickup of nitrogen from the fuel. As reported in BMI-1868, the irradiated Type 304 stainless steel claddings had sensitized microstructures characterized by carbide precipitates at grain boundaries and along deformation bands. In addition, several specimens had isolated regions near the cladding inner diameter that were susceptible to particularly heavy etched attack, Figure A-33. To check the possibility of fission-product or fuel reaction in these areas, samples of cladding from helium-bonded Specimen A-2 (18.2×10^{20} fissions per cm^3 at 25.4 kw per ft) and sodium-bonded Specimen B-3 (20.4×10^{20} fissions per cm^3 at 28.1 kw per ft) from Capsule BMI-50-4 were subjected to electron-microprobe analysis for cesium, cerium, zirconium, molybdenum, uranium, and plutonium in addition to the stainless steel constituents, iron, chromium, and nickel. The analyses revealed that no fission products, uranium, or plutonium were present. A slightly greater than normal concentration of chromium, probably in the form of iron-chromium carbide, was found in the grain boundaries.

A micro-Kjeldahl analysis of cladding from Specimen A-22 (Capsule BMI-50-7) showed the concentration of nitrogen in the cladding to be 360 ± 30 ppm, as opposed to 330 ± 30 ppm in an unirradiated control sample. Thus, no significant nitriding of the cladding occurred during irradiation.

On the basis of these results, it was concluded that the anomalous cladding microstructure was due to gross carbide precipitation at the grain boundaries, with the probability that the carbon was introduced as a surface contaminant during fabrication.

In Capsules BMI-50-6 and BMI-50-11 the irradiation conditions were more severe in terms of burnup and heat generation rate, respectively. Fuel specimens in Capsule BMI-50-6 were irradiated to burnups of 35.0×10^{20} to 48.6×10^{20} fissions per cm^3 (102,000 to 157,000 MWD/T). Heat generation rates of 29.5 to 39.7 kw per ft were attained in this capsule late in the irradiation.

Capsule BMI-50-11 was designed for the irradiation of specimens at high heat generation rates, nominally 40 kw per ft. Fuel specimens were irradiated to burnups

500X

FIGURE A-31. SECOND-PHASE MATERIAL FOUND IN THE FUEL OF THREE OUT OF FOUR SPECIMENS EXAMINED FROM CAPSULE BMI-50-5

Specimen A-6 is shown here.

FIGURE A-32. X-RAY INTENSITIES OF URANIUM AND PLUTONIUM AND URANIUM:PLUTONIUM RATIOS ACROSS THE RADIUS OF IRRADIATED (U, Pu)N SPECIMEN A-24 FROM CAPSULE BMI-50-7

of 15.9×10^{20} to 20.1×10^{20} fissions per cm^3 (52,500 to 58,500 MWD/T) at average heat generation rates of 41.6 to 49.0 kw per ft, with peak rates exceeding 50 kw per ft. Under these conditions, fuel-surface temperatures up to 1105 C and centerline temperatures in excess of 1600 C were realized.

500X

HC21909

FIGURE A-33. TYPE 304 STAINLESS STEEL CLADDING SODIUM BONDED TO HIGH-DENSITY (U, Pu)N SPECIMEN B-3 OF CAPSULE BMI-50-4

Note the fine grains near the ID. Electron-beam microprobe analysis indicated that heavily etched grain boundaries are rich in chromium, probably in the form of chromium carbide.

The specimen descriptions, irradiation conditions, and results of preliminary postirradiation examinations of Capsules BMI-50-6 and BMI-50-11 are summarized in Tables A-19 and A-20. Macroviews of the irradiated specimens from these two capsules are shown in Figures A-34 and A-35.

In Capsule BMI-50-6 (high-burnup experiment) both of the helium-bonded specimens experienced cladding strains of more than 4 percent. Expectedly, both claddings were ruptured. Specimen B-1 (10-mil sodium bond) also had a ruptured cladding; in the region of the rupture, the cladding had deformed 1.9 percent. Average cladding strain over the fueled region of this specimen was 0.6 percent. The other three specimens in the capsule were apparently sound and had experienced little or no cladding strain. Except for the helium-bonded specimens, no fuel-pellet swelling data are presently available for these specimens. On the basis of cladding diameter increases, fuel swelling in the helium-bonded specimens was on the same order as was exhibited by fuel from earlier capsule experiments. The cause of the cladding deformities and rupture in 10-mil sodium-bonded Specimen B-1 is uncertain and will be the subject of further investigations.

All the fuel specimens from Capsule BMI-50-11 (high heat-generation-rate experiment) exhibited some cladding deformation. However, only Specimen B-54 (10-mil sodium bond) had a visible cladding defect. The presence of fission gas in all the capsule compartments suggests that microdefects exist in the claddings of a number of these

TABLE A-19. IRRADIATION CONDITIONS AND PRELIMINARY SWELLING DATA FOR FUEL SPECIMENS IN CAPSULE BMI-50-6 (IRRADIATION CONDITIONS BASED ON THERMOCOUPLE DATA)

	Specimen Designation					
	A-4	A-3	B-2	B-1	C-2	C-1
Bond						
Type	Helium	Helium	Sodium	Sodium	Sodium	Sodium
Cold Gap, mils	<1	<1	10	10	20	20
Density, percent of theoretical						
Pellet	83.8	95.5	83.9	95.5	96.5	94.4
Smear	83.8(a)	95.5(a)	73.3	83.0	70.0	68.0
Burnup						
10^{20} Fissions per Cm^3	39.7	47.7	48.6	43.1	46.3	35.0
10^3 MWD/T(b)	130	132	157	123	131	102
Fuel-Surface Temperature(c), C						
Average	615	685	685	615	635	545
Maximum	725	800	800	720	750	645
Maximum Temperature at Fuel Center(c), C	1130	1205	1260	1070	1115	950
Linear Heat Generation, kw per ft						
Average(d)	22.6	26.2	26.5	23.4	25.0	19.5
Maximum	34.8	39.7	39.7	34.1	36.2	29.5
Cladding Diameter Increase, percent						
Maximum	5.8	5.2	0.3	1.9	0	0
Average	4.1	4.4	0.15	0.6	0	0
Fuel Diameter Increase, percent						
Maximum	6.6(e)	5.9(e)	(f)	(f)	(f)	(f)
Average	4.7(e)	5.0(e)	(f)	(f)	(f)	(f)
Cladding Condition	Failed	Failed	Sound	Failed	Sound	Sound

(a) Slip fit of fuel into cladding - essentially no clearance.

(b) Based on 200 Mev per fission.

(c) Capsule was relocated into higher flux positions for last six irradiation cycles. Irradiation temperatures are for these cycles.

(d) Time-weighted average for entire irradiation.

(e) Based on cladding deformation and assuming no clearance between fuel and cladding.

(f) Data not yet available.

TABLE A-20. IRRADIATION CONDITIONS AND PRELIMINARY SWELLING DATA FOR FUEL SPECIMENS IN CAPSULE BMI-50-11 (IRRADIATION CONDITIONS BASED ON THERMOCOUPLE DATA)

	Specimen Designation					
	A-43	A-44	B-43	B-54	C-43	C-44
Bond						
Type	Helium	Helium	Sodium	Sodium	Sodium	Sodium
Cold Gap, mils	<1	<1	10	10	20	20
Density, percent of theoretical						
Pellet	82.7	94.7	82.7	94.4	94.3	94.3
Smear	82.7(a)	94.7(a)	70.2	80.6	69.0	68.8
Burnup						
10^{20} Fissions per Cm^3	17.0	18.2	15.9	19.2	20.1	18.9
10^3 MWD/T(b)	55.7	52.5	58.5	55.0	57.5	54.5
Average Irradiation Temperature(c), C						
Fuel Surface	830	880	870	920	960	910
Fuel Center	1240	1310	1295	1375	1440	1360
Average Linear Heat Generation(c), kw per ft	41.6	44.5	44.0	46.5	49.0	46.4
Cladding Diameter Increase, percent						
Maximum	1.4	2.2	0.5	2.8	2.0	0.8
Average	0.8	1.7	0.2	1.2	1.0	0.2
Fuel Diameter Increase, percent						
Maximum	1.6(d)	2.4(d)	(e)	(e)	(e)	(e)
Average	0.9(d)	1.8(d)	(e)	(e)	(e)	(e)
Cladding Condition(f)	Sound	Sound	Sound	Failed	Sound	Sound

(a) Slip fit of fuel into cladding - essentially no clearance.

(b) Based on 200 Mev per fission.

(c) Time-weighted averages.

(d) Based on cladding deformation and assuming no clearance between fuel and cladding.

(e) Data not yet available.

(f) Based on macroappearance. The presence of fission gas in all the capsule compartments suggests that pinhole leaks exist in several of the specimens.

4X

2178-9

Specimen A-4
(Helium Bond)

4X

2180-1

Specimen A-3
(Helium Bond)

4X

2184-5

Specimen B-2
(10-Mil Sodium Bond)

FIGURE A-34. IRRADIATED SPECIMENS FROM CAPSULE BMI-50-6

Note that the claddings are ruptured on both helium-bonded specimens and on 10-mil sodium-bonded Specimen B-1.

4X

2186-7

Specimen B-1
(10-Mil Sodium Bond)

4X

2190-1

Specimen C-2
(20-Mil Sodium Bond)

4X

2188-9

Specimen C-1
(20-Mil Sodium Bond)

FIGURE A-34. (CONTINUED)

4X

2168-9

Specimen A-43
(Helium Bond)

4X

2166-7

Specimen A-44
(Helium Bond)

4X

2170-1

Specimen B-43
(10-Mil Sodium Bond)

FIGURE A-35. IRRADIATED SPECIMENS FROM CAPSULE BMI-50-11

Note that the only specimen with a visibly failed cladding is 10-mil sodium-bonded Specimen B-54.

4X

2172-3

Specimen B-54
(10-Mil Sodium Bond)

4X

2163-4

Specimen C-43
(20-Mil Sodium Bond)

4X

2162-2

Specimen C-44
(20-Mil Sodium Bond)

FIGURE A-35. (CONTINUED)

specimens. However, the failure of the cladding on Specimen B-54 is unusual in that it is oriented circumferentially and apparently is not related to hoop stresses in the cladding. This specimen is bowed, suggesting that it has been subjected to a bending moment. The cause of this failure will be sought in future detailed examinations.

It is interesting to note that the diametral swelling rates of the helium-bonded specimens from Capsule BMI-50-11 are approximately the same as were observed for helium-bonded specimens irradiated at lower heat generation rates. It is also noteworthy that the helium-bonded specimens experienced relatively large cladding deformations without rupturing their cladding.

Plans for Future Work

The postirradiation examination of fuel specimens from Capsules BMI-50-6 and BMI-50-11 will continue, with emphasis on determining the cause(s) of the two observed cladding failures in sodium-bonded specimens. Additionally, more detailed examinations of the sound specimens will be performed to establish the effects of high burnup and high heat generation rate on fuel swelling, fission-gas release, and fuel-cladding compatibility.

Preparation of EBR-II Fuel Pins

W. T. Langendorfer, M. D. Houston, E. O. Speidel, and O. L. Kruger

Objective of Program

To fabricate solid-solution ($U_{0.8}Pu_{0.2}$)N pellets by powder metallurgical techniques and clad them in well characterized Type 316 stainless steel for irradiation in the EBR-II.

Approach Being Used

Sintering techniques are being employed to fabricate ($U_{0.8}Pu_{0.2}$)N pellets of controlled density, size, and microstructure for EBR-II fuel-pin irradiation experiments. Pellets for the BMI-3 series capsules were prepared in Fiscal Year 1970. Design variables included fuel density (88.5 and 95 percent of theoretical), bonding medium (sodium or helium), and total diametral fuel-cladding gap (0.0025 to 0.0100 in.). Each fuel pin contains 10 in. of fuel.

In the general procedure to be used in preparation of EBR-II fuel pins, nominal ($U_{0.8}Pu_{0.2}$)N powder containing fully enriched uranium will be ball milled to reduce the particle size, cold pressed in hardened steel dies, sintered, and centerless ground, if necessary, to produce fuel pellets that are within ± 2.0 percent of the design densities and 0.0005 in. of the required diameters. The fuel pellets will be right circular cylinders having a length-to-diameter ratio of approximately one. Pellets for two of the BMI-3 series capsule loadings have a nominal 0.070-in. -diameter annular hole. Control pellets from each powder batch will be characterized with respect to chemistry, microstructure, density, and impurity levels.

Fuel pins consisting of (U, Pu)N pellets either helium or sodium bonded to tubular cladding will be assembled in a high-purity helium or argon atmosphere [to permit post-irradiation measurement of helium generated by the (n, α) reactions] and sealed by TIG welding. Type 316 stainless steel tubes which have been well characterized for defects and dimensional tolerances will be utilized. After plutonium decontamination, each sealed fuel pin will be helium leak checked, visually examined, and radiographed to verify the position of the fuel pellets and the overall quality of the welds. Sodium-bonded fuel pins are heated to a temperature in excess of the melting point of sodium and centrifuged; an eddy-current inspection is performed to assure a continuous, void-free sodium bond.

Significant Accomplishments During Fiscal Year 1970

The fabrication of pellets for seven fuel pins, each containing approximately 10 in. of fuel, was completed. The pellets were fabricated by cold pressing and sintering nominal $(U_{0.8}Pu_{0.2})N$ powders prepared by a hydride-nitride cycle on arc-cast uranium-20 w/o plutonium buttons.

Seven fuel pins each composed of $(U,Pu)N$ pellets stacked within a tube of Type 316 stainless steel cladding, were loaded in an atmosphere of high-purity helium. In three pins, the bonding medium between the fuel and cladding was helium while sodium bonding was utilized in the other four pins. After welding, each of the pins was tested in accordance with the program requirements and found acceptable for secondary encapsulation.

Summary of Research Carried Out

The fabrication of both high-density and low-density $(U_{0.8}Pu_{0.2})N$ pellets for fuel pins to be inserted in the EBR-II was completed. A summary of dimensional and density data is given in Table A-21 along with fuel-pin design data.

TABLE A-21. DATA FOR $(U_{0.8}Pu_{0.2})N$ FUEL PINS IN THE BMI-3 SERIES SCHEDULED FOR EBR-II IRRADIATION

Capsule	Pellet Quantity	Total Pellet Length, in.	Average Diameter of Fuel ^(a) , in.		Average Density of Fuel ^(b) , percent of theoretical	Fuel-Pin Design Data	
			ID	OD		Bonding Medium	Radial Gap Width, mil
BMI-3-2	44	9.8592	--	0.2745	88.4	Sodium	5.0 ^{+0.0} -1.0
BMI-3-3	42	10.0623	--	0.2744	91.3	Sodium	5.0 ^{+0.0} -1.0
BMI-3-4	50	9.9935	--	0.2707	93.9	Sodium	7.0 ^{+0.0} -1.0
BMI-3-5	41	10.0302	--	0.2848	90.4	Sodium	5.0 ^{+0.0} -1.0
BMI-3-6	48	10.1077	0.069 ^(c)	0.2701	94.7	Helium	2.5 ^{+0.0} -1.0
BMI-3-7	35	9.6670	--	0.2698	88.5	Helium	2.5 ^{+0.0} -1.0
BMI-3-8	46	9.9254	0.069 ^(c)	0.2699	89.8	Helium	2.5 ^{+0.0} -1.0

(a) ID given for annular pellets.

(b) Based on a theoretical density of 14.17 g per cm³.

(c) Except for $U_{natural}N$ end pellets, which will be solid and 88.5 percent of theoretical density.

Nominal $(U_{0.8}Pu_{0.2})N$ powders containing fully enriched uranium were prepared using a hydride-nitride cycle on arc-cast uranium-20 w/o plutonium buttons. Seven powder batches (A-30, A-32, A-33, A-34, A-35, A-36, and A-37) were synthesized to fabricate the seven pins. The as-synthesized powder was wet ball milled for 32 hr in a uranium-lined ball mill containing tungsten carbide-cobalt balls and nanograde hexane. After milling, the powder was vacuum dried at room temperature, and then pressed into pellet form in hardened steel dies using zinc stearate as a die lubricant. High-density pellets were sintered at 2100 C for approximately 10 hr under 1 atm of nitrogen while pellets for low-density pins were sintered at 1975 C for 6 hr under 1 atm of nitrogen. Annular pellets were prepared for Capsules BMI-3-6 and BMI-3-8.

Table A-22 shows the powder batch associated with its fuel pin along with the corresponding die diameter and the pressure used in cold pressing. All pellets were centerless ground to meet the dimensional requirements.

TABLE A-22. FABRICATION DATA FOR BMI-3-SERIES FUEL PELLETS

Capsule	Powder Batch	Die Diameter, in.	Pressing Pressure, tsi
BMI-3-2	A-36	0.344	15
BMI-3-3	A-35	0.344	15
BMI-3-4	A-30	0.338	15
BMI-3-5	A-35 and A-37	0.344	15
BMI-3-6	A-32 and A-33	0.338 ^(a)	15
BMI-3-7	A-34	0.338	15
BMI-3-8	A-32 and A-33	0.338 ^(a)	15

(a) Die contained a 0.088-in. -diameter center mandrel.

Characterization of the densified ($U_{0.8}Pu_{0.2}$)N EBR-II pellets involved density measurements, metallographic examination, and chemical analyses. Although chemical analyses were not conducted on pellets from every powder batch, control pellets were placed in storage for future analyses if necessary. Selected pellets from each batch with the exception of Batch A-37 were examined metallographically. With the exception of Batch A-36 all microstructures were single-phased. The microstructure of the pellet from Batch A-36 showed a second phase believed to be higher nitride. Typical microstructures for high-density and low-density EBR-II pellets are shown in Figure A-36, while typical chemical analyses are given in Table A-23.

TABLE A-23. TYPICAL CHEMICAL ANALYSES ON ($U_{0.8}Pu_{0.2}$)N PELLETS

Pellet Identification	Carbon, w/o	Nitrogen, w/o	Uranium, w/o	Plutonium, w/o
A-33-70	0.05	5.48	--	--
A-34-16	0.03	5.49	--	--
A-30-28	--	--	75.6	19.1
A-32-1	--	--	76.6	18.8

Seven fuel pins, each composed of (U,Pu)N pellets stacked within a tube of Type 316 stainless steel cladding, were loaded in an atmosphere of high-purity helium. The bonding medium between the fuel and cladding was helium for three of the pins, while sodium bonding was utilized in the other four pins. The cladding OD of all pins in this irradiation series (BMI-3) was held constant at 0.315 in. The cladding wall thickness and the sodium annulus were varied as part of the irradiation study. The end plugs were welded in. Only seven usable pins were generated because of welding problems associated with the eighth pin. Each of the pins was tested in accordance with the program requirements and found acceptable for secondary encapsulation.

500X

Etched

PL7921

a. Low-Density Pellet A-33-22

500X

Etched

PL7929

b. High-Density Pellet A-33-66

FIGURE A-36. TYPICAL MICROSTRUCTURES OF LOW - AND HIGH-DENSITY EBR-II PELLETS

Plans for Future Work

Pellets will be fabricated for a 19-pin fuel bundle and the pins loaded in Fiscal Year 1971.

EBR-II Irradiation-Capsule Assembly and Safety Analysis Preparation

E. O. Fromm, N. E. Miller, and J. W. Ray

Objective of Program

To design and fabricate irradiation capsules, encapsulate clad (U,Pu)N fuel pins, perform required nondestructive examinations, prepare the Data Package for the experiments, ship the completed capsules to the EBR-II, and perform irradiation surveillance for experiments in the EBR-II.

Approach Being Used

Standard EBR-II irradiation capsules are being used for this program. Both the capsule components and some cladding material which are of Type 304L stainless steel will be procured from ANL. Additional cladding material of Type 316L stainless steel will be procured commercially. The fuel-pin cladding will be sodium bonded to the outer capsule by centrifuging at 1000 F. Sodium levels and bond soundness will be verified by X-radiography and eddy-current testing.

Significant Accomplishments During Fiscal Year 1970

Seven EBR-II capsules designated BMI-2-1, -2-2, -2-3, -2-5, -2-6, -2-7, and -2-8, designed to operate at fuel-pin power ratings up to 40 kw per ft were completed and sent to the EBR-II for irradiation. The Quality Assurance Description document associated with these experiments was prepared and forwarded to the EBR-II site for review. The eddy-current equipment used for determination of bond soundness was modified to improve the stability; the sensitivity of the modified equipment was determined by the use of dummy capsules fabricated from material having properties which closely approximated the electrical properties of the components in the actual irradiation capsules.

Three EBR-II capsules in the third series (C-BMI-3-6, -3-7, and -3-8) designed to operate at fuel-pin power ratings of 30 to 40 kw per ft were assembled and nondestructively tested. The Experiment Description and Safety Analysis documents associated with the BMI-3 series experiments were prepared. The Quality Assurance Description document for the three completed capsules was also prepared.

Capsule BMI-1-3 was inserted in the EBR-II in Subassembly X-070 for Run 39B.

Summary of Research Carried Out

Eight EBR-II capsules containing (U,Pu)N fuel pins in pellet form were originally included in the BMI-2 series irradiation experiments. However, one capsule (BMI-2-4) did not meet the BCL quality assurance and was not included in the BMI-2 experiments. Therefore, there are only seven capsules instead of the eight originally planned. The design details and desired irradiation conditions for the seven capsules, designated BMI-2-1, -2-2, -2-3, -2-5, -2-6, -2-7, and -2-8, are given in Table A-24. All of the capsules contain a nominal 10-in. active fuel region within claddings of Type 316L stainless steel with either 0.010-, 0.015-, or 0.020-in.-thick walls. Argon is used as the cover gas in the inner clad assembly so that the amounts of helium and hydrogen generated by the (n, α) and (n,p) reactions and their release from the fuel can be determined after the irradiation. The clad elements are immersed in sodium within an outer capsule of Type 304L stainless steel which is 0.375 in. in OD with a 0.020-in. wall. The fuel cladding and end-cap materials were obtained commercially, whereas the outer capsules and end fittings were obtained from ANL and are standard EBR-II components.

TABLE A-24. DESCRIPTION OF THE BMI-2 SERIES OF $(U_{0.8}Pu_{0.2})N$ IRRADIATIONS IN THE EBR-II

Capsule	Fuel-Pin Cladding Thickness ^(a) , in.	Fuel-Cladding Radial Sodium Bond Thickness, in.	Fuel Diameter ^(b) , in.	Fuel Smear Density ^(c) , percent	Specific Power ^(d) , kw per ft	Target Burnup ^(e) , a/o
BMI-2-1	0.020	0.010	0.255	81.7	30.7-33.8	6
BMI-2-2	0.020	0.010	0.255	81.7	30.7-33.8	9
BMI-2-3	0.020	0.010	0.255	81.7	30.7-33.8	12
BMI-2-5	0.015	0.015	0.255	76.1	30.7-33.8	12
BMI-2-6	0.010	0.010	0.275	82.6	35.7-39.3	6
BMI-2-7	0.010	0.010	0.275	82.6	35.7-39.3	12
BMI-2-8	0.010	0.010	0.275	82.6	35.7-39.3	9

(a) All cladding is Type 316L stainless steel, 0.315 in. in OD.

(b) All capsules will contain a nominal 10-in. length of fuel axially centered within the EBR-II core.

(c) Based on a fuel-pellet density of 95 percent of theoretical; the theoretical density of $(U_{0.8}Pu_{0.2})N$ is 14.3 g per cm³.

(d) Range of specific powers in core Row 4 of the EBR-II operating at 50 Mw; for the specified fuel this corresponds to 9.54×10^{13} to 10.50×10^{13} fissions/(cm³) (sec).

(e) For $(U_{0.8}Pu_{0.2})N$ of 95 percent of theoretical density, a heavy atom burnup of 1 percent equals 3.27×10^{20} fissions per cm³.

Sodium bonding of the inner clad assemblies for the BMI-2 series was accomplished by centrifuging, and verification of the soundness of the bond was made by eddy-current techniques.

The seven sodium-bonded fuel pins were loaded into the outer capsules using a procedure similar to that used for the BMI-1-series capsules. Essentially, the encapsulation is done inside a dry box previously evacuated and backfilled with purified helium. The clad assembly is preferentially heated from the top down to melt the sodium so as not to disturb the sodium bond or strain the cladding. The hot assembly is then lowered into the capsule which contains approximately 5 g of molten sodium. The sodium in both annuli is cooled from the bottom up, the top end cap is Heliarc welded to the capsule, and the welds are nondestructively tested for soundness and leak tightness.

The sodium bond between the cladding and the outer capsule was also accomplished by centrifuging, and verification of the soundness of the bonds was made by eddy-current techniques.

The eddy-current equipment used to evaluate the integrity of the sodium bonds of both the inner and outer sodium annuli was modified to improve stability. As before, the sensitivity of the modified equipment was evaluated by means of dummy capsules fabricated from material having properties which closely approximated the electrical properties of the components of the actual clad fuel pins and irradiation capsules. Various known void configurations were simulated as a basis for the determination of the eddy-current equipment sensitivity. For the inner clad assembly it was possible to mask out the effects of pellet interfaces and offset pellets and still detect a void as small as 1/16 in. in diameter through the 0.010-in. -thick annulus. The minimum detectable void in the outer sodium annulus was of comparable size. No voids of this magnitude were detected in either annulus of the seven capsules in the BMI-2 series.

Work was initiated on the third set of EBR-II irradiation experiments, designated the BMI-3 series. The planned fabrication of eight capsules was reduced to seven when

welding difficulties were encountered late in the year with fuel-pin fabrication. The seven capsules in this group of (U, Pu)N fuel pins emphasize specific fuel-pin power ratings in the range of 30 to 40 kw per ft and burnups to 100,000 MWD/T. The design details for each capsule are summarized in Table A-25. Essentially, each capsule contains a nominal 10-in. active fuel length of (U, Pu)N fuel pellets within a 0.315-in. -OD Type 316 stainless steel cladding obtained from a commercial vendor. Four of the capsules contain a 0.005- or a 0.007-in. -thick radial sodium bond between fuel and cladding, while the other three have a 0.0025-in. -thick radial helium bond between the fuel and cladding. The fuel-pin dimensions and target burnups were established on the basis of the fuel swelling observed in the thermal flux irradiation of mixed-nitride fuels conducted by Battelle-Columbus. Thus, a particular objective of these experiments is to provide a quantitative comparison between the solid-fission-product swelling rates occurring during fast-flux irradiation with those observed in a predominately thermal-flux environment. Additionally, an optimum sodium-gap size is being sought. The helium-bonded pins were designed to compare the effectiveness of centralized and distributed porosity in accommodating fuel swelling and to observe the effect of cladding restraint on fuel swelling.

The Approval in Principle for BMI-3 series was prepared and forwarded to the AEC for review; approval was granted for the proposed irradiations. The Experiment Description and Hazards Analysis was prepared and is being reviewed prior to forwarding to the EBR-II Project.

Characterization and fabrication of the outer capsule components for all seven capsules was completed. Assembly of the first three capsules (C-BMI-3-6, -3-7, and -3-8) was completed. Essentially, the procedure for encapsulation into the outer capsule was identical to that used for the BMI-2 series. The sodium bond between the cladding and outer capsule was accomplished by centrifuging, and verification of the soundness of the bond was made by eddy-current techniques. No voids 1/16 in. in diameter or larger through the 0.010-in. -thick sodium annulus were detected. The Quality Assurance Description for the three capsules was prepared. Assembly of the remaining four capsules was begun.

Capsule BMI-1-3 was loaded into Position 12 of MK-A-19 Subassembly X-070, and the subassembly was inserted into Position 3E1 of the reactor grid for EBR-II Run 39B. This is the first mixed-nitride capsule to be irradiated in the EBR-II. The target burnup for the capsule (helium bond) is 3 a/o. At the end of EBR-II Run 42, the capsule had accumulated a total of 4435 reactor megawatt-days for a total burnup of about 2.4 a/o at an estimated maximum specific fuel-pin power of 25.8 kw per ft [9.1×10^{13} fissions/(cm³)(sec)].

Plans for Future Work

The irradiation of Capsules BMI-1-1, -1-2, -1-4, -2-1, -2-2, -2-3, -2-5, -2-6, -2-7, and -2-8 will be initiated. It is anticipated that these capsules will be incorporated into Subassembly X-086 and inserted in the EBR-II for Run 45.

The irradiation of Capsule BMI-1-3 will be terminated at the end of EBR-II Run 44; a peak fuel burnup of about 3.8 a/o is anticipated. The capsule will be returned to Battelle-Columbus in Cask BCL-4 for postirradiation examination after an appropriate cooling period.

The assembly of the four remaining capsules in the BMI-3 series will be completed, and the capsules will be nondestructively tested. All seven capsules will then be shipped to the EBR-II Irradiation Coordinator. The Quality Assurance Description for the four capsules with sodium-bonded fuel pins will be prepared. The Data Package containing the Experiment Description, Hazards Analysis, and the Quality Assurance Description (for all seven capsules) will be forwarded to the EBR-II Project for review.

TABLE A-25. BMI-3 SERIES OF (U,Pu)N FUEL-PIN IRRADIATIONS IN THE EBR-II

Capsule	Fuel-Pin Cladding ^(a) , in.		Bond Medium	Radial Bond Thickness, in.	Fuel Diameter ^(b) , in.	Fuel Density ^(c) , percent of theoretical	Specific Power ^(d) , kw per ft	Smear Density, percent of theoretical	Burnup ^(e) , a/o		Planned Burnup ^(f) , a/o	Reactor Megawatt-Days to Achieve Planned Burnup ^(g)
	ID	Wall							To Contact Cladding	To Yield 1 Percent Cladding Strain		
BMI-3-2	0.285	0.015	Sodium	0.005	0.275	88	31.0-38.9	81.8	7.6	10.2	7.5	19,687.5
BMI-3-3	0.285	0.015	Sodium	0.005	0.275	91	32.1-40.2	84.6	7.6	10.2	9	26,250
BMI-3-4	0.285	0.015	Sodium	0.007	0.271	95	32.4-40.8	85.9	11.0	13.8	12	26,250
BMI-3-5	0.295	0.010	Sodium	0.005	0.285	91	34.4-43.2	85.0	7.4	9.8	7.5	13,125
BMI-3-6	0.275	0.020	Helium	0.0025	0.270 (0.070)	95	30.0-37.8	85.4	3.8	--	6	13,125
BMI-3-7	0.275	0.020	Helium	0.0025	0.270	88.5	30.0-37.7	85.3	4.1	--	6	13,125
BMI-3-8	0.275	0.020	Helium	0.0025	0.270 (0.070)	88.5	28.0-35.2	79.6	4.1	--	6	13,125

(a) All cladding is Type 316 stainless steel, 0.315 in. in OD.

(b) Values in parentheses are the ID's of annual pellets.

(c) Based on a theoretical density of 14.3 g per cm³ for (U_{0.8}Pu_{0.2})N.

(d) Ranges of axial centerline specific power levels in Core Row 5 of EBR-II operating at 62.5 Mw.

(e) Based on a fuel swelling rate of 0.48% $\Delta V/V$ per 10²⁰ fissions per cm³ (1.5% $\Delta V/V$ per a/o burnup), and assuming that internal porosity is ineffective in accommodating fuel swelling. Cladding swelling due to fast neutron irradiation is assumed to be given by $\Delta V/V = 10^{-38} (\phi t)^{1.69} \left[\exp\left(-\frac{7808}{RT}\right) - \exp\left(-\frac{25300}{RT}\right) \right]$.

(f) For 95 percent dense (U_{0.8}Pu_{0.2})N, 1 a/o burnup equals 3.27 x 10²⁰ fissions per cm³; for 88.5 percent dense (U_{0.8}Pu_{0.2})N, 1 a/o burnup equals 3.05 x 10²⁰ fissions per cm³.

(g) Assuming irradiation in an average Core Row 5 location.

A 19-pin subassembly containing unencapsulated, Type 316 stainless steel-clad mixed-nitride fuel pins will be designed and the pins fabricated and sent to the EBR-II for irradiation. The pins will be designed for irradiation at 30 kw per ft to a burnup goal of 150,000 MWD/T. The tentative fuel and cladding parameters are as follows:

(U,Pu)N pellet diameter	0.260 in.
Fuel density	95 percent of theoretical
Sodium annulus	10-mil radial
Cladding material	Type 316 stainless steel
Cladding OD	0.310 in.
Cladding thickness	15 mil

The Approval in Principle will be prepared and forwarded to the AEC for review. The Data Package consisting of the Experiment Description, Safety Analysis, and Quality Assurance Description will be prepared and forwarded to the EBR-II Project for review.

The irradiation surveillance and performance analysis for all capsules in the EBR-II will be continued.

UN-PuN TREAT Analysis

R. Artigas, H. D. Gronbeck, and P. Cybulskis

Objective of Program

To perform transient irradiation tests on (U,Pu)N fuels in the TREAT reactor.

Approach Being Used

(U,Pu)N fuel specimens will be subjected to transients in the TREAT reactor in order to simulate the dynamic thermal behavior of fast-reactor fuels. These tests should help to establish the acceptability of mixed-nitride fuels for LMFBR application under operational transient and accident conditions.

Significant Accomplishments During Fiscal Year 1970

In order to accomplish the objectives of the program a tentative capsule design has been adopted. The adequacy of the conceptual capsule design from a heat-transfer viewpoint has been demonstrated by means of time-dependent thermal calculations for the (U,Pu)N-fueled experiments for a range of reactor transients. The correlation between neutron flux in the (U,Pu)N-fueled capsule and the TREAT reactor has been established through the computation of a figure of merit for this experiment.

Summary of Research Carried Out

Transient testing programs for other ceramic fuels, performed by General Electric, Atomics International, and Argonne National Laboratory in the TREAT facility, were reviewed in order to take full advantage of the background of information developed previously. The physical properties of the mixed nitrides were compared with those of the carbides and oxides in order to predict the relative behavior of the fuels under transient conditions. Parameters which must be varied in the program have been identified as: type of bond between fuel and cladding, transient magnitude, preirradiation history, fuel density, and transient time scale.

Analytical comparisons were made between the thermal response of nitride fuels during TREAT transients and the response of a nitride-fueled LMFBR to an accident

reactivity excursion. It was found that TREAT can provide an adequate simulation of the thermal transients that may be expected under LMFBR accident conditions.

Analytical and experimental questions concerning the TREAT tests were discussed with representatives of ANL, and energy releases of up to 80 Btu per in. of fuel were tentatively selected as the basis for the TREAT capsule design. The primary cause of cladding failure for the unirradiated specimens in the temperature range of interest (2500 to 5000 F) is expected to be the pressure due to the vaporization of the sodium bond during the transient, and not the vapor or decomposition pressure of the fuel.

In order to establish the pulse characteristics that would subject the (U,Pu)N fuels to temperatures in the range of interest (2500 to 5000 F) for significant periods of time and to develop the requirements for the detailed capsule design, a preliminary conceptual capsule design was adopted. A one-dimensional geometrical model suited for computational purposes and based on the conceptual design is illustrated in Figure A-37. The time-temperature behavior of the mixed-nitride-containing capsule when subjected to a flat-top transient was calculated by means of the ARGUS⁽¹⁾ code*.

Initially, the sodium-bond region in the capsule was treated as a stationary region with thermal conductivity k , but this resulted in the selection of prohibitively small time steps to assure numerical stability, especially at times near or during sodium-bond vaporization. The treatment of sodium-bond regions as flow regions with zero velocity and the use of three axial nodes permitted the use of somewhat larger computational time steps. The heat-transfer coefficient, h , for these sodium annuli was defined such that,

$$\bar{h} = \frac{\int \frac{1}{r} \left[\frac{\partial}{\partial r} \left(k_r \frac{\partial T}{\partial r} \right) \right] r dr}{\left(\frac{\Delta T}{\Delta r} \right) \int r dr},$$

where k , the thermal conductivity, was taken to be constant over r , and the very thin annular regions were approximated by slabs. This model was tested by making two ARGUS runs, one with an "exact" treatment and another with the above definition of h . The temperature distributions as a function of time for the two cases were essentially identical.

The thermal properties of sodium in the range of 400 to 1700 F were fitted to the following parabolic equations by means of a linear regression subroutine for use in the ARGUS code:

$$\text{Thermal conductivity} = k = 54.274258 - (0.0213924)T + (4.787088 \times 10^{-6})T^2,$$

$$\text{Density (liquid)} = \rho_L = 58.727 - (0.00756757)T,$$

$$\text{Volumetric specific heat} = \rho C_p = 20.139277 - (6.556376845 \times 10^{-3})T + (1.812281168 \times 10^{-6})T^2,$$

where T is the Fahrenheit temperature, k is given in Btu/(hr)(ft)(F), ρ in lb per ft³, and ρC_p in Btu/(ft³)(F).

It is expected that the helium overpressure, which is for all practical purposes the dominant pressure at any point in the sodium bond, will not exceed 2 atm before boiling can occur. The vapor pressure of sodium exceeds 2 atm at about 1800 F. For the present analysis it was, therefore, assumed that, if the bond temperature exceeds the temperature at which the vapor pressure of sodium is greater than 2 atm, all the liquid sodium in the bond is displaced by sodium vapor. This is a reasonable, although conservative, assumption since at 2 atm the ratio of liquid to vapor densities is approximately 1300 and only a small portion of the sodium must vaporize to fill the fuel-cladding gap.

* Extensive programming modifications to the ARGUS code were made for adaptation to Battelle's CDC-6400 computer.

FIGURE A-37. ONE-DIMENSIONAL MODEL OF TREAT CAPSULE
(Not Drawn to Scale)

In an attempt to determine the performance of the capsule, several "flat-top" transients, all within the tentative design criterion for total energy release of 80 Btu per in., were investigated. In a flat-top or clipped-burst transient the power rises rapidly to a high level and is maintained at that level for a brief period of time, of the order of seconds, followed by reactor shutdown. This is in contrast to a fast burst in which the power rises exponentially to a peak value and then immediately decreases to a low level. A flat-top transient generating a specified power density in the experimental fuel can be related to the average TREAT reactor power by use of the figure of merit. For these initial calculations, the figure of merit derived by General Electric for mixed-oxide irradiations in the TREAT reactor (1.12×10^{-4} watt/cm³ per watt of reactor power) was utilized. The time-temperature behavior of a representative UN-PuN experiment is illustrated in Figures A-38 through A-41 for the inner four capsule regions for four different flat-top transients. The four transients produced pseudo-steady-state power levels in the UN-PuN fuel specimen of 75, 60, 50, and 40 kw per ft at TREAT powers of 70, 55.5, 47, and 37 Mw, respectively. Figure A-42 shows the time-temperature behavior after the end of the reactor pulse for the case involving a power level of 50 kw per ft. Figure A-43 illustrates the time-temperature behavior of the fuel hot-spot for the four pulses. Figures A-44 and A-45 show the time-temperature history of the outer capsule components (beryllium, sodium, niobium, sodium, 1000 aluminum) for two different pulses.

The results of these calculations illustrate the effect of the rate of energy release on the behavior of the experimental fuel pin. For the pulse producing 75 kw per ft, under the assumptions previously noted, sodium-bond vaporization is seen to occur 2.65 sec after the start of the transient at a total TREAT energy release of about 186 Mw-sec. For the pulse producing 60 kw per ft, bond vaporization is predicted at 6.5 sec at an energy release of about 361 Mw-sec. For the pulse producing a pseudo-steady-state power level of 50 kw per ft, sodium-bond vaporization is not predicted to occur during the approximately 10-sec duration of the pulse even though the total TREAT energy release is 432 Mw-sec. As would be expected, the lower-power transients provide more time for the redistribution of energy to the heat sinks within the capsule, thus allowing a greater total energy release without exceeding a threshold such as the vaporization of the sodium bond. When sodium-bond vaporization does occur, essentially adiabatic heatup of the fuel can follow as a result of the low thermal conductivity of the sodium vapor. However, prediction of the thermal behavior of the fuel after bond vaporization is highly uncertain because of the lack of understanding about the thresholds and mechanisms of sodium boiling, the expulsion and reentry of liquid sodium in narrow annuli, etc. The situation is further complicated by the possibility of cladding failure as the temperatures in the experiment approach the regime in which bond vaporization (boiling) may be expected. The study of the above phenomena is, of course, one of the prime objectives of the fuel-element transient testing program.

In view of the uncertainties in predicting such effects at the onset of sodium-bond vaporization and the subsequent thermal behavior of the fuel pin, the calculations discussed herein can only be used to identify the types of transients which will take the experiments into regimes of interest. Thus, consideration of the results of the above calculations indicate that TREAT transients of the flat-top or clipped-burst type should produce pseudo-steady-state power levels in sodium-bonded UN-PuN fuels of about 50 kw per ft or more to reach conditions of interest from an overpower transient or accident viewpoint.

It should be noted that the experiment power levels (kw per ft) cited in this discussion do not correspond directly to the specific powers of steady-state irradiations. In the latter, the flowing coolant is maintained at a constant temperature and, from the point of view of the experimental fuel pin, provides an infinite heat sink. In the TREAT capsule, on the other hand, there is no heat transferred external to the capsule and only a finite heat capacity is available for accommodating the transient energy release. Thus, in the

FIGURE A-38. TIME-TEMPERATURE BEHAVIOR OF THE INNER FOUR REGIONS OF A UN-PuN CAPSULE SUBJECTED TO A 3.1-SEC FLAT-TOP TRANSIENT GENERATING 75 KW PER FT IN A FUEL AT A TREAT POWER OF 70 MW

FIGURE A-39. TIME-TEMPERATURE BEHAVIOR OF THE INNER FOUR REGIONS OF A UN-PuN CAPSULE SUBJECTED TO A 6.98-SEC FLAT-TOP TRANSIENT GENERATING 60 KW PER FT IN A FUEL AT A TREAT POWER OF 55.5 MW

FIGURE A-40. TIME-TEMPERATURE BEHAVIOR OF THE INNER FOUR REGIONS OF A UN-PuN CAPSULE SUBJECTED TO A 9.2-SEC FLAT-TOP TRANSIENT GENERATING 50 KW PER FT IN A FUEL AT A TREAT POWER OF 47 MW

FIGURE A-41. TIME-TEMPERATURE BEHAVIOR OF THE INNER FOUR REGIONS OF A UN-PuN CAPSULE SUBJECTED TO A 10-SEC FLAT-TOP TRANSIENT GENERATING 40 KW PER FT IN A FUEL AT A TREAT POWER OF 37 MW

FIGURE A-42. TIME-TEMPERATURE BEHAVIOR OF THE UN-PuN CAPSULE AFTER THE END OF THE REACTOR PULSE OF 50 KW PER FT

FIGURE A-43. TIME-TEMPERATURE BEHAVIOR OF FUEL HOT SPOT FOR THE FOUR PULSES

FIGURE A-44. TIME-TEMPERATURE BEHAVIOR OF THE OUTER CAPSULE FOR A 10-SEC PULSE GENERATING A POWER LEVEL OF 40 KW PER FT IN A FUEL

FIGURE A-45. TIME-TEMPERATURE BEHAVIOR OF THE OUTER CAPSULE FOR A 9.2-SEC PULSE GENERATING A POWER LEVEL OF 50 KW PER FT IN A FUEL

latter case, operation at even very low power levels for prolonged periods of time could lead to overheating of the experiment. In this connection, thermal reactor irradiations of UN-PuN fuels have been performed at continuous power levels approaching 50 kw per ft, whereas such an experimental power level could not be extended for more than 10 sec in the TREAT capsule without the expectation of possible fuel-pin failure. The energy release prior to sodium-bond vaporization and/or fuel-pin failure in TREAT will also depend on the initial temperature of the experiment; in the present analysis a starting temperature of 400 F has been assumed.

When the thermal behavior of the outer capsule components is examined it appears that the conceptual design includes sufficient heat capacity in the outer aluminum heat sink to accommodate the transient energy releases of interest (see Figures A-44 and A-45). The maximum average temperature rise in the outer aluminum region, as defined in Figure A-37, can be found to be

$$T_{\max} - T_{\text{initial}} = \left[\int_{\Delta t} Q dt \right] \times 0.5578, \quad (\text{A-12})$$

where Q refers to the experiment power in kw per ft and Δt is the duration of the pulse in seconds. The temperatures are in degrees Fahrenheit. For a flat-top transient

$\int_{\Delta t} Q dt = Q \cdot \Delta t$. Using Equation (A-12), the maximum average temperature rise in the outer aluminum, when a power level of 60 kw per ft is used for 6.5 sec, is 217 F. At any given time the hottest spot in the aluminum could be somewhat higher than this temperature rise predicts; see, for example, Figure A-46. This is an asymptotic, adiabatic, temperature increase and the actual temperature should be somewhat less than this value.

For the calculations discussed above, the power distribution and figure of merit as determined by GE for the mixed-oxide transient irradiations were utilized. In order to determine a figure of merit for the (U,Pu)N TREAT capsule, a one-dimensional, multi-group, integral transport code, THERMOS⁽²⁾, was used. A set of thermal cross sections to be used with a two-group diffusion code, 2DB⁽³⁾, was also generated. The transport-theory code gave the detailed neutron flux distribution within the UN-PuN experiment and the diffusion code was used to normalize the THERMOS results to an average reactor power.

For the THERMOS calculations, the reactor, or that part of the reactor immediately surrounding the test cell, was taken to be "normal core fuel cells"⁽⁴⁾; that is, 89.05 percent by volume of core graphite, 2.31 percent Zircaloy-3 cladding, and 8.64 percent void. The core graphite, also described in Reference (4), is 99.9585 percent by volume carbon (with a density of 1.72 g per cm³), 4.21 x 10⁻⁴ percent boron, 2.188 x 10⁻² percent iron, 1.787 x 10⁻² percent U²³⁵, and 1.32 x 10⁻³ percent U²³⁸. The (U,Pu)N capsule was assumed to be placed in a 4 by 4-in. test cell at the center of the TREAT core. The results of the THERMOS calculations are given in Figures A-47 and A-48, and the number densities used in the calculation in terms of nuclide per unit volume are given in Table A-26. The mixed-nitride fuel was assumed to have a density of 95 percent of theoretical, and to contain 80 w/o UN and 20 w/o PuN. The uranium isotopic composition was assumed to be that of natural uranium, and the plutonium as 89.6 percent Pu²³⁹, 8.8 percent Pu²⁴⁰, and 1.6 percent Pu²⁴¹. For computational purposes the test capsule was divided into four regions: (1) fuel; (2) a volume-homogenized region of sodium, stainless steel, and sodium; (3) a volume-homogenized region of beryllium, sodium, niobium, and sodium; and (4) an aluminum outer region. Figure A-48 also compares the power distribution for the (U,Pu)N TREAT capsule with the power distribution of mixed-oxide fuel of General Electric Company. A higher peak-to-average power ratio is present in the mixed-nitride fuel. The differences are attributed primarily to differences in fuel radii and fuel composition. These differences in power distribution are expected to make little difference in the overall temperature distribution within the capsule.

FIGURE A-46. ALUMINUM HOT-SPOT TEMPERATURE AS A FUNCTION OF TIME

FIGURE A-47. SOURCE-NORMALIZED THERMAL FLUX AS A FUNCTION OF POSITION IN (U, Pu)N FUEL IN TREAT TEST CELL

FIGURE A-48. POWER DISTRIBUTION (ARBITRARY NORMALIZATION) OF (U, Pu)N FUEL AND A MIXED OXIDE AS A FUNCTION OF POSITION IN TREAT TEST CELL

TABLE A-26. NUMBER DENSITIES USED IN THE INTEGRAL TRANSPORT CALCULATION

Element	Number Density, nuclides per unit volume $\times 10^{-24}$	
	(U,Pu)N Capsule	TREAT Reactor
Carbon	--	0.076796
Boron	--	5.1144×10^{-7}
Iron	0.0843	2.0445×10^{-5}
Uranium-235	0.0001871	7.706×10^{-6}
Uranium-238	0.025798	5.622×10^{-7}
Tin	--	1.794×10^{-6}
Zirconium	--	0.0009722
Plutonium-239	0.0057945	--
Plutonium-240	0.0005691	--
Plutonium-241	0.0001035	--
Sodium	0.0254	--
Aluminum	0.0602	--
Beryllium	0.1236	--
Niobium	0.0545	--
Nitrogen	0.03245	--

From the THERMOS results, thermal-group parameters were determined for the (U,Pu)N capsule. A cell calculation was also performed for the TREAT core using the same code, and a set of thermal cross sections was determined for the reactor.

A set of fast cross sections was generated by the use of a Fourier Transform 54-group Fast Spectrum Code, FORM⁽⁵⁾. Cross sections were generated for both the TREAT core and the (U,Pu)N capsule.

The reflector compositions were taken as described in Table A-27; some of the impurities were neglected. The thermal spectrum was assumed to be Maxwellian for the computation of thermal parameters for the reflector materials. The fast cross sections were obtained from FORM.

TABLE A-27. REFLECTOR COMPOSITIONS

Material	Amount of Indicated Element Present, v/o		
	Carbon	Zirconium	Aluminum
Upper reflector	65.39	3.98	15.67
Zirconium-clad reflector	89	2.31	--
Aluminum-clad reflector	87	--	4.6
Permanent reflector	90.57	--	1.89

For computational purposes the TREAT reactor was geometrically represented in a symmetrical R-Z geometry, as shown in Figure A-49. The two-dimensional diffusion code, 2DB, was used to compute power and flux distributions. Modification was required in using this code for a thermal reactor, since it defines Σ_{tr} as $\Sigma_a + \Sigma_s$. Σ_{tr} was computed properly, with Σ_s defined as $\Sigma_s (1-\mu)$ for the present calculations. Axial and radial flux distributions were computed. The reactor core was assumed to have no control rods; control rods were included in the upper reflector, and no test hole was included. Figures A-50 and A-51 compare the fission rates as measured by the use of

FIGURE A-49. R-Z REPRESENTATION OF THE TREAT REACTOR
(NOT TO SCALE)

FIGURE A-50 COMPUTED AND MEASURED AXIAL FISSION RATES IN THE TREAT CORE

FIGURE A-51 COMPUTED AND MEASURED RADIAL FISSION RATES IN THE TREAT CORE

U^{235} foils⁽⁴⁾, and as computed by this analysis. The measured fission rate in the lower half of the reactor is higher because it contains no control rods.

An experiment was next included in the test hole with a (U, Pu)N specimen about 2.5 in. long. A combination of the THERMOS run and the normalizing 2DB run was used to determine a figure of merit, i. e., the ratio of the specific power in the experimental fuel specimen to the average reactor power. This figure of merit determines the desired TREAT reactor power for a specified energy release in the fuel. The figure of merit, FOM, is somewhat dependent upon the particular fuel specimen to be irradiated, and it therefore must be determined for each case. The computed FOM for this analysis, which should be representative for UN-PuN experiments, is

$$\text{FOM} \approx 1.8 \times 10^{-4} \text{ watt/cm}^3 \text{ per watt of reactor power}$$

This compares with a FOM of 1.12×10^{-4} watt/cm³ per watt of reactor power, as computed by G. E. for mixed-oxide irradiations in TREAT. The higher fissile atom density of the nitride fuel compared to the oxide fuel is believed to account for the larger figure of merit. The difference implies that lower TREAT reactor powers are going to be required than indicated previously. The value of the FOM will be recomputed for each particular experiment and experimental capsule using many of the neutronics parameters and results determined here.

Plans for Future Work

During the next fiscal year the detailed design of the TREAT capsule will be performed and the capsule will be fabricated; engineering and safety analyses will be performed and the transient irradiation of one UN-PuN-fueled experiment will be carried out.

- (1) Schoeberle, D. F., et al., "A Method of Calculating Transient Temperatures in a Multiregion, Axisymmetric, Cylindrical Configuration, The ARGUS Program", ANL-6654 (November, 1963).
- (2) Toppel, B. J., and Boksys, I., "The Argonne-Revised THERMOS Code", ANL-7023 (March, 1965).
- (3) Little W. W., Jr., and Hardie, R. W., "2DB User's Manual", BNWL-831 (1968).
- (4) Okrent, D., et al., "The Reactor Kinetics of the Transient Reactor Test Facility (TREAT)", ANL-6174 (September, 1960).
- (5) McGoff, D. J., "FORM, A Fourier Transform Fast Spectrum Code", NAA-SR-5766 (September, 1960).

Model Development for Irradiation-Induced Swelling of (U, Pu)N

S. K. Batra

Objective of Program

To develop a mathematical model for the swelling of nuclear fuels whose mechanical behavior is representative of that believed to be occurring when (U, Pu)N fuel surrounded by liquid sodium is irradiated in the low flux range, and to evaluate the influence various parameters may have on the rate of swelling.

Approach Being Used

A purely mechanical approach is adopted in meeting this objective. A quantitative analysis of an idealized model of a clad fuel element is used to provide further insight into the swelling problem and to suggest ways in which swelling can be retarded.

Significant Accomplishments During Fiscal Year 1970

The possibility of controlling fuel swelling during irradiation by incorporation of a controlled porosity in the fabricated pellets is being evaluated. Preliminary results show no influence of variations in density, from 80 to 95 percent of theoretical, on the diametral expansion of the clad fuel.

Summary of Research Carried Out

The motivation for the development of the model is to evaluate the possibility of eliminating liquid sodium in the annulus around nitride fuels in LMFBR fuel rods. The model developed makes the following assumptions to analyze the problem:

- (1) The fuel has uniform porosity throughout the deformation process. No new pores are generated during burnup.
- (2) The fuel material is approximated by polyhedral cells associated with each pore. The deformation behavior of the polyhedral cell is approximated by the deformation behavior of a spherical shell of equivalent volume.
- (3) The pressure of the fission gases in the pores is assumed to be negligible; surface-tension effects are neglected.
- (4) The fuel and cladding obey a nonlinear creep law.
- (5) Isothermal creep is assumed.
- (6) The solid fuel material is allowed to change its density through volumetric expansion due to fission atom production. This is introduced in the creep law in the following manner:

$$\dot{\epsilon} = A \left| \sigma^* \right|^n \exp (-Q/RT).$$

The equation expresses the relationship between the strain rate, $\dot{\epsilon}$, and the stress, σ^* , at the temperature, $T(K)$, for a material whose activation energy is Q (cal per mole). R is the gas constant and A and n are constants describing the creep properties of the material. The stress is so formulated as to make dilation, a measure of the volume change locally, equal to zero for all times. Therefore, to introduce volumetric expansion due to fission-product atoms, the equation is modified as

$$\dot{\epsilon} = A \left| \sigma^* \right|^n \exp (-Q/RT) + 1/3 \mu \Gamma,$$

where μ is the volumetric expansion caused by a fission-product atom and Γ is the fission rate.

- (7) A state of hydrostatic stress, which is equal to the reactive internal pressure of the cladding, is assumed to prevail in the fuel material.
- (8) Changes in volume of a radial slice of fuel are constrained to occur in the radial direction.
- (9) No gap is assumed to exist between the fuel and the cladding.
- (10) The cladding acts to restrain volume expansion of the solid fuel into the available porosity of the fuel.

This mathematical model is analyzed numerically. The program has been coded in the G. E. time-sharing system.

Using the model, the following case for nitride fuel was evaluated:

Inner radius of the cladding = 0.1475 in.
 Outer radius of the cladding = 0.1575 in.
 Fission rate = 7.5×10^{13} fissions/(cm³)(sec)
 Creep strength of the fuel (1000 C) = 3000 psi
 Creep strength of the cladding (700 C) = 7500 psi
 Creep stress exponent of the fuel = 3.0
 Creep stress exponent of the cladding = 4.0
 Volumetric expansion = 3×10^{-22} cm³ per fission.

Calculations were obtained for initial material density levels of 95 and 80 percent of theoretical. The results of these calculations are plotted in Figure A-52. They show

that for the postulated behavior and for these density levels the influence of porosity on swelling is negligible. Thus, the initial indication is that little benefit can be gained by increases in the fuel porosity, irrespective of the swelling restraint by the cladding.

FIGURE A-52. SWELLING BEHAVIOR OF CLAD NITRIDE FUELS INITIALLY 80 TO 95 PERCENT DENSE

The volumetric expansion caused by fission-product atoms is assumed to be $3 \times 10^{-22} \text{ cm}^3$ per fission in this mathematical model, and the fission rate is $7.5 \times 10^{13} \text{ fissions}/(\text{cm}^3)(\text{sec})$.

Plans for Future Work

To fully explore the potential of the porosity level in the retardation of fuel swelling, further parametric evaluations are planned. In particular, lower values of μ , more characteristic of fuel swelling due to solid fission-product atoms, will be examined. Alternatively, the porosity of an annular fuel geometry as a possible mechanism for retarding fuel swelling will be explored.

✓ TECHNOLOGY OF NUCLEAR FUELS FOR
ADVANCED FAST REACTORS (AEC-DRDT) ✓

D. L. Keller and W. Chubb

The objective of this program is to obtain information on the basic causes of changes in the properties and dimensions of the most promising fuel candidates for improved or advanced types of fast reactors as well as for current concepts. Data obtained in this program will provide a unique description of the in-pile behavior of those portions of LMFBR fuels which operate at temperatures from 1300 to 2000 C. Such data will allow determination of the relative contributions of those parts of the fuel operating above 1300 C, of those parts operating below 1300 C, and of the cladding to the overall fuel-element swelling behavior. The data will enhance assessment of the performance of present LMFBR fuel concepts under all credible operating conditions and will tend to validate subsequent use of current fuels at more efficient temperature levels. A model describing the mechanical interactions of the various parts of the fuel element will be developed to allow extrapolation of the experimental data to all temperatures of interest to LMFBR's.

Included in the program is (1) an irradiation study in which the dimensions and other physical properties of oxide, and, to a lesser extent, nitride and carbide, fuels are being determined as a function of burnup and irradiation temperature, (2) a study focused on the mechanisms of swelling in nuclear fuels in which theoretical models describing the generation and movement of gaseous fission products, including solubility and chemical diffusivity factors, bubble formation, and overall swelling processes, are being formulated and evaluated by comparison with the behavior and properties of actual fuels, (3) a fuel materials development effort in which fuels suited to the assessment of various technological concepts under study in the program are prepared and exhaustively characterized, (4) a materials properties study in which chemical and mechanical properties that might influence the behavior under irradiation of refractory fuels are investigated, and (5) a capsule development effort in which capsules tailored to the special requirements of the irradiation study are designed and prepared for use in the BRR and the MTR or ETR.

Irradiation Behavior of Oxide Fuels at High Temperatures

R. F. Hilbert, W. J. Zielenbach, D. E. Lozier,
R. B. Clark, and V. W. Storhok

Objective of Program

To investigate the irradiation behavior of oxide fuels at surface temperatures from 1200 to 1900 C.

Approach Being Used

Several UO_2 specimens are being irradiated in order to study swelling, fission-gas release, and restructuring of UO_2 at surface temperatures from 1200 to 1900 C. The effects of density, axial centerline holes, venting of fission gases, stoichiometry, and the addition of PuO_2 are also being studied. One specimen in each capsule starting with Capsule HT-BRR-9 will be monitored for the pressure of gas collecting inside its cladding during the irradiation to determine the extent and timing of gas release. Fission gas released from the fuel to the interior of the cladding will be conducted to one side of a metal diaphragm located in the cool zone of the capsule. An externally controlled and measured pressure source will act on the opposite side of the diaphragm

to balance the fission-gas pressure. The balance of pressures will be determined by sensing the deflection of the diaphragm with an electrical contact.

Six specimens of UO_2 were irradiated in Capsule HT-BRR-9 to study swelling, fission-gas release, and restructuring of UO_2 as a function of surface temperature. Specifically, Capsule HT-BRR-9 contained the fuels described in Table B-1.

TABLE B-1. DESCRIPTION OF UO_2 SPECIMENS IRRADIATED IN CAPSULE HT-BRR-9

Design Cladding Temperature, C	Geometry	Nominal Density, percent of theoretical	U^{235} Enrichment, percent
1900(a)	110-mil axial hole	97	20
1700	55-mil axial hole	97	10
1900	Solid	90	20
1700	110-mil axial hole	97	20
1500	110-mil axial hole	97	10
1900	Solid	90	20

(a) Gas pressure monitored.

Four specimens of UO_2 and two specimens of $\text{UO}_2\text{-PuO}_2$ were irradiated in Capsule HT-BRR-11 to determine the effects of stoichiometry, as-fabricated porosity, and the addition of PuO_2 on the swelling and gas-release behavior of UO_2 at 1700 C. In addition, a portion of the experiment was designed to determine the restraint to swelling of these fuels at 1700 C by a cladding with a strength approximating that of stainless steel at 600 C. The fuels irradiated in Capsule HT-BRR-11 are given in Table B-2.

TABLE B-2. DESCRIPTION OF THE SPECIMENS IRRADIATED AT 1700 C IN CAPSULE HT-BRR-11

Fuel	Geometry	Nominal Density, percent of theoretical	Cladding Thickness, in.
$\text{UO}_2\text{-x}$	110-mil axial hole	96	0.020(a)
UO_2	55-mil axial hole	80	0.020
$\text{UO}_2\text{-8 w/o PuO}_2$	110-mil axial hole	96	0.040
UO_2	110-mil axial hole	96	0.040
$\text{UO}_2\text{+x}$	110-mil axial hole	96	0.020
$\text{UO}_2\text{-8 w/o PuO}_2$	110-mil axial hole	96	0.020

(a) Gas pressure monitored.

Three specimens of UO_2 and three specimens of $\text{UO}_2\text{-PuO}_2$ were irradiated in Capsule HT-BRR-12 to study the temperature dependency of restructuring, columnar grain growth, and gas-bubble formation. The capsule was neutron radiographed at selected times early in the irradiation and at the end of each cycle (about 500 hr) in an attempt to determine whether restructuring occurred (as evidenced by center-void formation). The duration of the irradiation was based primarily on the timing and the nature of changes seen on the neutron radiographs. The irradiation was short (only two cycles) to minimize the chances of the structure being altered by inadvertent

overtemperature conditions. The fuels irradiated in Capsule HT-BRR-12 are described in Table B-3.

TABLE B-3. DESCRIPTION OF THE SPECIMENS IRRADIATED IN CAPSULE HT-BRR-12

Fuel	Design Cladding Temperature, C	Description
UO ₂	1500	90 percent dense, gas-pressure monitor
UO ₂ -8 w/o PuO ₂	1700	90 percent dense
UO ₂	1700	90 percent dense, 110-mil axial hole
UO ₂ -8 w/o PuO ₂	1500	90 percent dense
UO ₂	1300	90 percent dense
UO ₂ -8 w/o PuO ₂	1300	90 percent dense

Capsule HT-BRR-14 will contain oxide fuel specimens and will be primarily aimed at determining the mechanism of gas release from and swelling of UO₂. The capsule will contain the fuel specimens shown in Table B-4. The fully dense UO₂ specimens are designed to study lenticular pore movement and columnar grain growth as a function of temperature and in the absence of as-fabricated porosity. The specimen with the annular tungsten foil at the midradius and the specimen with the depleted UO₂ annulus are designed to interrupt the sweeping action of lenticular voids. Hopefully, interrupting the flow of lenticular voids will permit the formation of observable fission-gas bubbles in the columnar grains. The UO₂ specimen with the gas monitor is designed to determine the timing and extent of fission-gas release at temperatures where lenticular void migration by vapor transport of UO₂ is slow or nonexistent.

TABLE B-4. DESCRIPTION OF THE SPECIMENS TO BE IRRADIATED IN CAPSULE HT-BRR-14

Fuel	Nominal Density, percent of theoretical	Centerline Hole Diameter, in.	Design Cladding Temperature, C	Description
UO ₂	96	0.110	1300	Gas monitor
UO ₂	95	0.055	1450 ± 50	Annular tungsten foil at fuel midradius
UO ₂	95	0.055	1450 ± 50	Annular region of depleted UO ₂ on fuel OD at fuel axial midplane
UO ₂	100	0.110	1700	--
UO ₂	100	0.110	1700	Vented cladding
UO ₂ -8 w/o PuO ₂	90	None	1500	--

Most of the specimens in HT-BRR series capsules consist of a column of pellets or slugs of fuel 1 in. long contained in tungsten-26 w/o rhenium claddings approximately

1.44 in. long with an OD of 0.25 in. and a wall thickness of 20 mils, as shown in Figure B-1. Two specimens in Capsule HT-BRR-11 have a cladding thickness of 40 mils and an OD of 0.29 in.

Dimensional changes in the specimens are determined after each cycle of irradiation by measurements from neutron radiographs. The postirradiation examination includes (when appropriate) dimensional measurements, fission-gas-release measurements, and metallography.

Significant Accomplishments During Fiscal Year 1970

On the basis of the swelling rates observed on a cycle-by-cycle basis (a cycle consists of 3 weeks of irradiation) for a number of specimens in this program, the external swelling of UO_2 appears to be temperature-dependent and essentially linear as a function of burnup. At cladding surface temperatures below about 1600 C, external swelling rates generally were less than 8 v/o per 10^{20} fissions per cm^3 . Above 1600 C, swelling rates increased with temperature to a cladding surface temperature of about 1750 C, where external swelling rates were nearly four times as great. This behavior shows that UO_2 can severely deform its cladding at these temperatures even though gas release is high.

A gas-pressure monitor indicated that a UO_2 specimen which operated at a cladding surface temperature of 1840 C released fission gas at nearly the same rate as it was generated. This high gas release was continuous after the first few hours of irradiation. Retained-gas measurements performed during the postirradiation examination indicated that all the specimens that operated at cladding surface temperatures of 1475 C and above released about 90 percent of their fission gas. The UO_2 in these specimens formed columnar grains extending from the cladding to the center of the sample. At a cladding surface temperature of 1325 C, the UO_2 released about 75 percent of the gas produced during the irradiation and consisted of short columnar and enlarged equiaxed grains.

The above-mentioned specimen of UO_2 which operated at a cladding surface temperature of 1840 C with a gas-pressure monitor attached continued to swell even though the cladding failed after a burnup of 0.5×10^{20} fissions per cm^3 . This behavior demonstrates that the diametral increase of this specimen was not caused by an increase of the gas pressure contained within the cladding. The gas-pressure monitor registered 29 psig before failure and zero after the cladding rupture. A review of the irradiation history of all the specimens revealed no relation between the amount of swelling and the number of thermal cycles (to ambient temperature). Thus, thermal ratcheting can probably be discounted as a major contributor to the swelling. On the basis of these observations, it is concluded that the swelling of UO_2 at high temperatures is caused by the precipitation and growth of fission-gas bubbles within the UO_2 prior to the release of the gas at external surfaces of the UO_2 .

A theory to explain these observations postulates that the uranium dioxide swells by the formation of small, relatively immobile fission-gas bubbles. This swelling results in small, permanent, external dimensional changes. Periodically, portions of the uranium dioxide are swept by lenticular voids. This vapor-phase zone-refining process reconstitutes the uranium dioxide down the temperature gradient, maintaining the density of the oxide essentially constant. The vapor-phase transport and redensification of the oxide occur in such a way that external dimensional changes are not recovered. The large external dimensional changes occurring when this sequence is repeated many times represent the summation of a large number of repetitive steps involving small density decreases in the uranium dioxide followed by redensification by the zone-refining process. The zone-refining process is instrumental in collecting fission gas and in forming channels for gas release. Although probably not the sole mechanism of gas release, the process is a major mechanism of gas release from uranium dioxide at temperatures over 1600 C.

FIGURE B-1. STANDARD CONFIGURATION OF SPECIMENS IRRADIATED IN THE BRR

Summary of Research Carried Out

During Fiscal Year 1970, the irradiation and postirradiation examinations of Capsules HT-BRR-9 and HT-BRR-12 were completed. Irradiation of Capsule HT-BRR-11 was completed late in the fiscal year, and postirradiation examination was initiated. Fabrication and encapsulation of the specimens in Capsule HT-BRR-14 were completed and the irradiation was started.

The irradiation conditions and dimensional changes of the UO_2 and $\text{UO}_2\text{-PuO}_2$ specimens in Capsules HT-BRR-9, -11, and -12 are given in Tables B-5 through B-7. Note that the final dimensional data taken from neutron radiographs are in excellent agreement with the postirradiation micrometer measurements. Neutron radiographs, which illustrate the general condition of the specimens, are shown in Figures B-2 through B-4. A plot of external volumetric swelling rate as a function of cladding surface temperature, Figure B-5, shows that the external dimensions of UO_2 and $\text{UO}_2\text{-PuO}_2$ clad with 20 or 40 mils of tungsten-rhenium alloy increase with increasing temperature from 1250 to 1900 C. (It should be noted that the data shown in Figure B-5 represent the external volumetric swelling rate of each specimen for the entire irradiation and that the temperatures represent an average of the temperatures of each reactor cycle.) There are differences between specimens, such as cladding thickness and density; however, the data given in Figure B-5 show that temperature is the most significant variable with respect to swelling of oxide fuels at high temperatures. The swelling data given in Figure B-5 can be separated into three loosely defined temperature regimes on the basis of microstructural observations. The irradiation behavior of UO_2 and $\text{UO}_2\text{-PuO}_2$ in each of these temperature regimes is discussed below, and a model of oxide fuel swelling at high temperatures is presented.

External swelling data for several oxide fuel specimens that operated at cladding surface temperatures from 1260 to 1390 C are shown in Figure B-6. In this range of surface temperatures, the external volumetric swelling rates were nearly linear as a function of burnup and varied from about 0.5 to 5 percent per 10^{20} fissions per cm^3 , while fission-gas release was about 75 percent. There was little apparent difference in the external swelling behavior between the UO_2 and $\text{UO}_2\text{-8 w/o PuO}_2$ fuels or between two specimens of $\text{UO}_2\text{-8 w/o PuO}_2$ with different cladding thicknesses. Since the specimens with different cladding thickness (4P and 5P in Capsule HT-BRR-11) contain 110-mil axial holes, it may be that differences in internal swelling will be measured in the postirradiation examination. Note on Figure B-6 that 80 percent dense UO_2 Specimen 360 exhibited a lower external fuel volume increase when irradiated to a higher burnup than the other specimens. Neutron radiographs (Figure B-3) indicate that the axial hole was larger and that, therefore, the specimen was densified by the end of the first irradiation cycle. Because the specimen densified early in the irradiation, the effect of the initial porosity on the swelling during the rest of the irradiation is not clear at this time. A study of the microstructure during the postirradiation examination may provide some explanation for the improved behavior of this specimen.

In the case of UO_2 Specimen 342 from Capsule HT-BRR-9, which was irradiated at an average surface temperature of 1325 C, it is possible to derive a direct correlation between the initial and final porosities of the fuel and the amount of swelling. A typical microstructure of Specimen 342 after irradiation shows that the fuel has a nearly equiaxed grain structure (Figure B-7). The specimen has exhibited some grain growth, including some columnar growth; the grain size shown in Figure B-7 is approximately twice the preirradiation grain size. A typical view of the microstructure near the fuel midradius at a higher magnification (Figure B-7a) shows that most of the visible (resolvable) porosity is located at the grain boundaries. There has been a limited amount of pore movement to grain boundaries probably by the vaporization-condensation mechanism and, perhaps, some grain-boundary migration by grain growth up the temperature gradient.

TABLE B-5. IRRADIATION CONDITIONS AND DIMENSIONAL CHANGES FOR UO₂ SPECIMENS
IN CAPSULE HT-BRR-9

Specimen	UO ₂ Composition	BRR Cycle	Temper- ature, C	Estimated Accumulated Burnup, 10 ²⁰ fissions per cm ³	Maximum Diameter of Center- line Hole, in.	External Dimensional Changes ^(a) , percent			
						Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
339	97 percent dense; 110-mil center- line hole; gas- pressure monitor	1	1890	0.26	0.120	0.4	0.4	1.1	2.0
		2	1880	0.59	0.130	2.9	2.3	3.3	7.9
		3	1840	0.82	0.142	3.7	3.5	4.4	11.4
		4	1840	1.15	0.160	4.4	4.0	5.2	13.8
		5	1775	1.45	0.176	4.4	4.6	5.3	15.2
		6	1800	1.78	0.180	6.0	5.3	5.2	16.6
		7	1850	2.08	0.180	8.2	7.5	9.8	24.8
		8	1860	2.34	0.180	8.0	8.2	10.8	27.2
						[14.8]	[8.2]		[27.2]
343	97 percent dense; 55-mil center- line hole	1	1475	0.19	0.055	-0.2	-0.2	0.6	0.2
		2	1450	0.43	0.057	0.0	0.0	0.4	0.5
		3	1430	0.60	0.057	2.0	1.8	0.5	4.1
		4	1470	0.84	0.057	2.6	1.8	0.7	4.4
		5	1425	1.06	0.059	2.2	1.9	0.8	4.6
		6	1475	1.30	0.060	3.5	3.3	0.2	6.8
		7	1520	1.52	0.070	4.4	3.2	1.0	7.4
		8	1555	1.71	0.070	5.8	5.2	1.2	11.7
						[4.0]	[3.8]		[8.8]
345	90 percent dense	1	1575 ^(b)	0.26	0.055	0.1	0.1	3.4	3.6
		2	1675	0.59	0.071	4.8	2.6	4.0	9.4
		3	1710	0.82	0.085	6.3	5.4	3.9	14.6
		4	1760	1.15	0.115	7.3	5.9	7.2	20.3
		5	1700	1.45	0.126	7.7	5.9	8.5	21.7
		6	1700	1.78	0.142	7.9	6.6	11.0	26.3
		7	1720	2.08	0.147	10.4	9.1	14.5	32.7
		8	1735	2.34	0.147	11.6	10.7	17.5	38.8
						[11.4]	[9.9]		[37.3]
341	97 percent dense; 110-mil center- line hole	1	1600	0.27	0.110	0.2	0.2	0.5	1.0
		2	1650	0.62	0.120	0.0	0.0	0.7	0.7
		3	1580	0.86	0.120	1.1	0.7	1.0	2.3
		4	1700	1.21	0.120	3.2	3.0	0.6	6.8
		5	1650	1.52	0.134	4.0	3.7	0.6	8.2
		6	1630	1.87	0.136	7.7	6.0	0.3	12.7
		7	1655	2.19	0.145	8.1	7.3	2.9	17.5
		8	1665	2.46	0.153	8.8	8.0	4.4	20.3
						[7.1]	[7.1]		[18.6]
342	97 percent dense; 110-mil center- line hole	1	1325	0.19	0.110	0.2	0.3	0.1	0.7
		2	1325	0.43	0.110	-0.4	-0.4	0.7	-0.2
		3	1260	0.60	0.110	1.2	0.3	0.7	1.3
		4	1360	0.86	0.110	1.0	0.9	0.8	2.6
		5	1340	1.09	0.110	1.6	0.7	0.6	2.1
		6	1300	1.33	0.110	4.2	2.5	0.5	5.6
		7	1330	1.55	0.110	3.4	2.5	0.4	5.5
		8	1350	1.74	0.110	2.6	2.3	0.0	4.6
						[2.3]	[2.2]		[4.4]

TABLE B-5. (Continued)

Specimen	Composition	Cycle	Temperature, C	Estimated Accumulated Burnup, 10^{20} fissions per cm^3	Maximum Diameter of Center- line Hole, in.	External Dimensional Changes ^(a) , percent			
						Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
344	90 percent dense	1	1570	0.25	0.040	0.4	0.5	-0.4	0.6
		2	1620	0.57	0.060	0.0	0.0	0.8	0.7
		3	1570	0.79	0.064	1.2	0.6	0.6	1.7
		4	1730	1.12	0.100	4.9	3.7	4.8	12.7
		5	1725	1.42	0.114	6.3	4.7	9.3	19.8
		6	1600	1.74	0.122	4.7	3.9	10.5	18.3
		7	1630	2.03	0.122	8.5	7.5	11.2	26.2
		8	1650	2.28	0.130	8.5	7.6	10.0	25.2
						[7.6]	[7.2]		[24.1]

(a) Values in brackets are based on micrometer measurements of diameter; all other measurements were taken from neutron radiographs.

(b) On the basis of the shell temperature opposite Specimen 345 and the specimen behavior during the first cycle (fuel irradiation and centerline voiding), it is believed that the specimen operated at a temperature at least 200 C higher than indicated. The cladding thermocouple may be shorted near the specimen in a lower temperature region, thus causing the low temperature reading.

TABLE B-6. IRRADIATION CONDITIONS AND DIMENSIONAL CHANGES FOR SPECIMENS IN CAPSULE HT-BRR-11

Specimen	Description	BRR Cycle	Temperature, C	Estimated Accumulated Burnup, 10^{20} fissions per cm^3	External Dimensional Changes ^(a) , percent			
					Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
358	UO ₂ -x: 96 percent dense, 0.110-in. axial hole, gas-pressure monitor	1	1680	0.21	0.7	0.8	2.7	4.3
		2	1410	0.45	-0.1	-0.1	2.0	1.8
		3	1430	0.73	0.9	1.1	1.7	3.9
		4	1420	0.97	0.3	0.4	3.3	4.1
		5	1380	1.19	0.5	0.6	2.7	3.9
		6	1380	1.41	0.4	0.5	1.5	2.5
		7	1380	1.64	1.8	1.2	1.8	4.2
		8	1370	1.86	2.8	1.6	2.0	5.2
					[0.8]	[0.5]		[3.0]
360	UO ₂ : 80 percent dense, 0.055-in. axial hole	1	1530	0.23	0.4	0.5	-1.7	-0.7
		2	1370	0.50	0.3	0.3	0.5	1.1
		3	1390	0.81	1.3	1.5	-0.1	2.9
		4	1380	1.08	0.8	1.0	0.0	1.9
		5	1400	1.33	0.6	0.7	0.3	1.1
		6	1400	1.58	0.4	0.5	-0.3	0.7
		7	1400	1.84	1.8	1.3	-0.3	2.9
		8	1390	2.09	1.9	1.8	0.4	4.0
					[1.2]	[0.8]		[2.0]
4P	UO ₂ -8 w/o PuO ₂ : 96 percent dense, 0.110-in. axial hole, 0.040-in. -thick cladding	1	1460	0.18	-0.1	-0.2	1.2	0.8
		2	1280	0.39	0.3	0.4	0.9	1.7
		3	1300	0.63	-0.3	-0.5	1.8	0.8
		4	1290	0.84	0.2	0.3	1.5	2.1
		5	1300	1.03	0.7	1.0	1.3	3.3
		6	1300	1.22	0.2	0.2	1.5	1.9
		7	1290	1.42	0.6	0.5	1.5	2.5
		8	1270	1.61	0.9	0.7	1.7	3.1
					[0.5]	[0.5]		[2.7]
359	UO ₂ : 96 percent dense, 0.110-in. axial hole, 0.040-in. -thick cladding	1	1695	0.23	0.3	0.4	0.9	1.8
		2	1500	0.51	0.3	0.4	2.3	3.2
		3	1530	0.84	0.2	0.2	1.4	2.2
		4	1530	1.12	0.6	0.8	1.9	3.5
		5	1550	1.38	0.7	0.9	1.2	3.0
		6	1550	1.64	0.6	0.8	0.6	2.2
		7	1550	1.91	2.3	2.2	0.7	5.1
		8	1550	2.17	3.1	2.6	1.0	6.2
					[3.4]	[3.0]		[6.0]
303	UO ₂ +x: 96 percent dense, 0.110-in. axial hole	1	1630	0.21	0.2	0.2	2.6	3.1
		2	1500	0.48	0.3	0.4	2.3	3.1
		3	1510	0.79	0.2	0.2	1.8	2.2
		4	1510	1.06	0.6	0.7	2.5	3.9
		5	1520	1.31	0.4	0.4	2.5	4.3
		6	1520	1.56	0.4	0.5	2.4	3.4
		7	1510	1.82	1.4	1.6	4.0	7.2
		8	1500	2.07	2.7	1.8	4.1	7.7
					[2.8]	[2.3]		[8.7]

TABLE B-6. (Continued)

Specimen	Description	BRR Cycle	Temperature, C	Estimated Accumulated Burnup, 10^{20} fissions per cm^3	External Dimensional Changes ^(a) , percent			
					Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
5P	UO ₂ -8 w/o PuO ₂ : 96 percent dense, 0.110-in. axial hole	1	1425	0.14	0.6	0.7	0.9	2.1
		2	1320	0.33	0.1	0.1	1.2	1.4
		3	1320	0.55	0.7	0.9	2.4	4.2
		4	1310	0.74	0.6	0.8	2.0	3.6
		5	1320	0.92	0.8	0.9	1.6	3.4
		6	1300	1.10	0.3	0.4	1.4	2.2
		7	1280	1.28	0.6	0.3	1.7	2.3
		8	1260	1.45	1.5	0.8	1.5	3.1
					[0.7]	[0.6]		[2.7]

(a) Values in brackets are based on micrometer measurements of diameter; all other measurements were taken from neutron radiographs.

TABLE B-7. IRRADIATION CONDITIONS AND DIMENSIONAL CHANGES FOR SPECIMENS IN CAPSULE HT-BRR-12

Specimen	Description	Cycle	Temperature, C	Estimated Accumulated Burnup, 10^{20} fissions per cm^3	External Dimensional Changes ^(a) , percent			
					Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
364	UO ₂ : 90 percent dense, gas-pressure monitor	5 hr	1475	<0.05	0.1	0.1	-0.2	0.0
		50 hr	1485	<0.05	0.0	0.0	-0.6	-0.7
		1 (643 hr)	1530	0.38	-0.2	-0.2	0.1	-0.3
		2 (1065 hr)	1520	0.63	1.4 [1.8]	0.8 [1.2]	0.9	2.4 [3.3]
1P	UO ₂ -8 w/o PuO ₂ : 90 percent dense	5 hr	1675	<0.05	0.0	0.0	-1.6	-1.6
		50 hr	1690	<0.05	0.6	0.7	-0.4	1.0
		1	1710	0.36	1.0	1.1	1.5	3.8
		2	1700	0.60	1.9 [1.6]	1.6 [1.4]	2.0	5.3 [4.8]
365	UO ₂ : 90 percent dense, 0.110-in. axial hole	5 hr	1500	<0.05	0.5	0.6	0.6	1.8
		50 hr	1470	<0.05	0.5	0.6	0.8	1.9
		1	1490	0.46	0.2	0.3	1.4	2.0
		2	1490	0.77	3.3 [2.2]	2.7 [2.3]	1.7	7.1 [6.3]
2P	UO ₂ -8 w/o PuO ₂ : 90 percent dense	5 hr	1530	<0.05	0.5	0.6	0.0	1.1
		50 hr	1510	<0.05	-0.2	-0.2	0.0	-0.4
		1	1500	0.31	0.1	0.1	1.4	1.7
		2	1490	0.52	1.3 [1.0]	1.3 [0.9]	1.7	4.2 [3.5]
370	UO ₂ : 90 percent dense	5 hr	1325	<0.05	0.3	0.4	1.1	1.8
		50 hr	1265	<0.05	0.2	0.2	0.7	1.1
		1	1260	0.29	0.3	0.4	1.3	2.0
		2	1260	0.48	1.4 [0.7]	0.8 [0.5]	1.4	2.9 [2.4]
3P	UO ₂ -8 w/o PuO ₂ : 90 percent dense	5 hr	1325	<0.05	0.6	0.8	0.5	2.0
		50 hr	1270	<0.05	0.6	0.7	0.0	1.4
		1	1260	0.23	0.0	0.0	0.5	0.5
		2	1260	0.38	2.6 [0.8]	1.4 [0.8]	0.5	3.3 [2.1]

(a) Values in brackets are based on micrometer measurements of diameter; all other measurements were taken from neutron radiographs.

FIGURE B-2. NEUTRON RADIOGRAPHS OF THE UO₂ SPECIMENS IN CAPSULE HT-BRR-9

Specimen 358
 $\text{UO}_2\text{-x}$
 96 percent dense
 0.110-in. axial hole
 Gas-pressure monitor

Specimen 360
 UO_2
 80 percent dense
 0.055-in. axial hole

Specimen 4P
 $\text{UO}_2\text{-8 w/o PuO}_2$
 96 percent dense
 0.110-in. axial hole
 0.040-in. -thick cladding

Specimen 359
 UO_2
 96 percent dense
 0.110-in. axial hole
 0.040-in. -thick cladding

Specimen 303
 $\text{UO}_{2+\text{x}}$
 96 percent dense
 0.110-in. axial hole

Specimen 5P
 $\text{UO}_2\text{-8 w/o PuO}_2$
 96 percent dense
 0.110-in. axial hole

Preirradiation

FIGURE B-3. NEUTRON RADIOGRAPHS OF CAPSULE HT-BRR-11

Specimen 364
 UO_2
 90 percent dense
 Gas-pressure monitor

Specimen 1P
 UO_2 -8 w/o PuO_2
 90 percent dense

Specimen 365
 UO_2
 90 percent dense
 0.110-in. axial hole

Specimen 2P
 UO_2 -8 w/o PuO_2
 90 percent dense

Specimen 370
 UO_2
 90 percent dense

Specimen 3P
 UO_2 -8 w/o PuO_2
 90 percent dense

FIGURE B-4. NEUTRON RADIOGRAPHS OF CAPSULE HT-BRR-12

FIGURE B-5. EXTERNAL VOLUMETRIC SWELLING RATE AS A FUNCTION OF CLADDING SURFACE TEMPERATURE FOR UO_2 AND $\text{UO}_2\text{-PuO}_2$ SPECIMENS FROM CAPSULES HT-BRR-9, HT-BRR-11, AND HT-BRR-12

FIGURE B-6. EXTERNAL VOLUME INCREASE OF THE FUEL AS A FUNCTION OF BURNUP FOR UO_2 AND $\text{UO}_2\text{-PuO}_2$ SPECIMENS IRRADIATED AT CLADDING SURFACE TEMPERATURES FROM 1260 TO 1390 C

400X

As Polished

HC23416

a. View Near the Fuel Midradius

Note that there are few visible fission-gas bubbles within the UO_2 grains, and that the large pores are of the irregular type that is usually interconnected.

Etched

HC23657

b. Partial Cross Section from Cladding to Centerline

Note that many grains 20 to 40 μ wide are elongated to 40 to 60 μ in the direction of the temperature gradient.

FIGURE B-7. TYPICAL MICROSTRUCTURE OF UO_2 SPECIMEN 342 FROM CAPSULE HT-BRR-9

This specimen was irradiated to a burnup of 1.74×10^{20} fissions per cm^3 at an average cladding surface temperature of 1325 C.

There are few resolvable pores within the UO_2 grains. The porosity at the grain boundaries was determined by quantitative metallography to be 9 percent of the fuel volume. Since the fuel contained 3 v/o porosity before irradiation, the density decrease of the fuel, determined from these measurements, was 6 percent. This is in good agreement with the sum of the measured external fuel volume increase of 4.4 percent and a 10-mil decrease in diameter of the axial hole to account for an additional 4 v/o increase. The fact that this specimen swelled both radially inwardly and outwardly at this temperature is especially noteworthy.

Microstructures of Specimens 370 and 3P (Figures B-8 and B-9) from Capsule HT-BRR-12, which were irradiated to lower burnups, are generally similar in appearance to Specimen 342 from Capsule HT-BRR-9, although Specimen 370 shows less porosity agglomerated at the grain boundaries and some resolvable porosity within the grains. The lack of an axial hole (and partial accommodation of swelling by the hole) may also account for the relatively high swelling rate exhibited by these specimens compared to that of Specimen 342 (see Figure B-6).

The larger pores shown in Figures B-7, B-8, and B-9 are of the irregular type that has been shown previously to be highly interconnected. This degree of interconnected porosity could be consistent with the high rate of gas release (67 to 75 percent) provided that there is a high mobility of gas to move gas from the fuel to the interconnected porosity. It seems likely that the 2 to 6 percent volume increase of these specimens is caused by the growth of discrete gas bubbles prior to and in the process of becoming interconnected. Many of these bubbles are visible at grain boundaries in Figures B-7 through B-9 and some are to be seen within the grains. The mechanism by which the majority of the fission gases reaches the open grain-boundary porosity is uncertain at this time.

External swelling data for several specimens that were irradiated at cladding surface temperatures from 1475 to 1550 C are shown in Figure B-10. In this temperature range, the external volumetric swelling rates were also linear as a function of burnup and varied from about 3 to 8 percent per 10^{20} fissions per cm^3 . Gas release ranged from 60 to 91 percent and the microstructures varied considerably from specimen to specimen. Many of the specimens (see Figures B-11 through B-13) were composed of columnar grains associated with lenticular voids from the cladding to the center of the fuel pellet. Specimen 2P from Capsule HT-BRR-12 had columnar grains elongated in the direction of heat flow, but there were few well-shaped lenticular voids to be seen. An explanation for this will be offered later. Specimen 364 from Capsule HT-BRR-12 showed a nearly equiaxed grain structure near the cladding and more pronounced columnar grains and lenticular voids in the hotter central regions of fuel (Figure B-13). These observations suggest that this range of cladding surface temperatures, corresponding to minimum fuel temperatures between 1550 and 1650 C is the minimum temperature for rapid restructuring under the conditions of these irradiations. Specimen 359, which had a 40-mil thick cladding and an axial centerline hole, exhibited a lower degree of swelling compared to the swelling of other specimens (Figure B-10). An explanation of this apparent improvement will be deferred until sections of this specimen have been examined microstructurally.

Microstructures of UO_2 Specimens 343 and 365 (Figures B-11 and B-12) show that these specimens have columnar grains and many lenticular voids from the cladding to the centerline. The multitude of lenticular voids present near the center of Specimen 365 (Figure B-12) is probably the result of migration and collection of as-fabricated porosity. (Note that Specimen 365 was irradiated for only two reactor cycles.) In contrast, the "chevron"-shaped voids that are seen in Specimen 343 (Figure B-11), which had undergone eight cycles of irradiation, are believed to be typical of voids migrating within large crystals and perhaps were formed from fission gases within a columnar grain of fuel that was previously "restructured". These observations are incorporated in the discussion and theory of oxide fuel swelling which is presented at the end of this section.

500X

Etched

HC24189

FIGURE B-8. TYPICAL MICROSTRUCTURE OF UO_2 SPECIMEN 370 FROM CAPSULE HT-BRR-12

This specimen was irradiated to a burnup of 0.48×10^{20} fissions per cm^3 at an average cladding surface temperature of 1260 C.

500X

As Polished

HC24028

FIGURE B-9. TYPICAL MICROSTRUCTURE OF UO_2 -8 w/o PuO_2 SPECIMEN 3P FROM CAPSULE HT-BRR-12

This specimen was irradiated to a burnup of 0.38×10^{20} fissions per cm^3 at an average cladding surface temperature of 1260 C.

FIGURE B-10. EXTERNAL VOLUME INCREASE OF THE FUEL AS A FUNCTION OF BURNUP FOR UO₂ AND UO₂-PuO₂ SPECIMENS IRRADIATED AT CLADDING SURFACE TEMPERATURES FROM 1475 TO 1550 C

HC23628

FIGURE B-11. TYPICAL MICROSTRUCTURE OF UO_2 SPECIMEN 343 FROM CAPSULE HT-BRR-9

This specimen was irradiated to a burnup of 1.71×10^{20} fissions per cm^3 at an average surface temperature of 1475 C. Note the columnar grains, generally 25 to 50 μ wide and 100 to 1000 μ long.

HC24114-15

FIGURE B-12. TYPICAL MICROSTRUCTURE OF UO_2 SPECIMEN 365 FROM CAPSULE HT-BRR-12

This specimen was irradiated to a burnup of 0.77×10^{20} fissions per cm^3 at an average surface temperature of 1490 C.

The microstructure of UO₂ Specimen 364 (Figure B-13) shows that there is pronounced columnar grain growth in the central regions of the fuel and that the grain structure is more equiaxed near the cladding. The gas pressure monitored over this specimen as a function of burnup is shown in Figure B-14. There was very little gas release until a burnup of about 0.3×10^{20} fissions per cm³ (500 hr at temperature). Then, the gas release increased, initially in steps and then more continuously to a rate of about 100 percent. The cumulative fission-gas release at the end of the irradiation, as indicated by the pressure monitor, was about 60 percent. (A postirradiation analysis which showed that the specimen had released 81 percent of its fission gas is in reasonably good agreement.) Reactor shutdowns had little effect on gas release during the course of the irradiation, indicating that thermal-stress cracking was not directly responsible for a significant amount of gas release. The "incubation" period of 500 hr before a high rate of gas release and the structure observed in Figure B-13 are difficult to understand. Apparently, the processes of fission-gas agglomeration and channel opening which result in high gas-release rates take time to get started, but once started, the overall process is highly efficient. As mentioned previously, the actual mechanism by which gases reach the open channels in equiaxed-grained fuel is unclear at this time.

The typical microstructure of UO₂-8 w/o PuO₂ Specimen 2P, irradiated at an average surface temperature of 1495 C, is shown in the etched condition in Figure B-15. This specimen contains grains that are elongated in the direction of heat flow, but individual lenticular voids are evidently not responsible for this elongation. However, all large pores are apparently migrating toward the center of the specimen. A higher-magnification view of some of these pores (Figure B-16) shows that several pores may act in concert to produce elongated grains. The photograph also shows "trails" behind the pores that have been revealed by etching with a mixture of H₂SO₄ and H₂O₂, suggesting that the "trails" represent composition (probably plutonium) differences. The large size of the pores and the "trails", which are the same width as the pores, suggests that their motion must be, to a large extent, dependent on the evaporation-condensation mechanism. The reason that the voids are not more lenticular in shape or more distinctly faceted on their condensing surfaces may be due to their low speed at this temperature or to a high gas pressure in the bubbles.

A plot of external volume increases as a function of burnup for UO₂ and UO₂-8 w/o PuO₂ specimens that operated at average cladding surface temperatures above 1640 C is given in Figure B-17. Here, also, swelling is linear as a function of burnup. Such large amounts of external swelling at these temperatures tend to contradict the common belief that oxide fuels do not swell at these temperatures where gas release is high. The data of Figure B-17 show that fuel at these temperatures applies a stress outwardly on its cladding.

A gas-pressure monitor indicated that Specimen 339, which operated at an average surface temperature of 1840 C, released nearly 100 percent of its fission gas from the start of the irradiation. This high release has been confirmed by results of retained-gas measurements. In fact, all the specimens that exhibited columnar grain growth from the cladding to the fuel centerline released greater than 80 percent of their fission gas.

It has been suggested that the pressure of released fission gases could deform the cladding and that the fuel would heat up further because of a fuel-cladding gap and swell to follow the cladding. This view can be discounted, at least for these specimens, since Specimen 339 swelled 3 percent radially at pressures less than 30 psig and continued to swell throughout the irradiation to a radial deformation of over 8 percent even though the pressure monitor indicated that a cladding failure relieved the gas pressure at 3 percent deformation and a burnup of about 0.5×10^{20} fissions per cm³. It also has

Etched

HC24122-25

FIGURE B-13. TYPICAL MICROSTRUCTURE OF UO_2 SPECIMEN 364 FROM CAPSULE HT-BRR-12

This specimen was irradiated to a burnup of 0.63×10^{20} fissions per cm^3 at an average surface temperature of 1525 C.

FIGURE B-14. PRESSURE MONITORED IN UO_2 SPECIMEN 364 AS A FUNCTION OF BURNUP

Etched

HC24358-59

FIGURE B-15. TYPICAL MICROSTRUCTURE OF $\text{UO}_2\text{-8 w/o PuO}_2$ SPECIMEN 2P FROM CAPSULE HT-BRR-12

This specimen was irradiated to a burnup of 0.52×10^{20} fissions per cm^3 at an average surface temperature of 1495 C. The location of the photograph in Figure B-16 is indicated by a box.

750X

Etched

HC24280

FIGURE B-16. HIGH-MAGNIFICATION VIEW OF $\text{UO}_2\text{-8 w/o PuO}_2$ SPECIMEN 2P TAKEN NEAR THE FUEL MIDRADIUS

Note the "trails" behind the pores. The temperature of this region of fuel is estimated to be 1700 ± 100 C.

FIGURE B-17. EXTERNAL VOLUME INCREASE OF THE FUEL AS A FUNCTION OF BURNUP FOR UO₂ AND UO₂-PuO₂ SPECIMENS IRRADIATED AT CLADDING SURFACE TEMPERATURES FROM 1640 TO 1900 C

been suggested that the cladding could be deformed by a thermal ratcheting mechanism. Deformation by such a mechanism should be related to the thermal cycling history of the specimens. A review of the thermal records of these specimens revealed absolutely no correlation between the number or the timing of thermal cycles and the amount or timing of diametral swelling. On the basis of these observations, it must be concluded that swelling is caused by the precipitation and growth of fission-gas bubbles within the fuel prior to gas release.

The microstructures of UO_2 Specimens 339 and 344 are shown in Figures B-18 and B-19. These microstructures show the fuel to be composed of columnar grains from the cladding to the fuel centerline. Very few lenticular voids were found in Specimen 339, which operated at a cladding surface temperature of 1840 C (Figure B-18). (Note the high density of the UO_2 in this specimen whose external volume increased 27 percent while the gas-pressure monitor recorded zero internal pressure.) Lenticular voids with their typical faceted surfaces are visible in the structures of specimens irradiated at surface temperatures of 1640 and 1475 C (Figures B-19 and B-11). These observations suggest that the speed of lenticular voids increases with increasing temperature, resulting in void removal and high-density fuel at 1840 C. The microstructure of UO_2 -8 w/o PuO_2 Specimen 1P (see Figure B-20), which had only two cycles of irradiation (compared to eight cycles for Specimens 339, 344, and 343), shows a considerable number of lenticular voids (that are probably a result of agglomeration and migration of as-fabricated porosity) and, at higher magnification, several "chevron"-shaped voids (see Figure B-21), which are second-generation or follow-on voids.

The higher-magnification view of Specimen 1P (Figure B-21) shows smaller pores moving in a columnar grain being created by a large lenticular pore. This observation is further evidence that the migration of pores of various sizes and shapes is a continuous, repetitive process in oxide fuels at high temperatures. A high-magnification view of a void in Specimen 344 is shown in Figure B-22. This void apparently was in motion just before the end of the irradiation, since material on the lower, colder side of the void is essentially free of small fission-gas bubbles while small, spherical fission-gas bubbles are apparently about to be overtaken and swept up by the lenticular void. The width of the columnar grain being created by the void is much the same as that of adjacent columnar grains, suggesting that all have been created by lenticular void sweeping. The parallel sides of these columnar grains suggest that the voids remain the same size as they traverse the radius of the fuel, and it follows that the voids must lose any fission gas they sweep up about as fast as they zone refine it out of the fuel. Columnar grains with diverging sides imply that the void, or voids that created it, was growing and possibly accumulating fission gas. Columnar grains with converging sides imply that the void was getting smaller as it traversed the fuel. Figures B-18 and B-19 show columnar grains with nearly parallel sides extending full width to the cladding, suggesting that lenticular voids can originate at the cladding- UO_2 interface. In Figure B-16, the structure suggests that lenticular voids can originate from porosity collected at the grain boundaries of UO_2 . The structure shown in Figure B-22 suggests that lenticular voids can originate at cracks or as the result of the growth of fission-gas bubbles.

The above data contain the following observations which should be explained by any theory or model of UO_2 behavior at high temperatures:

- (1) The external dimensional increase of UO_2 clad with tungsten-rhenium alloy increases with increasing temperature from 1325 to 1900 C.
- (2) The external dimensional increase of UO_2 clad with tungsten-rhenium alloy increases linearly with burnup between 1325 and 1900 C to a burnup of at least 2.3×10^{20} fissions per cm^3 .
- (3) Large external dimensional changes can occur in UO_2 fuel elements at high temperatures while little or no density change occurs in the UO_2 itself.

400X

HC23734

a. High-Magnification View of Fuel

Note that there are few fission-gas bubbles larger than $1\ \mu$ in diameter within the grains of UO_2 .

HC23659

b. Partial Cross Section from Cladding to Centerline

Note the columnar grains $50\ \mu$ wide and $500\ \mu$ long extending from the cladding to the central void. Also note the relative thicknesses of fuel and cladding and that deformation was proceeding at a high rate under these conditions.

FIGURE B-18. TYPICAL MICROSTRUCTURE OF UO_2 SPECIMEN 339

This specimen was irradiated to a burnup of 2.34×10^{20} fissions per cm^3 at an average surface temperature of $1840\ \text{C}$.

HC23618

FIGURE B-19. TYPICAL MICROSTRUCTURE OF UO_2 SPECIMEN 344 FROM CAPSULE HT-BRR-9

This specimen was irradiated to a burnup of 2.28×10^{20} fissions per cm^3 at an average surface temperature of 1640 C. Note the columnar grains, generally 50μ wide and 800μ long.

HC24126-28

FIGURE B-20. TYPICAL MICROSTRUCTURE OF UO_2 -8 w/o PuO_2 SPECIMEN 1P FROM CAPSULE HT-BRR-12

This specimen was irradiated to a burnup of 0.60×10^{20} fissions per cm^3 at an average surface temperature of 1705 C.

750X

Etched

HC24281

750X

Etched

HC24282

FIGURE B-21. HIGH-MAGNIFICATION VIEWS OF $\text{UO}_2\text{-8 w/o PuO}_2$ SPECIMEN 1P TAKEN ABOUT ONE-THIRD OF THE RADIUS IN FROM THE FUEL SURFACE

500X

Etched

HC23584

FIGURE B-22. POSTIRRADIATION MICROSTRUCTURE OF UO_2 SPECIMEN 344 IRRADIATED AT A SURFACE TEMPERATURE OF 1640 C

A section is shown near the inside diameter where the temperature was near 1800 C. Fission-gas bubbles and voids should be moving toward the hot centerline void which is the black area at the top of this photograph. Note that the UO_2 formed by condensation on the cold side of the lenticular void is faceted and virtually bubble-free. It appears that the lenticular void is moving faster than the other bubbles which, because of their uniform size, appear to be relatively stationary.

- (4) External dimensional changes of clad UO_2 fuel elements can occur in the absence of internal pressure from fission gas released from the fuel.
- (5) External dimensional changes of clad UO_2 can occur at high temperatures even though the UO_2 releases as much as 90 percent of its fission gas at any given time.
- (6) Gas release from UO_2 is approximately 90 percent complete at temperatures over 1600 C at heat ratings of 2.5 to 3.5 kw per ft.
- (7) The structure of UO_2 irradiated at temperatures over 1600 C at heat ratings of 2.5 to 3.5 kw per ft consists of long columnar grains often associated with lenticular voids. It is apparent that these lenticular voids move through the UO_2 , probably by a vapor transport process, overtaking smaller fission-gas bubbles and depositing fully dense fuel behind them.

In order to explain these observations, the following theory is proposed. It is postulated that: (1) the fundamental processes controlling mobility of highly insoluble gas atoms in UO_2 , as in any crystalline solid, are such that a large proportion of the fission gas precipitates inside particles of fuel, causing swelling; (2) at high temperatures lenticular voids are formed in UO_2 and they periodically sweep through the fuel, collecting fission gases and redensifying the fuel; and (3) in the interval of time between passages of lenticular voids, a new population of small, relatively stationary fission-gas bubbles forms and swells the UO_2 .

The tendency of gas bubbles to swell as more and more fission gas precipitates in them places a stress on the surrounding fuel that is a fundamental consequence of the tendency for the gas to precipitate; as a result, pressures in bubbles are in excess of surface tension restraint (see the section of this report on "Gas-Bubble Nucleation and Growth"). As in all fuels, the swelling stresses are transmitted throughout the fuel and its cladding; strain therefore results, primarily by creep at high temperatures. The stresses will be partly relieved to produce a steady-state condition; because of the temperature gradients in UO_2 , this usually means that the highest stresses are found near the cladding. Under these conditions, the cladding will be deformed to the extent that its creep strength dictates, thereby producing a strong temperature dependency in the rates of external volume increase. The fact that the gas bubbles causing swelling are periodically swept out of UO_2 at high temperatures does not eliminate dimensional changes because a new set of bubbles will form. The sweeping event, however, does halt the growth of the preexisting bubbles, produces significant gas release, and redensifies the fuel. This means that the external volume increase of clad UO_2 does not proceed exponentially at high temperatures. It proceeds linearly in a series of steps, and possibly at a slightly lower rate than for fuels which retain a higher proportion of their fission products.

Figure B-23 illustrates how this process results in steady-state and essentially linear deformation as a function of burnup. In the first step (1 to 2), the fuel swells by the formation of small fission-gas bubbles, which apparently do not move fast enough to get out without causing swelling. In the second step (2 to 3), a lenticular void sweeps through the swollen fuel, depositing pure, dense UO_2 behind it and rejecting gases and other fission products into radial arrays. In the third step (4 to 5), the purified UO_2 swells again by the formation of a new set of small fission-gas bubbles. And so on. The theory hypothesizes that in the first step a density decrease of, for example, 0.2 to 2 v/o occurs in the UO_2 . If the UO_2 contains a centerline void, perhaps the cladding strain and the external volume increase of the UO_2 might range up to as much as 0.5 v/o, depending upon the temperature, the temperature gradient, and the corresponding strengths of the fuel and the cladding. A significant part of the density decrease in the

FIGURE B-23. SCHEMATIC DIAGRAM OF THE SWELLING PROCESS IN URANIUM DIOXIDE AT HIGH TEMPERATURES

UO₂ may go to partly fill the centerline void. Subsequently, in the second step, the passage of a lenticular void through each sector of the fuel redensifies the UO₂ restoring the centerline void to its original size plus up to 0.5 v/o and leaving the cladding strained an equal amount. The repetition of the complete sequence sixty times would result in an external volume increase of as much as 30 percent, further causing a corresponding increase in the volume of the centerline void, and a relatively small increase or decrease in the density of the UO₂.

Any large discontinuity in the UO₂ such as preexisting porosity, a fission-gas bubble, or a crack is a potential source of a lenticular void. The lenticular void takes shape because UO₂ has an appreciable vapor pressure ($>10^{-2}$ torr) above 1600 C and vapors evaporated into a void in solid UO₂ containing a temperature gradient will condense in appreciable quantities on the colder side of the void. The condensate forms as pure crystalline UO₂ containing little or no fission products, and because crystallization occurs preferentially on certain close-packed planes (111), the cold side of a lenticular void grows as one or more of these planes. This evaporation-condensation process is an efficient zone-refining process that periodically sweeps the UO₂ clean of fission-gas atoms and small bubbles. Lenticular voids are predicted to move at rates which depend upon both the temperature, which provides the UO₂ vapor, and upon the temperature difference across the void, which provides the free energy to activate the several processes involved (see the section of this report entitled "Mechanisms of Bubble Migration"). The repeated passage of lenticular voids is believed to be responsible for the large, dense, straight-sided columnar grains generally observed in irradiated UO₂. It is predicted that such repeated passages will eventually deposit the fission products they collect at the sides of these columnar grains, thereby forming the elongated radial voids frequently observed in irradiated UO₂ (see Figures B-11 and B-18 through B-20). The fact that these radial voids should be highly interconnected is believed to be the reason for the rapid, nearly steady-state release of gas from UO₂ during irradiation. It is important to recognize that the primary predicted consequences of lenticular void action are the redensification of the fuel in the direction of heat extraction and the gleaning of fission gases from the fuel. The voids are not expected to transport gas in great quantity, and only secondarily assist in opening radial channels. It is also noteworthy that theory predicts that a lenticular void originating in a large, single crystal or columnar grain will usually maintain the crystal orientation surrounding it and not create a new grain within the old. It follows that once oxide fuels have "restructured" into columnar grains of a size characteristic of the temperature of the fuel and its composition, repeated passages of small lenticular voids through these large grains will have the effect of maintaining the density and macroscopic appearance of the fuel almost constant. It might be said that "restructuring" occurs only once, but that redensification, repurification, and gas release are continuing processes.

If this theory describing the processes of lenticular void behavior and the processes of dimensional change in the presence of lenticular voids and columnar grains is correct, then it appears that the basic cause of external volume increases of UO₂ fuel elements at high temperatures is (as usual) related to bubble formation and that the lenticular-void, zone-refining process represents primarily a process of fuel reconstitution and gas collection.

This theory suggests that it is reasonable to divide a cylindrical UO₂ fuel pin for analytical purposes into a series of annular regions, each spanning a small range of temperature. Each of the more central regions will exert a stress on the regions outside it in accordance with its temperature and strength. The outer regions and the cladding will respond by straining and deforming outwardly in accordance with their yield strengths or creep strengths. The resultant behavior for one particular cladding at temperatures from 1260 to 1900 C is shown in Figure B-5. The significance of these

results to designers of liquid-metal-cooled reactors may be illustrated by noting that the creep strength of the cladding, tungsten-26 w/o rhenium, at 1400 C is equivalent to that of the same thickness of annealed Type 316 stainless steel between 750 and 800 C. Furthermore, if consideration is given to the slightly different geometries of the specimens and typical fast-breeder fuel-pin designs, it can be shown that the 20-mil-thick tungsten-rhenium claddings at 1400 C are equivalent in creep-stress-restraint capability to the design thicknesses of annealed Type 316 stainless steel at 750 to 770 C. Similarly, the 40-mil-thick tungsten-rhenium claddings at 1400 C provide a creep stress restraint equivalent to typical fast-breeder cladding design thicknesses of stainless steel at about 700 C. The results show that UO_2 does exert a significant outward stress at high temperatures in spite of high fractional gas release. If the contributions to restraint and swelling provided by the regions of UO_2 below 1300 C and by the stainless steel cladding can be accurately assessed by existing models of the behavior of UO_2 fuel pins, then the data provided here can be incorporated into these models to describe the contribution of the hotter regions of the UO_2 .

In addition, the theory incorporates the phenomenon of lenticular void migration, which is basically a process of fractional crystallization and zone refining in the vapor state. This process provides a rapid and effective mechanism for collecting not only fission gases, but also other fission products, such as ruthenium. The process also should be effective in redistributing plutonium and all other elements possessing any degree of solubility in UO_2 .

Plans for Future Work

The postirradiation examination of Capsule HT-BRR-11 will be continued with emphasis on determining gas-release characteristics and the relationships between microstructures and fuel swelling and gas-release behavior.

The irradiation of specimens in Capsule HT-BRR-14 will continue toward a target burnup of 2×10^{20} fissions per cm^3 .

Irradiation Behavior of Tungsten- UO_2 Cermets at High Temperatures

R. F. Hilbert, W. J. Zielenbach, and V. W. Storhok

Objective of Program

To investigate the irradiation behavior of tungsten- UO_2 cermets at surface temperatures from 1600 to 1800 C.

Approach Being Used

Several specimens of tungsten- UO_2 have been irradiated in HT-BRR-series capsules to evaluate the effect of various modifications on the behavior of the cermet. A tungsten- UO_2 cermet represents a major modification to bulk UO_2 . The thermal conductivity of the tungsten- UO_2 cermet is estimated to be about three times higher than that of bulk UO_2 . In contrast, the thermal conductivity of tungsten-UN or tungsten-UC cermets differs little from that of the bulk fuels.

Capsule HT-BRR-3 contained two specimens of 94 percent dense tungsten-50 v/o UO_2 cermet clad with 20 mils of tungsten-26 w/o rhenium.

Capsule HT-BRR-6 contained two specimens of tungsten-42 v/o UO_2 -28 v/o porosity clad with 40 mils of tungsten-26 w/o rhenium. One of the two porous tungsten- UO_2 cermet specimens was vented to the capsule.

Significant Accomplishments During Fiscal Year 1970

The specimens of tungsten-42 v/o UO_2 -28 v/o porosity with 40-mil-thick claddings irradiated in Capsule HT-BRR-6 experienced no external diameter changes after a burnup of 1.65×10^{20} fissions per cm^3 at approximately 1640 C. This result was attributed mainly to rapid gas release through the porosity (80 percent gas release), and to a lesser extent to accommodation of swelling by the porosity and to an increase in external restraint provided by the thick cladding. The ability of the cermet to retain an open pore structure at high temperatures is believed to be an important factor in the nonswelling behavior exhibited. In contrast, the 94 percent dense tungsten-50 v/o UO_2 cermets clad with 20 mils of tungsten-26 w/o rhenium and irradiated earlier in Capsule HT-BRR-3 swelled to a diameter increase of about 16 percent before gas release was enhanced by the development of interconnected porosity; at this point, the external swelling ceased.

The venting of one of the porous tungsten- UO_2 cermet specimens to the capsule had no effect on swelling, when results were compared with those for the unvented specimen. This indicates that at the burnup level attained the stress exerted on the cladding by the pressure of released gas, in spite of a high rate of gas release, was not sufficient to deform the cladding of the unvented specimen.

Summary of Research Carried Out

The tungsten-42 v/o UO_2 -28 v/o porosity specimens in Capsule HT-BRR-6 were irradiated at temperatures around 1640 C to burnups near 1.7×10^{20} fissions per cm^3 during Fiscal Year 1969. The postirradiation examination of these specimens was completed in Fiscal Year 1970. The irradiation conditions and dimensional changes of the porous tungsten- UO_2 cermets from Capsule HT-BRR-6 are given in Table B-8. A comparison of external fuel volume increase as a function of burnup, given in Figure B-24, for these porous cermets and the high-density tungsten- UO_2 cermets from Capsule HT-BRR-3, shows a large improvement in swelling behavior for the porous cermet. It should be noted that the indicated volumetric decrease of the porous cermets is caused by a fuel length decrease that resulted from a loss of fuel by vaporization from the top of the pellet. The porous cermets from Capsule HT-BRR-6 showed negligible diameter changes. The postirradiation examination was aimed primarily at determining the reasons for the absence of swelling in the porous cermet.

The postirradiation microstructure of the high-density cermets in Capsule HT-BRR-3 showed a partial redistribution of the UO_2 toward the fuel OD, and considerable voidage and tearing of the cermet matrix toward the fuel ID (see BMI-1848, August, 1968, page 26). On the basis of these microstructural changes and the swelling curve (Figure B-24), it was hypothesized that the high-density cermet swelled at a high rate until there was a sufficient degree of surface-connected porosity available for gas release and, at this point, external swelling ceased.

A metallographic cross section of porous tungsten- UO_2 cermet Specimen 319 from Capsule HT-BRR-6 (Figure B-25) shows a partial redistribution of the UO_2 toward the fuel OD and of the voidage toward the fuel ID. Presumably the redistribution of the voidage and UO_2 occurred by vapor transport of the UO_2 down the thermal gradient. The neutron radiographs indicate that significant redistribution had occurred by the end of the fourth cycle of irradiation. Since no change in swelling rate was observed, it appears that the redistribution of the voidage and densification of the UO_2 cermet structure near the cladding did not affect the swelling behavior. Fission-gas-retention measurements indicated that 80 percent of the gas was released during this irradiation at 1640 C. A higher magnification view of the UO_2 -cermet structure (Figure B-26) shows a relatively small amount of fission-gas porosity at the UO_2 grain boundaries, and an even smaller amount of porosity within the UO_2 grains.

TABLE B-8. IRRADIATION CONDITIONS AND DIMENSIONAL CHANGES FOR THE POROUS
TUNGSTEN-UO₂ CERMET SPECIMENS IN CAPSULE HT-BRR-6

Specimen	Composition	Specimen Variable	Cycle	Surface Temperature, C	Estimated Accumulated Burnup, 10 ²⁰ fissions per cm ³	External Dimensional Changes ^(a) , percent			
						Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
319	Tungsten-42 v/o UO ₂ -28 v/o porosity	40 mils of tungsten-rhenium cladding	1	1600	0.20	0.0	0.0	-2.1	-2.1
			2	1680	0.47	0.7	0.8	-3.3	-1.7
			3	1620	0.62	0.8	0.8	-4.6	-3.0
			4	1635	0.94	0.3	0.2	-6.1	-5.7
			5	1640	1.21	(b)	(b)	(b)	(b)
			6	1650	1.49	-0.1	-0.4	-6.7	-7.5
			7	1630	1.67	0.1	-0.2	-7.7	-8.1
						[0.5]	[0.3]		[-7.1]
321	Tungsten-42 v/o UO ₂ -28 v/o porosity	Vented; 40 mils of tungsten-rhenium cladding	1	1590	0.20	1.1	1.6	-2.1	-1.1
			2	1630	0.47	2.1	2.4	-5.3	-0.5
			3	1660	0.62	1.9	1.8	-5.2	-1.6
			4	1670	0.94	1.4	1.5	-6.8	-3.9
			5	1670	1.21	(b)	(b)	(b)	(b)
			6	1650	1.48	1.0	0.9	-8.0	-6.4
			7	1640	1.65	0.8	0.9	-8.0	-6.2
						[0.0]	[0.0]		[-8.0]

(a) Values in brackets are based on micrometer measurements of diameter; all other measurements were taken from neutron radiographs.

(b) Data for the fifth cycle are unavailable.

FIGURE B-24. EXTERNAL FUEL VOLUME INCREASE AS A FUNCTION OF BURNUP FOR TUNGSTEN-UO₂ CERMETS FROM CAPSULES HT-BRR-3 AND HT-BRR-6

25X

FIGURE B-25. TYPICAL MICROSTRUCTURE OF TUNGSTEN-42 v/o UO_2 -28 v/o POROSITY SPECIMEN 319

This specimen was irradiated to a burnup of 1.67×10^{20} fissions per cm^3 at surface temperatures of 1640 C. Note that there is still porosity in the fuel and that there has been some movement of UO_2 toward the cladding.

500X

HC23094

FIGURE B-26. TYPICAL MICROSTRUCTURE OF TUNGSTEN-42 v/o UO_2 -28 v/o POROSITY SPECIMEN 319

Note that the UO_2 grains are relatively free of fission-gas porosity.

On the basis of these results, it appears that the improved swelling behavior of the porous tungsten- UO_2 cermets can be attributed primarily to enhanced fission-gas release through the open porosity and to a lesser extent to the restraint offered by the thick (40 mils) cladding and to the accommodation of swelling by the voidage.

In another section of this report, it is postulated that, in bulk UO_2 , fission gases precipitate as small bubbles which are subsequently swept up by the larger bubbles and other voids that move out of the grains by a vaporization-condensation mechanism. The migration and rejection of these larger bubbles and voids by the vaporization-condensation mechanism represents a redensification process that maintains bulk UO_2 at a relatively constant and high density. This redensification process negates any effect that as-fabricated porosity would have on enhancing gas release or accommodating swelling.

In cermet fuels the situation is somewhat different from that in bulk oxide; certainly the temperature gradients are lower. Presumably, the fission gases within the UO_2 grains in a cermet form small bubbles which tend to grow and move out of the grains by the same vaporization-condensation mechanism. However, the tungsten matrix provides a mechanical barrier that precludes long-range migration of larger voids. Any preexisting porosity or porosity that forms as a result of the arrival of gas bubbles and voids at fuel particle-matrix interfaces tends to remain or stop at the tungsten barrier. Thus, in porous cermets, the channels introduced for or developed by the release of the gases upon their ejection by grains tend to remain open. Also, the stationary channels provide space for accommodation of any swelling of the UO_2 particles, provided the cladding and tungsten matrices are sufficiently strong to force swelling into voids.

Plans for Future Work

There are no plans for additional investigations of cermet fuels at this time.

Irradiation Behavior of Nitride Fuels
at High Temperatures

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Objective of Program

To investigate the irradiation behavior of nitride fuels at surface temperatures from 1200 to 1900 C.

Approach Being Used

Several specimens of UN and tungsten-UN were or are being irradiated to study the swelling and fission-gas-release behavior of UN at high temperatures. Variations of the amount and configuration of porosity, the effect of cladding restraint, and the effect of grain size on the swelling behavior of UN are being investigated. The timing of gas release, the effects of a nitrogen overpressure (to control the stoichiometry), and the effects of additions of PuN are also being studied.

Five specimens of UN were irradiated in Capsule HT-BRR-10 to help elucidate the effects of grain size, uniformly distributed porosity, and temperature on the swelling and gas-release behavior of UN. The timing and magnitude of gas release were measured by monitoring the fission-gas pressure on the 80 percent dense UN specimen. Specifically, the fuels listed in Table B-9 were irradiated.

TABLE B-9. DESCRIPTION OF UN SPECIMENS IRRADIATED IN CAPSULE HT-BRR-10

Design Cladding Temperature, C	Fuel Characteristics	U ²³⁵ Enrichment, percent
1700(a)	Fine grained; 80 percent dense	20
1700	Fine grained; 99 percent dense	10
1700	Fine grained; 99 percent dense	10
1700	Large grained; cast	12
1500	Fine grained; 99 percent dense	10

(a) Gas pressure monitored.

To determine whether increasing the nitrogen content or "stoichiometry" of UN has any influence on gas mobility and release, Capsule LRL-2 operated with a slight nitrogen overpressure. Other variables in the experiment were grain size and porosity. Specifically, the specimens listed in Table B-10 were irradiated at surface temperatures of approximately 1500 C. The 10 percent enriched fuel in these specimens was in the form of annular cylinders approximately 0.10 in. in ID by 0.20 in. in OD by 0.75 in. long. The cylinders were clad with 0.020-in. -thick tungsten-26 w/o rhenium. A disk of depleted UN 0.03 in. thick separated the bottom of the fuel from the bottom end cap. A 0.13-in. gap existed between the top of the specimen and the top end cap, and a vent hole penetrated the cladding wall at this location. The nitrogen overpressure was applied from a vented U₂N₃ specimen within the inner capsule which was heated electrically to temperatures up to about 700 C. Specimens M and K had a 0.06-in. -thick annular disk of 10 percent enriched, 95 percent dense UN added to the top of the fuel column, reducing

the gap between the fuel and top end cap to 0.07 in. All specimens had a nominal 100-mil axial hole except Specimens O and L (arc-melted material), which had such a hole penetrating the top two-thirds of the fuel length while the bottom third was a solid disk. The thermocouple well in Specimens O, J, K, M, and P was 90 mils in diameter so that some centerline void space was available to accommodate swelling in all specimens.

TABLE B-10. DESCRIPTION OF UN SPECIMENS IRRADIATED IN CAPSULE LRL-2

Specimen (in Order From Top of Capsule)	UN Type ^(a)	Nominal Fuel Density ^(b) , percent of theoretical	Thermocouples	
			Centerline	Surface
O	Arc melted	96, 97.5, 99	Yes	Yes
L	Arc melted	96, 99, 97.5	No	Yes
J	High density, fine grained	98	Yes	No
K	Low density	75	Yes	Yes
M	Low density	75	Yes	No
N	High density, coarse grained	98	No	Yes
P	High density, coarse grained	98, 98	Yes	No

(a) All specimens are 10 percent enriched, and all were designed to operate near 1500 C.

(b) Specimens O and L each consist of three pieces of fuel with densities as indicated, top to bottom of specimen. Specimen P consists of two pieces of fuel, both 98 percent dense.

Capsule HT-BRR-13 contains three specimens of UN and one specimen of UN-8 w/o PuN designed to be irradiated at 1700 C. Two of the UN specimens are 93 percent dense, one with a sound cladding and one with a cladding slit every 90 deg (to eliminate cladding restraint) in order to test the effect of cladding restraint (or lack of restraint) on the swelling and gas-release behavior of UN. A 75 percent dense UN specimen has a gas-pressure monitor to investigate the timing and magnitude of gas release from porous UN. The effect of PuN additions on the swelling and gas-release behavior of UN is being studied by comparison of the above specimen with a 75 percent dense specimen of UN-8 w/o PuN.

Except for the variations mentioned, each specimen consists of slugs of fuel in a column 1 in. long contained in a tungsten-26 w/o rhenium cladding with an OD of 0.25 in. and a wall thickness of 20 mils, as shown earlier in Figure B-1.

Dimensional changes in the specimens are determined after each cycle of irradiation by measurements from neutron radiographs. The postirradiation examination includes (when appropriate) dimensional measurements, fission-gas-release (retention) measurements, and metallography.

Significant Accomplishments During Fiscal Year 1970

Two different types of swelling behavior apparently corresponding to two different types or compositions of UN have been observed in UN-base fuels at about 1700 C. One type is characterized by initial swelling rates of the order of 10 to 20 v/o per 10^{20} fissions per cm^3 . After a high degree of interconnected porosity is developed in this type of UN, there is little or no additional swelling. The second type is characterized by initial swelling rates of the order of 2 to 4 v/o per 10^{20} fissions per cm^3 , a low mobility of fission gases, and gradually increasing swelling rates throughout the irradiation.

The swelling of both types of UN was observed to take place primarily by the growth of fission-gas bubbles at grain boundaries. However, the growth of these bubbles apparently involved only a small fraction of the fission gas available, at least in the

second type of fuel. Decreased swelling rates were realized in both types of fuel by minimizing grain-boundary area, as by the use of large-grained material or by substituting porosity for most of the grain boundaries. The effect of interconnected porosity in both types of UN-base fuels seems to be to eliminate the formation of large gas bubbles at grain boundaries by venting the gas that is mobile enough to appear at grain boundaries.

The addition of 24 v/o porosity to a tungsten-UN cermet in Capsule HT-BRR-7 (see BMI-1870, August, 1969) resulted in a specimen which exhibited diametral and volume changes of less than 1.5 percent upon irradiation to 1.8×10^{20} fissions per cm^3 at an average surface temperature of 1760 C. Postirradiation analyses have shown that 83 percent of the fission gas produced during the irradiation was released from the cermet. Therefore, in this specimen, it was suggested that the large improvement in dimensional stability over that of the high-density cermet fuel was related to the ease of release of fission gas through the interconnected porosity. The open structure eliminates pockets of high gas pressure and inhibits the transmission of stresses to the cladding.

The UN specimens in Capsule LRL-2 showed cladding diameter increases of less than 1 percent and external fuel volume increases of less than 4 percent upon irradiation to about 2.1×10^{20} fissions per cm^3 at 1400 to 1600 C. Gas bubbles were observed at a magnification of 500 diameters at grain boundaries but not within the grains.

Summary of Research Carried Out

During Fiscal Year 1970, the postirradiation examinations of the UN and tungsten-UN cermet specimens in Capsules HT-BRR-7, HT-BRR-10, and LRL-2 were completed. The UN and UN-8 w/o PuN specimens in Capsule HT-BRR-13 completed three cycles of an irradiation that is still in progress.

Table B-11 summarizes the irradiation conditions and dimensional changes of the UN specimens in Capsule HT-BRR-10. Measurements obtained in the Battelle-Columbus Hot-Cell Facility with a micrometer are also given in Table B-11; they are in excellent agreement with the data taken from neutron radiographs.

Preirradiation and postirradiation neutron radiographs of the UN specimens from Capsule HT-BRR-10 are shown in Figure B-27. Postirradiation photomicrographs of these specimens (Figure B-28) show that, with the exception of the large-grained UN specimen (350), all the specimens ruptured their claddings.

A graphical comparison of the swelling data on the 80 and 99 percent dense UN specimens in Capsule HT-BRR-10 with the two 70 percent dense UN specimens in Capsule HT-BRR-7 and with the five 97 percent dense UN and tungsten-UN cermet specimens from Capsules HT-BRR-3 and HT-BRR-4 is shown in Figure B-29. A most striking observation that can be made from Figure B-29 is that the UN from these four capsules has exhibited two different types of swelling behavior. The five UN specimens (three of bulk UN and two tungsten-75 v/o UN cermets) from Capsules HT-BRR-3 and HT-BRR-4 exhibited high initial swelling, after which there was essentially no further swelling (see BMI-1848, August, 1968, for additional data on these specimens). The UN specimens from Capsules HT-BRR-10 and HT-BRR-7 (see BMI-1870, August, 1969, for data on Capsule HT-BRR-7) demonstrated small dimensional changes early in the irradiation with an increased swelling rate in the later stages of the irradiation. Since the UN specimens in Capsule HT-BRR-10 were known to be hyperstoichiometric before irradiation, the possibility exists that the differences in swelling behavior are related to differences in stoichiometry.

The first type of UN behavior mentioned (specimens from Capsules HT-BRR-3 and HT-BRR-4) was characterized by rapid growth of fission-gas bubbles and the agglomeration of bubbles in the grain boundaries to form channels (Figure B-30) accompanied by a

TABLE B-11. IRRADIATION CONDITIONS AND DIMENSIONAL CHANGES FOR UN SPECIMENS
IN CAPSULE HT-BRR-10

Specimen	UN Composition	BRR Cycle	Temper- ature, C	Estimated Accumulated Burnup, 10^{20} fissions per cm^3	External Dimensional Changes ^(a) , percent			
					Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
348	80 percent dense; gas-pressure monitor	1	1720	0.27	0.2	0.2	0.3	0.7
		2	1650	0.59	0.2	0.2	0.8	1.2
		3	1650	0.91	0.6	0.7	0.7	2.1
		4	1700	1.23	3.1	2.8	1.0	6.7
		5	1750	1.52	6.2	5.9	2.5	14.4
		6	1725	1.83	11.8	10.2	3.0	23.5
		7	1700 ^(b)	2.10	16.8	14.5	4.2	33.2
351	99 percent dense; fine grained	1	1550	0.24	0.3	0.3	0.1	0.8
		2	1580	0.55	0.0	0.0	0.7	0.6
		3	1600	0.86	0.4	0.5	0.5	1.6
		4	1640	1.17	1.6	1.1	0.6	2.8
		5	1640 ^(b)	1.45	3.8	2.6	1.8	7.1
		6	1625	1.75	6.5	4.4	1.7	10.5
		7	1625	1.99	7.5	5.4	2.5	13.2
					[8.3]	[5.2]		[12.9]
352	99 percent dense; fine grained	1	1550 ^(b)	0.24	-0.3	-0.4	0.2	-0.6
		2	1580	0.55	0.3	0.3	0.9	1.6
		3	1600	0.86	0.5	0.6	0.6	1.8
		4	1640	1.17	3.5	2.4	1.5	6.5
		5	1640	1.45	5.2	3.1	1.9	8.1
		6	1625	1.75	5.8	3.8	1.8	9.6
		7	1625	1.99	6.8	5.8	2.3	13.8
					[7.4]	[5.1]		[12.5]
350	Cast; large grained	1	1600	0.27	0.4	0.4	0.6	1.5
		2	1665	0.63	0.0	0.0	0.8	0.7
		3	1690	0.99	0.7	0.9	1.1	2.9
		4	1660	1.35	0.5	0.6	1.3	2.5
		5	1670	1.68	2.2	1.7	1.5	4.9
		6	1620	2.03	2.6	2.3	1.7	6.4
		7	1600 ^(b)	2.30	4.0	3.2	2.2	8.6
					[3.2]	[2.3]		[6.8]
353	99 percent dense; fine grained	1	1460	0.22	0.1	0.1	0.3	0.4
		2	1540	0.52	-0.2	-0.2	1.1	0.6
		3	1580	0.82	0.6	0.8	1.2	2.8
		4	1560	1.12	0.8	1.0	1.3	3.3
		5	1570	1.40	2.1	1.3	1.5	4.1
		6	1520	1.69	3.3	2.2	1.7	6.1
		7	1505	1.91	6.2	4.4	1.8	10.5
					[4.7]	[3.6]		[9.0]

(a) Values in brackets are based on micrometer measurements of diameter; all other measurements were taken from neutron radiographs. No micrometer measurements were made of Specimen 348.

(b) Temperature estimated from inner-shell thermocouple after specimen thermocouple failed.

FIGURE B-27. NEUTRON RADIOGRAPHS OF UN SPECIMENS IN CAPSULE HT-BRR-10

Specimen 348; 85 Percent Dense; Gas-Pressure Monitor

Specimen 351; 98 Percent Dense; Fine Grained

Specimen 352; 98 Percent Dense; Fine Grained

Specimen 350; Cast; Large Grained

Specimen 353; 98 Percent Dense; Fine Grained

FIGURE B-28. POSTIRRADIATION PHOTOMACROGRAPHS OF THE UN SPECIMENS FROM CAPSULE HT-BRR-10

In all cases, the magnification is 4X.

FIGURE B-29. A COMPARISON OF EXTERNAL VOLUME INCREASE AS A FUNCTION OF BURNUP FOR UN SPECIMENS FROM CAPSULES HT-BRR-3, HT-BRR-4, HT-BRR-7, AND HT-BRR-10

large amount of fuel swelling; then after channels were developed by interconnection or overlap of the bubbles at the grain boundaries, it is believed that gas-release rates to external surfaces increased and that external dimensional changes ceased. Analysis of the UN indicated that more than 97 percent of the fission gas produced had been released.

500X

HC21321

FIGURE B-30. TYPICAL MICROSTRUCTURE OF UN SPECIMEN 288 (INITIALLY 97 PERCENT DENSE) FROM CAPSULE BRR-3

This specimen was irradiated to a burnup of 2.51×10^{20} fissions per cm^3 at surface temperatures of about 1680 C. Note the regions in the UN grains which are relatively free of fission-gas porosity.

The microstructure of fine-grained UN Specimen 351 from Capsule HT-BRR-10 (Figure B-31) shows that most of the larger pores and, therefore, most of the easily resolvable porosity, are found at grain boundaries; however, at high magnification a large population of small pores, which probably contain most of the fission gas, is seen within the fuel. Quantitative metallography measurements have shown that the UN, originally 99 percent dense, now contains about 8 percent easily resolvable porosity at the grain boundaries. The discrepancy between the measured external volume increase of the fuel, 12.9 percent, and the measured density change, 7 percent, is attributed primarily to a multitude of unresolvable, small bubbles within the grains. Duplicate Specimen 352 was similar in both behavior and microstructural appearance. The microstructure of Specimen 353 (fine-grained) is shown in Figure B-32. This specimen was 99 percent dense before irradiation, but was irradiated at a slightly lower average surface temperature of 1530 C than Specimens 351 and 352. As in the case of Specimens 351 and 352, a large proportion of the observable fission-gas porosity is located at UN grain boundaries.

100X

HC23616

500X

HC23720

a. Low Magnification

b. Higher Magnification

FIGURE B-31. TYPICAL MICROSTRUCTURE OF UN SPECIMEN 351 IRRADIATED TO A BURNUP OF 1.99×10^{20} FISSIONS PER CM^3 AT AN AVERAGE SURFACE TEMPERATURE OF 1600 C

Note that most of the large pores are associated with grain boundaries.

100X

HC23610

FIGURE B-32. TYPICAL MICROSTRUCTURE OF UN SPECIMEN 353 IRRADIATED TO A BURNUP OF 1.91×10^{20} FISSIONS PER CM^3 AT AN AVERAGE SURFACE TEMPERATURE OF 1530 C

Most of the fission-gas porosity is associated with grain boundaries.

Fission-gas release was measured to be less than 4 percent for Specimens 351 and 353. Since the microstructures suggest a high degree of interconnection of the grain-boundary porosity to the fuel surface, this gas-release measurement indicates that only a small fraction of the gas in the fuel was actually responsible for the grain-boundary swelling. It seems likely that a combination of diffusion of the small amount of fission gas formed in the immediate vicinity of the grain boundaries to the grain boundaries and the high concentration or availability of vacancies at the grain boundaries swells the fuel. There was no evidence of preferential alignment of fission-gas porosity in grain boundaries perpendicular to the temperature gradient, as was observed by Albrecht, et al. (1).

Typical microstructures of UN Specimen 350 (large-grained), as shown in Figures B-33 and B-34, reveal that, in the absence of grain boundaries, there has been little growth of fission-gas bubbles and a somewhat lower amount of external fuel swelling (see Figure B-29). This large-grained specimen of UN, which retained nearly 100 percent of its fission gases, swelled somewhat less than the fine-grained UN, even though it was irradiated to a greater burnup at a slightly higher temperature. Apparently, a reduction in the grain-boundary area has improved the dimensional stability of the UN. The belief that elimination of grain boundaries as a preferred site for growth of bubbles will reduce swelling of UN at these temperatures is also supported by the results obtained on irradiation of 70 percent dense UN in Capsule HT-BRR-7. The 30 v/o porosity, which was fabricated into the UN at the grain boundaries, resulted in a significant improvement in the external swelling behavior when compared with that of high-density UN (Figure B-29) despite comparable fission-gas-release rates (<20 percent gas release).

A further hint that there may be a difference in the UN to account for the differences in external swelling and gas-release behavior between the UN from Capsule HT-BRR-3 and the UN from Capsule HT-BRR-7 is seen by comparing the microstructures presented in Figures B-30 and B-35. The microstructure of the UN from Capsule HT-BRR-3 (Figure B-30) shows fairly large regions which are free of fission-gas porosity, while the UN shown in Figure B-35 from Capsule HT-BRR-7 (completely described in BMI-1870, August, 1969) has fission-gas porosity in the form of small bubbles throughout most of the UN grains.

The gas-pressure monitor attached to 80 percent dense UN Specimen 348 in Capsule HT-BRR-10 indicated that the instantaneous gas-release rate increased, as shown in Figure B-36, to a rate of about 25 percent just prior to cladding failure at a burnup of 1.14×10^{20} fissions per cm^3 . The cumulative gas release at this burnup was about 15 percent. A postirradiation measurement which indicated a total gas release of 39 percent after a burnup of 2.1×10^{20} fissions per cm^3 is in general agreement with the data obtained from the monitor.

A close examination of the microstructure of Specimen 348 did not provide an explanation for the high swelling rate observed in the last four cycles of the irradiation (Figure B-29). In previous irradiations, the microstructures of UN specimens that exhibited "breakaway" swelling were found to contain free uranium metal. The presence of uranium metal indicated that the UN in these "breakaway" samples had become deficient in nitrogen. The UN specimens in Capsule HT-BRR-10 were known to be rich in nitrogen before irradiation, and it was considered possible that the sharp increase in the external swelling rate of Specimen 348 might be due to loss in nitrogen after a cladding failure. However, neither the microstructure of Specimen 348 nor those of Specimens 351 and 352 in the regions of anomalous swelling behavior contained observable uranium metal. Small amounts of uranium metal are difficult to detect even in unirradiated UN.

FIGURE B-33. LOW-MAGNIFICATION COMPOSITE OF CAST UN SPECIMEN 350

This specimen was irradiated to a burnup of 2.3×10^{20} fissions per cm^3 at surface temperatures around 1640 C. Note that there are very few large bubbles present.

500X

HC23425

FIGURE B-34. MICROSTRUCTURE OF CAST UN SPECIMEN 350 FROM CAPSULE HT-BRR-10

Note that the porosity is very small, on the order of 1μ in diameter.

750X

HC22939

FIGURE B-35. MICROSTRUCTURE OF UN SPECIMEN 322 (INITIALLY 70 PERCENT DENSE) FROM CAPSULE HT-BRR-7

This specimen achieved a burnup of 1.72×10^{20} fissions per cm^3 at surface temperatures of about 1660°C . There is fission-gas porosity generally throughout the UN grains, except very near some faceted surfaces.

FIGURE B-36. PLOT OF FISSION-GAS PRESSURE AS A FUNCTION OF BURNUP AS MEASURED BY THE NULL-BALANCE TRANSDUCER ATTACHED TO SPECIMEN 348 IN CAPSULE HT-BRR-10

25X

FIGURE B-37. TYPICAL MICROSTRUCTURE OF TUNGSTEN-51 v/o UN-24 v/o POROSITY SPECIMEN 328

This specimen was irradiated to a burnup of 1.83×10^{20} fissions per cm^3 at surface temperatures of ~ 1760 C. Note that the porosity is still distributed throughout the fuel.

The irradiation behavior of two 97 percent dense tungsten-75 v/o UN cermet specimens is also depicted by the curve shown for 97 percent dense bulk UN from Capsule HT-BRR-3 in Figure B-29. Apparently, the behavior of the tungsten-UN cermets is similar to that of nitrogen-deficient bulk fuel at temperatures near 1700 C. The apparent saturation of swelling was attributed to release of fission gases through interconnected channels associated with UN grain boundaries and tungsten-UN interfaces. The addition of 24 v/o porosity to a tungsten-UN cermet resulted in a material, Specimen 328 (Capsule HT-BRR-7), which exhibited external diametral and volume changes of less than 1.5 percent upon irradiation to 1.83×10^{20} fissions per cm^3 at an average surface temperature of 1760 C (see BMI-1870, August, 1969). A metallographic cross section of the porous cermet (Figure B-37) shows that the porosity remains distributed throughout the fuel. A photomicrograph taken at a higher magnification (Figure B-38) shows regions of UN relatively free of fission-gas porosity, as was observed in the bulk UN in Figure B-30. Postirradiation analyses have shown that 83 percent of the fission gas produced during the irradiation was released from the cermet. Therefore, in this specimen, it is likely that the large improvement in dimensional stability over that of the high-density cermet fuel is related to the ease of release of fission gas through the interconnected porosity and to the inability of fission gas to develop high pressures and transmit high stresses to the cladding.

500X

HC23065

FIGURE B-38. TYPICAL MICROSTRUCTURE OF TUNGSTEN-51 v/o UN-24 v/o POROSITY SPECIMEN 328 FROM CAPSULE HT-BRR-7

Note that there are regions in the UN grains which are free of observable fission-gas porosity.

It is interesting to note that in Capsule HT-BRR-7, where both bulk UN and tungsten-UN cermet fuels fabricated with a large amount of porosity were irradiated, in one case there was high gas retention (bulk UN) and in the other case there was high gas release (tungsten-UN cermet). A review of the fabrication records indicated that the UN used in the cermet fuel was from a different batch than that of the bulk UN. Such altered circumstances might provide an opportunity for a compositional change to develop in the UN to account for the variation in gas-release behavior.

Table B-12 summarizes the irradiation conditions and external dimensional changes of the UN specimens irradiated in Capsule LRL-2. The micrometer measurement data reported in Table B-12 indicate that the external diametral swelling of the cladding (and of the fuel) was less than 1 percent in all cases. In agreement with these data, postirradiation photomicrographs show the claddings of all specimens to be in excellent condition (Figure B-39). External fuel length and volume changes were also small, and close to the limits of experimental error. In general, the changes were too small for any effects of grain size and density to be distinguished. Specimens N and P, which operated at temperatures about 100 C higher than most of the other specimens, exhibited slightly larger dimensional changes, suggesting an increase in the swelling of UN with temperature.

Metallographic examination, however, provided some information on the effects of grain boundaries and gas-bubble growth. Microstructures of the coarse-grained and fine-grained UN Specimens P and J showed extensive fission-gas porosity at the grain boundaries and no optically resolvable porosity within the grains (Figures B-40 and B-41). No optically resolvable fission-gas porosity was noted within the grains of any of the UN. Fission-gas release was found to be 5 percent or less in all cases, even though two specimens contained 25 v/o porosity, indicating that fission-gas mobility in the UN was low under the conditions of the irradiation. Thus, as with the UN irradiated in Capsule HT-BRR-10, it seems likely that the porosity that developed at the grain boundaries formed as a result of a combination of the small amount of fission gas in the immediate vicinity of the grain boundaries and a high concentration of vacancies in the boundaries. Indications of preferential growth of gas bubbles in grain boundaries oriented across the path of heat flow were observed only in Specimen J (Figure B-41; compare with Specimen P in Figure B-40).

An 8 v/o increase in the porosity of Specimen J was measured by Quantimet techniques. The specimen showed little, if any, external diametral swelling, but possibly some length increase. However, the central void decreased in diameter from 98 to 91 mils (representing a 4 v/o increase in the volume of the fuel). The external swelling of 2 v/o plus the inward swelling of 4 v/o thus accounts for three-fourths of the new porosity observed in the microstructure, as shown in Figure B-41. The amount of mechanical deformation in the radial direction is consistent with the apparent growth of bubbles in grain boundaries oriented in the circumferential direction. It appears that the preferred circumferential growth of gas bubbles is related to stress-induced migration of fission gases along the grain boundaries; or stated another way, the fine-grained UN has been less able to restrain creep stresses in the radial direction than in the circumferential direction, so that deformation by grain separation has been greatest in the radial direction, thereby opening circumferential cracks.

Table B-13 summarizes the irradiation conditions and dimensional changes of the UN and UN-PuN specimens in Capsule HT-BRR-13. Neutron radiographs of the specimens are shown in Figure B-42. Because of the anomalous swelling behavior of Specimens 371 and 380, dimensional measurement data are not reported. Apparently, the UN in these specimens sintered and shrank away from the cladding early in the first cycle of irradiation, and has since been redepositing by vapor transport on the cladding (Figure B-42). Further details of the extent of this behavior will be deferred until the

TABLE B-12. IRRADIATION CONDITIONS AND DIMENSIONAL CHANGES FOR SPECIMENS IN CAPSULE LRL-2

Specimen ^(a)	UN Composition	BRR Cycle	Centerline Temperature, C	Estimated Accumulated Burnup, 10^{20} fissions per cm^3	External Dimensional Changes ^(b) , percent			
					Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
O	Arc melted, large grained	1	1550	0.27	-2.2	-2.6	1.6	-3.6
		2	1410	0.52	0.0	0.0	0.8	0.8
		3	1440	0.78	0.5	0.5	0.4	1.5
		4	1440	0.99	0.4	0.4	1.0	1.9
		5	1425	1.18	0.4	0.5	0.9	1.9
		6	1420	1.44	0.0	0.0	1.9	1.9
		7	1410	1.71	2.0	0.7	1.8	3.3
		8	1425	1.92	0.6	0.3	1.8	2.4
					[0.0]	[0.0]		[1.8]
L	Arc melted, large grained	1	1620 ^(c)	0.29	-2.1	-2.6	0.6	-4.5
		2	1510	0.57	-0.8	-1.0	0.5	-1.5
		3	1540	0.86	-0.4	-0.5	1.0	0.1
		4	1540	1.09	0.2	0.2	0.8	1.2
		5	1535	1.30	0.0	0.0	1.2	1.2
		6	1530	1.58	0.7	0.9	1.4	3.2
		7	1520	1.87	0.9	0.6	1.3	2.6
		8	1530	2.09	0.8	0.0	0.6	0.6
					[0.0]	[0.0]		[0.6]
J	98 percent dense, fine grained	1	1590	0.30	-1.0	-1.2	0.5	-1.9
		2	1450	0.58	-1.4	-1.8	-0.1	-3.6
		3	1450	0.87	-0.7	-0.9	-0.6	-2.3
		4	1470	1.10	0.2	0.2	1.2	1.7
		5	1455	1.32	-1.0	-1.2	0.5	-1.9
		6	1450	1.60	0.2	0.2	1.2	1.7
		7	1440	1.90	0.3	-0.1	0.6	0.3
		8	1435	2.13	0.5	0.2	1.4	1.8
					[0.0]	[0.0]		[1.4]
M	75 percent dense	1	1580	0.26	-1.6	-2.0	-0.1	-4.0
		2	1470	0.50	-0.7	-0.9	-0.2	-1.9
		3	1470	0.75	0.1	0.1	0.1	0.3
		4	1480	0.95	0.1	0.1	0.0	0.2
		5	1460	1.14	0.1	0.1	0.2	0.4
		6	1460	1.39	0.9	1.0	0.2	2.3
		7	1450	1.65	0.9	0.6	0.6	1.8
		8	1435	1.85	1.1	0.6	0.4	1.6
					[-0.3]	[-0.4]		[-0.4]
K	75 percent dense	1	1575	0.26	-2.1	-2.6	0.5	-4.6
		2	1475	0.50	0.2	0.2	0.8	1.3
		3	1460	0.75	0.7	0.8	1.1	2.7
		4	1480	0.95	0.0	0.0	1.0	1.1
		5	1465	1.14	0.3	0.4	1.2	2.0
		6	1460	1.39	0.6	0.7	1.6	3.0
		7	1460	1.65	1.5	1.1	1.7	3.9
		8	1435	1.85	0.6	0.3	1.9	2.5
					[-0.3]	[-0.4]		[1.1]
N	98 percent dense, coarse grained	1	1680 ^(c)	0.30	-1.9	-2.4	0.1	-4.6
		2	1620	0.58	-0.3	-0.4	0.2	-0.5
		3	1570	0.87	0.1	0.1	1.5	1.7
		4	1525	1.10	0.6	0.7	0.8	2.2
		5	1600	1.32	-0.2	-0.3	0.5	-0.1
		6	1600	1.61	0.5	0.6	1.2	2.5
		7	1585	1.91	1.4	1.0	1.6	3.6
		8	1570	2.14	0.5	0.1	2.0	2.2
					[0.6]	[0.7]		[3.4]
P	98 percent dense, coarse grained	1	1635	0.29	-1.6	-2.0	-0.9	-3.0
		2	1580	0.57	0.0	-0.1	-0.1	-0.2
		3	1540	0.85	0.0	0.0	1.1	1.1
		4	1580	1.08	0.5	0.6	0.4	1.6
		5	1555	1.29	-0.5	-0.6	1.4	0.1
		6	1550	1.57	0.9	1.1	0.4	2.6
		7	1530	1.86	2.4	1.4	1.5	4.3
		8	1505	2.08	1.7	0.8	1.8	3.4
					[0.4]	[0.5]		[2.8]

(a) All specimens are UN and all have 0.100-in. centerline holes. Each specimen is 10 percent enriched in U^{235} .

(b) Values in brackets are based on micrometer measurements of diameter, all other measurements were taken from neutron radiographs.

(c) Normalized centerline temperatures.

Specimen O
Arc melted
Large grained

Specimen L
Arc melted
Large grained

Specimen J
98 percent dense
Fine grained

FIGURE B-39. POSTIRRADIATION PHOTOMACROGRAPHS OF THE UN SPECIMENS
IRRADIATED IN CAPSULE LRL-2 (~4X)

Specimen M
75 percent dense

Specimen K
75 percent dense

Specimen N
98 percent dense
Coarse grained

Specimen P
98 percent dense
Coarse grained

FIGURE B-39. (CONTINUED)

500X

HC23755

FIGURE B-40. TYPICAL MICROSTRUCTURE OF COARSE-GRAINED UN SPECIMEN P

Note that most of the observable porosity is associated with grain boundaries.

500X

HC23749

FIGURE B-41. TYPICAL MICROSTRUCTURE OF FINE-GRAINED UN SPECIMEN J NEAR MIDRADIUS

Note that most of the observable porosity is associated with grain boundaries.

UN Specimen 371
73 percent dense
Gas-pressure monitor

UN Specimen 382
93 percent dense

UN-8 w/o PuN Specimen 374
78 percent dense

UN Specimen 380
93 percent dense
Slit cladding

FIGURE B-42. NEUTRON RADIOGRAPHS OF THE UN AND UN-PuN SPECIMENS
IN CAPSULE HT-BRR-13

irradiation is completed and the specimens have undergone a complete postirradiation examination. However, this type of vapor transport was observed in Specimens 322 and 323 in Capsule HT-BRR-7 and in Specimens 336 and 337 in Capsule HT-BRR-8 (BMI-1870, August, 1969).

TABLE B-13. IRRADIATION CONDITIONS AND DIMENSIONAL CHANGES FOR THE UN AND UN-8 w/o PuN SPECIMENS IN CAPSULE HT-BRR-13

Specimen	Description	BRR Cycle	Average Temperature, C	Estimated Accumulated Burnup, 10^{20} fissions per cm^3	External Dimensional Changes, percent			
					Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
371	UN:	1	1660	0.30	No measurements ^(a)			
	75 percent dense	2	1675	0.59				
	gas-pressure monitor	3	1690	0.89				
382	UN:	1	1690 ^(b)	0.33	-0.4	-0.5	-0.3	-1.3
	93 percent dense	2	1700	0.64	-0.2	-0.2	0.2	-0.2
		3	1700	0.97	0.4	0.5	0.8	1.8
374	UN-8 w/o PuN:	1	1710	0.30	0.0	0.0	1.0 ^(c)	1.0
	75 percent dense	2	1690	0.59	0.2	0.2	-0.9 ^(c)	-1.5
		3	1650	0.89	0.7	0.8	-2.7 ^(c)	-1.1
380	UN:	1	1575 ^(b)	0.27	No measurements ^(a)			
	93 percent dense	2	1575	0.53				
	slit cladding	3	1550	0.80				

(a) Because of the anomalous behavior of the fuel in this specimen, no dimensional measurements are reported. See text for an explanation of specimen behavior.

(b) Temperature estimated from inner-shell thermocouple after specimen thermocouple failed.

(c) These values do not account for the fuel transferred to the inside of the top end cap.

After three cycles of irradiation at temperatures near 1700 C, 93 percent dense UN Specimen 382 is exhibiting relatively small dimensional changes. The external fuel volume increase of 1.8 percent at a burnup of about 1×10^{20} fissions per cm^3 is in excellent agreement with the swelling data presented for the nitrogen-rich UN (Figure B-29).

The 75 percent dense specimen of UN-8 w/o PuN, which exhibited a small diameter change after three cycles of irradiation at approximately 1680 C, formed a central void and some material, a high neutron absorber, presumably plutonium-rich, transferred to the inside of the top end cap (Figure B-42).

The gas-pressure monitor attached to 75 percent dense UN Specimen 371 indicated that the gas-release rate was negligible for the first half-cycle of irradiation but increased to a rate near 100 percent after the second cycle of irradiation (Figure B-43). The cumulative gas release, when the transducer ceased operation, was about 65 percent. Considering the large degree of fuel movement in this specimen, this amount of gas release is not surprising. The delay in achieving a high rate of gas release suggests that the gas operates to produce channels for gas release in the fuel.

FIGURE B-43. PLOT OF FISSION-GAS PRESSURE AS A FUNCTION OF BURNUP AS MEASURED BY THE NULL-BALANCE TRANSDUCER ATTACHED TO SPECIMEN 371 IN CAPSULE HT-BRR-13

Plans for Future Work

The irradiation of the UN and UN-PuN specimens in Capsule HT-BRR 13 will continue toward a target burnup of about 2×10^{20} fissions per cm^3 .

- (1) Albrecht, E. D., et al., "A High-Temperature Irradiation and Post-Irradiation Analysis of Uranium Nitride Fuel", UCRL-50727 (August 7, 1969); also UCRL-71703 (August 15, 1969).

Irradiation Behavior of Carbide Fuels at High Temperatures

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Objective of Program

To investigate the irradiation behavior of carbide fuels at surface temperatures from 1200 to 1900 C.

Approach Being Used

Early experiments in the HT-BRR irradiation series showed that dense UC and tungsten-UC cermet s swelled steadily at high rates when irradiated at temperatures above 1600 C to burnups up to 2.5×10^{20} fissions per cm^3 (BMI-1848). Only slight tendencies toward decreased swelling rates with increasing burnup were observed and no improvements in swelling behavior were realized by the introduction of centerline holes. The continued high swelling rates were attributed to relatively high fission-gas retention (58 percent at 1675 C) that was associated with a tendency for the fission gases to precipitate and form relatively small, discrete bubbles.

A variety of modifications of UC were or are being irradiated in attempts to either accommodate swelling internally (within the cladding) or to enhance fission-gas release or to enhance the strength of the cladding relative to that of the fuel. Because of extremely high fuel temperatures (2000 to 2200 C), the use of a 10-mil annular gap around a bulk UC specimen proved to be totally ineffective as a method of preventing cladding strain at a cladding surface temperature of about 1600 C (BMI-1870). Swelling of a copper-UC cermet was much greater than expected because the cermet separated into an annular ring of solid UC on the fuel outer diameter plus a central core of copper-rich liquid (BMI-1870).

A 60 percent dense specimen of crushed, minus 230-mesh particles of UC was irradiated in Capsule HT-BRR-10 to determine whether the gas-release behavior of UC can be modified by providing built-in gas-release channels and by lessening the distance fission gas must migrate to reach these channels; or whether the porosity is used to accommodate swelling and reduce the stress on the cladding. A 1-mil-thick tungsten foil was used as a barrier between the UC powder and the cladding in an attempt to reduce the rate of deterioration of the cladding by carbon diffusion into it.

Capsule HT-BRR-13 contains two specimens of 60 percent dense UC to test the effect of buffering with tungsten on fuel-cladding reactions and on the swelling and gas-release behavior of porous UC. One of the specimens contains a 1-mil-thick tungsten foil external buffer at the fuel-cladding interface, while the other is internally buffered with 5 w/o tungsten in the UC and no tungsten foil.

All specimens consist of a column of fuel 1 in. long contained in tungsten-26 w/o rhenium claddings with an OD of 0.25 in. and a wall thickness of 20 mils, as shown earlier in Figure B-1.

Dimensional changes in the specimens are determined after each cycle of irradiation by measurements from neutron radiographs. The postirradiation examination includes dimensional and density measurements, fission-gas-release measurements, and metallography.

Significant Accomplishments During Fiscal Year 1970

The 60 percent dense specimen of crushed UC particles irradiated in Capsule HT-BRR-10 showed a low initial swelling rate and a final external fuel volume increase of 7 percent after a burnup of 2×10^{20} fissions per cm^3 at 1530 C. This result compares favorably with external volume increases of about 35 percent at the same burnup at 1680 C in dense UC. However, the intermediate swelling rates of the two 60 percent dense UC specimens that are being irradiated in Capsule HT-BRR-13 at 1690 C suggests that a significant part of the improved swelling behavior of the specimen that operated at 1530 C is attributable to its lower irradiation temperature. The postirradiation microstructure of the specimen that operated at 1530 C suggested that the lack of bonded interparticle contacts and attendant inability of the swelling fuel to transmit stresses to the cladding was a major factor in eliminating external dimensional changes during the first half of the irradiation. The formation of solid bonds at the interparticle contacts by sintering led to a gradual increase in swelling rates during the last half of the irradiation. The specimens of loose-packed UC particles that are being irradiated at 1690 C have possibly experienced increased rates of swelling of individual particles and also increased rates of sintering and bonding at interparticle contacts and, thus, are experiencing higher rates of external fuel volume increase.

Summary of Research Carried Out

The irradiation and postirradiation examination of the 60 percent dense UC specimen in Capsule HT-BRR-10 was completed. The 60 percent dense UC specimens in Capsule HT-BRR-13 have completed three cycles of irradiation, and the irradiation is still in progress.

The irradiation conditions and dimensional changes of the 60 percent dense UC specimens from Capsules HT-BRR-10 and HT-BRR-13 are given in Table B-14. Neutron radiographs (Figure B-44) indicate that the specimens are in good condition. Also, a postirradiation photomicrograph of Specimen 354 from Capsule HT-BRR-10 (Figure B-45) shows no gross failures in the tungsten-26 w/o rhenium cladding.

TABLE B-14. IRRADIATION CONDITIONS AND DIMENSIONAL CHANGES FOR 60 PERCENT DENSE UC SPECIMENS IN CAPSULES HT-BRR-10 AND HT-BRR-13

Specimen and Capsule	Description of Fuel	BRR Cycle	Average Temperature, C	Estimated Accumulated Burnup, 10^{20} fissions per cm^3	External Dimensional Changes ^(a) , percent			
					Maximum Cladding OD	Average Fuel OD	Fuel Length	Average Fuel Volume
354, HT-BRR-10	60 percent dense UC, loose-packed particles, 1-mil-thick tungsten foil	1	1550	0.25	0.2	0.2	-2.8	-2.4
		2	1485	0.57	2.1	1.3	-2.4	0.1
		3	1500(b)	0.89	1.6	1.2	-1.9	0.3
		4	1540	1.21	1.7	0.8	-1.6	0.1
		5	1540	1.50	4.0	2.4	-1.3	3.5
		6	1520	1.81	3.6	2.7	0.8	6.3
		7	1520	2.06	4.3	3.2	2.5	8.9
					[3.6]	[2.4]		[7.3]
377, HT-BRR-13	60 percent dense UC, loose-packed particles, 1-mil-thick tungsten foil	1	1675(c)	0.26	2.7	1.7	-2.6	0.8
		2	1700	0.51	2.1	1.6	-0.7	2.5
		3	1680	0.77	3.7	2.7	-0.1	5.3
379, HT-BRR-13	60 percent dense UC, loose-packed particles, internal buffer of 5 w/o tungsten	1	1680(c)	0.25	0.4	0.4	-1.4	-0.6
		2	1690	0.49	2.8	1.7	-1.0	2.4
		3	1660	0.74	4.7	3.5	-0.8	6.2

(a) Values in brackets are based on micrometer measurements of diameter; all other measurements were taken from neutron radiographs.

(b) Temperatures were estimated from inner-shell thermocouple after specimen thermocouple failed.

(c) Temperatures were approximately 225 C hotter for the first 40 min of the first irradiation cycle.

External fuel volume changes as a function of burnup for the 60 percent dense UC specimens are compared with those for specimens of high-density, cast UC in Figure B-46. The 7 percent external fuel volume increase of one 60 percent dense UC specimen (354) at 1530 C compares favorably with volume increases of about 35 percent at the same burnup at 1680 C in dense UC. However, the higher swelling rate of the other two, Specimens 377 and 379 (Capsule HT-BRR-13), at about 1690 C suggests that the lower temperature of Specimen 354 (1530 C) had a significant influence on the results. This conclusion must be regarded as tentative until the irradiation and postirradiation examination of the specimens from Capsule HT-BRR-13 are completed.

A metallographic cross section of Specimen 354 (Figure B-47) shows the specimen to be in good condition; considerable grain growth ($62\ \mu$ before irradiation; $200\ \mu$ after irradiation) and a partial redistribution of fuel toward the cladding have occurred. The presence of small fission-gas bubbles in the UC and the number of interconnections between particles of UC near the cladding (Figure B-48) suggest that the 2.4 percent measured external diametral increase exhibited by the specimen is primarily the result of swelling of this outer region of fuel.

CAPSULE HT-BRR-10

UC Specimen 354
60 percent dense
1-mil-thick tungsten foil

Preirradiation

Postirradiation

CAPSULE HT-BRR-13

UC Specimen 379
60 percent dense
Internal buffer of 5 w/o tungsten

UC Specimen 377
60 percent dense
1-mil-thick tungsten foil

Preirradiation

Third Cycle

FIGURE B-44. NEUTRON RADIOGRAPHS OF 60 PERCENT DENSE UC SPECIMENS FROM CAPSULES HT-BRR-10 AND HT-BRR-13

4X

P1862-63

FIGURE B-45. POSTIRRADIATION PHOTOMACROGRAPH OF 60 PERCENT DENSE UC SPECIMEN 354 FROM CAPSULE HT-BRR-10

FIGURE B-46. A COMPARISON OF THE EXTERNAL VOLUME INCREASE OF UC SPECIMENS OF DIFFERENT DENSITIES AND TEMPERATURES FROM THE HT-BRR SERIES

The high degree of swelling of the high-density, large-grained UC specimens (35 v/o at 2×10^{20} fissions per cm³) irradiated at 1680 C was, to a large extent, attributed to retention of 58 percent of the fission gas in the dense UC in the form of discrete, spherical bubbles of sizes up to about 7 μ in diameter (BMI-1848, Figure 17). Microstructures of Specimen 354 irradiated in Capsule HT-BRR-10 at 1530 C (Figures B-48 and B-49) show few discrete, spherical bubbles greater than 2 μ in diameter in the 60 percent dense UC Specimen 354. These observations indicate that the difference in dimensional stability between the two configurations of UC is roughly consistent with the difference in size of the fission-gas bubbles.

An explanation for a part of the improved dimensional stability of low-density UC as exemplified in Specimen 354 is related to the temperature difference, 1530 C versus 1680 C. The observation of smaller bubbles in the low-density UC relative to the size of bubbles in the high-density UC supports this point of view. Larger bubbles would be expected with increasing temperatures, provided that vapor-transport processes were relatively inactive. However, a comparison of Figures B-47, B-48, and B-49 shows that as temperature increases from surface to centerline of this specimen the size of the bubbles remains the same, although the particle size increases at least three times (the latter effect is more obvious in Figure B-47). The faceted surfaces and gradients of porosity in particles shown in Figure B-49 suggest that the major mechanism of grain growth in this specimen has been by vapor transport, a process that could become active in UC near 1700 or 1800 C. It is noteworthy that the location of small bubbles in Figures B-48 and B-49 relative to surfaces and in the presence of small temperature gradients shows that these small bubbles are stationary relative to the surfaces. The location of bubbles near surfaces also implies that diffusion to surfaces is a relatively inactive mode of gas release.

The above observations suggest that the negligible swelling of Specimen 354 for four cycles of irradiation compared to 25 v/o swelling of high-density UC at the same burnup must be related to the lack of bonded contacts between the UC particles in Specimen 354 early in the irradiation. This loose contact between particles minimized the

FIGURE B-47. LOW-MAGNIFICATION COMPOSITE OF 60 PERCENT DENSE UC SPECIMEN 354

This specimen was irradiated to a burnup of 2.06×10^{20} fissions per cm^3 at an average surface temperature of 1530 C. Note that the fuel is more dense near the cladding and that there is porosity in the cladding. The original particle size of 62μ has increased to 200μ .

500X

HC23609

FIGURE B-48. MICROSTRUCTURE AT THE FUEL-CLADDING INTERFACE OF 60 PERCENT DENSE UC SPECIMEN 354

Note the small fission-gas pores in the relatively dense UC near the cladding.

500X

HC23721

FIGURE B-49. TYPICAL MICROSTRUCTURE OF 60 PERCENT DENSE UC SPECIMEN 354 AT HIGH MAGNIFICATION

Note the small fission-gas pores in the particles of UC. Faceted surfaces are present on the right side of most particles of UC and gradients of porosity are associated with these faceted surfaces. Also note the close association of pores with many surfaces on the left side of most particles of UC.

transfer of stress from the swelling UC fuel to the cladding. The growth of these contacts by swelling of individual particles, by vapor transport of UC, and by sintering, and the subsequent growth of fission-gas bubbles in the particles near the cladding must have been responsible for the gradual increase in swelling rates during the last three cycles of irradiation of Specimen 354.

Specimens 377 and 379 in Capsule HT-BRR-13, which operated at about 1690 C for three cycles of irradiation, probably experienced higher particle swelling rates, higher sintering rates, and more rapid interparticle bonding than Specimen 354 in Capsule HT-BRR-10. As a result, higher initial swelling rates are observed for the Capsule HT-BRR-13 specimens.

There is some porosity in the cladding of Specimen 354 (Figure B-47). However, the low degree of degradation of the cladding observed in this specimen, which had a 1-mil-thick tungsten foil at the fuel-cladding interface, represents a great improvement over that observed for the high-density UC specimens, which had no tungsten foil.

After three cycles of irradiation, there was no apparent difference in swelling behavior between Specimen 377, which has a 1-mil-thick tungsten foil at the fuel-cladding interface, and Specimen 379, which has 5 w/o tungsten added as an internal buffer.

Plans for Future Work

The irradiation of the 60 percent dense UC specimens in Capsule HT-BRR-13 will continue toward a target burnup of 2×10^{20} fissions per cm^3 .

Fission-Gas Diffusion and Solubility

R. L. Ritzman, R. B. Price, R. B. Clark, and D. L. Morrison

Objective of Program

To determine fission-gas diffusion, solubility, and bubble nucleation and agglomeration processes in refractory fuels.

Approach Being Used

Postirradiation fission-gas-release measurements are being made as a function of fission-product concentration for neutron-activated specimens by annealing them at temperatures from 1300 to 1800 C. Fission-gas solubility and diffusion coefficients and the effects of fission-gas precipitation will be deduced from the kinetics of the observed release. The influence of an irradiation environment on precipitation processes is also being examined using the postactivation annealing technique.

Significant Accomplishments During Fiscal Year 1970

The determination of fission-gas diffusion rates in $(\text{U}, \text{Pu})\text{O}_2$ was unsuccessful because of unexpected reactions between the mixed oxide and container materials. Preliminary measurements of fission-gas diffusion in UC, UN, and UO_2 indicated that diffusivities in UN and UO_2 are one to two orders of magnitude lower than in UC under comparable conditions. Thus, migration rates of fission gases in uranium oxide and nitride cannot be inferred from data that has been obtained on UC.

Summary of Research Carried Out

Work was primarily directed at obtaining fission-gas release and diffusion measurements from mixed oxides and, when this effort failed, investigating the differences in fission-gas release between UC, UN, and UO_2 .

Mixed-Oxide Fuel. An attempt was made to prepare high-density specimens of $(U_{0.92}Pu_{0.08})O_2$ from physically mixed powders of UO_2 and PuO_2 . The powders were blended and wet ball milled for 8 hr to uniformly disperse the PuO_2 component. Chemical analysis of the blended powder showed 300 ppm iron as the major contaminant. Cylindrical pellets were mechanically pressed from the blended powders. The resulting compacts were outgassed and presintered at 900 C in a vacuum to a density of 70 to 80 percent of theoretical. The presintered pellets were centerless ground to a diameter of approximately 0.460 in. and loaded into double-walled stainless steel capsules. These capsules were placed in a graphite container which was then loaded into an autoclave for gas-pressure bonding at 1250 C and 10,000 psi for 2 hr. Leak checks of the capsules showed no evidence of leaks before or after bonding.

The stainless steel cladding was removed from the bonded specimens by machining. Density measurements, oxygen-to-metal ratios, metallographic examination, and chemical analyses were made on the specimens after bonding. Density measurements indicated the material was 98 ± 1 percent of theoretical density. The oxygen-to-metal ratio of the gas-bonded specimens was 1.980 ± 0.005 , consistent with measurements on sintered mixed oxides. Chemical analysis of the material after gas-pressure bonding indicated iron and aluminum contents of 520 ppm and 210 ppm, respectively. Metallographic examinations confirmed the density measurement, but suggested the possible existence of included impurities.

Samples were machined from the gas-pressure-bonded specimens and irradiated at ambient temperature (<150 C) to an exposure of 8.6×10^{14} fissions per cm^3 . One of the activated samples was subsequently heated in a tungsten crucible at 1300 C in a specially designed induction furnace under 2 to 3 mm of helium pressure. A higher rate of fission-gas release than anticipated was obtained and the sample, after cooling, showed evidence of reaction with the tungsten crucible in which it had rested. The mixed-oxide sample lost nearly 3 percent of its weight during the anneal, and, since a corresponding quantity of fission gas was measured, it is probable that most of the gas release occurred from the region of the sample that was affected by the reaction with tungsten. Such a reaction was not expected because earlier work had shown mixed-oxide fuels to be compatible with tungsten-base alloys at temperatures up to 1700 C⁽¹⁾.

Additional heatings of unactivated mixed-oxide samples were performed in tungsten crucibles under vacuum and helium atmospheres without improvement. A metallographic section of one of these samples showed the presence of a reaction zone on the surfaces that had contacted tungsten and also revealed numerous internal fissures within the mixed-oxide material. The presence of excessive gas(es) in the mixed oxide was suspected, so a specimen was exposed to an outgassing treatment by heating very slowly to 1300 C in molybdenum under a slightly reducing atmosphere. When this specimen was reheated in tungsten in the induction furnace, the results again gave excessive weight loss and visual evidence of reaction with the metal container. It was concluded that specimen outgassing was not the cause of the incompatibility. Also, the problem could not be correlated specifically with any particular fuel sample, tungsten crucible, heating temperature, or furnace atmosphere. The behavior was general and common to both unirradiated and irradiated mixed-oxide samples. Perhaps the iron and aluminum impurities in the pressure-bonded material initiated the reactions that were observed, but this has not been confirmed. Nevertheless, it was clear that accurate fission-gas diffusion data could not be obtained with the existing material and that considerable effort might be required to resolve the problem. On this basis, work on this segment of the program was terminated.

Fission-Gas Release From UC, UN, and UO_2 . Pilot experiments were performed to obtain preliminary comparisons of fission-gas release from UC, UN, and UO_2 under the same conditions of fission exposure and postactivation heating. Specifically, two specimens each of arc-cast UC, single-crystal UO_2 , and 97 percent dense compacted

UN were neutron activated at ambient temperature to 2.2×10^{14} fissions per cm^3 . Then each pair of specimens was heated for 6 to 12 hr, one at 1400 C and the other at 1600 C. The UC specimens were heated in vacuum, the UN in the appropriate nitrogen overpressure to maintain stoichiometry at temperature, and the UO_2 in 0.1 atm of helium. The release of Xe^{133} was measured continuously during all the anneals.

The release of Xe^{133} from all samples was characterized by an initially rapid release followed by a lower rate that tended toward parabolic time dependence. In some cases release rates increased near the end of the run, indicative of surface reactions with gaseous contaminants. Sample weight changes supported this observation, and in such cases the initial portion of the gas-release curve was used to obtain diffusion-coefficient estimates. The fractional release of fission gas from UN and UO_2 was similar at both postactivation annealing temperatures, but significantly lower than the fractional release from UC. At 1600 C the UN and UO_2 release fractions were about a fifth of that for UC and at 1400 C, about a third. However, release fractions for the present UC samples were only about one-half to one-third of values that had been obtained in earlier UC studies⁽²⁾ under equivalent conditions. Therefore, the rate of fission-gas migration in UN and UO_2 may be even lower, compared to UC, than is indicated by the present results.

The fission-gas-release curves were analyzed in terms of the Hurst⁽³⁾ model, which approximates the perturbing effects of fission-gas precipitation on diffusion from a solid fuel body. The diffusion-coefficient values obtained from this analysis for the three fuels studied in the present series of experiments are listed in Table B-15. The values for UC in the table are lower by a factor of five than those reported in earlier UC studies⁽²⁾. Taking both the former and the more recent data into account, it appears that Xe^{133} diffusivities in UN and UO_2 are one to two orders of magnitude lower than in UC under comparable conditions. Therefore, the rates of migration of fission gases in UN and UO_2 cannot be inferred from data that have been obtained for the UC system. The results obtained here for UO_2 may be high because of suspected oxygen pickup by the fuel during the anneals. For example, MacEwan and Morel⁽⁴⁾, using similar conditions and the Hurst method of data analysis, obtained a diffusion coefficient for xenon in UO_2 at 1400 C of $8.2 \times 10^{-15} \text{ cm}^2$ per sec. The diffusivities listed in Table B-15 should be considered preliminary crude estimates and subject to verification by additional measurements.

TABLE B-15. ESTIMATED Xe^{133} DIFFUSION COEFFICIENTS
FOR UC, UN, AND UO_2

Fuel Material	Estimated Xe^{133} Diffusion Coefficient at Indicated Temperature, cm^2 per sec	
	1400 C	1600 C
UC	3×10^{-12}	8×10^{-11}
UN	2×10^{-13}	2×10^{-12}
UO_2	4×10^{-13}	2×10^{-11}

Plans for Future Work

During the next year a small effort is planned to perform additional fission-gas-release experiments with single-crystal UO_2 . The work will concentrate on obtaining

accurate xenon diffusivities as a function of temperature for use in analytical models of fission-gas-bubble formation and growth.

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- (2) Ritzman, R. L., Price, R. B., and Morrison, D. L., "Fission-Gas Diffusion and Solubility", in "Progress on High-Temperature Fuels Technology During August, 1968, Through July, 1969. Annual Report", BMI-1870 (August, 1969), pp 88-98.
- (3) Hurst, D. G., "Diffusion of Fission Gas" (AECL-1550), CRRP-1124 (November, 1962).
- (4) MacEwan, J. R., and Morel, P. A., "Migration of Xenon Through a UO_2 Matrix Containing Trapping Sites", Nucl. Appl., 2, 158-170 (1966).

Evaluation of Fission-Gas Bubbles in Nuclear Fuels

R. L. Ritzman, A. J. Markworth, and R. B. Price

Objective of Program

To evaluate by means of scanning electron microscopy and optical microscopy the morphology and dynamics of fission-gas-bubble distributions in lightly irradiated nuclear fuels, and to relate these to current theories as well as to other recently obtained data.

Approach Being Used

Scanning-electron-microscope (SEM) and optical-microscope (OM) examinations are being made of the bubble sizes and concentrations in neutron-activated nuclear fuel specimens as a function of fission exposure, annealing temperature, and time at temperature. The concentration and size of fission-gas bubbles are being measured, and the observed bubble distributions are being quantitatively assessed in terms of current theories of bubble precipitation, growth, migration, and re-solution.

Significant Accomplishments During Fiscal Year 1970

Scanning electron microscopy and optical microscopy were used to evaluate fission-gas-bubble distributions in lightly irradiated, hyperstoichiometric UC. Interpretation of the results led to the conclusion that the character of bubble distributions is sensitive to material composition and postactivation annealing temperature. If the composition of the UC and the annealing temperature favor the existence of UC_2 second phase during heating, then gas-bubble networks will form preferentially at the UC_2 platelets. If the conditions favor solid-solution formation during heating, then two populations of gas bubbles will form, one containing large pores located at grain and some subgrain boundaries and a second containing much smaller bubbles, which are homogeneously dispersed within the UC grains.

Scanning electron microscopy was also used to search for small fission-gas bubbles on a fracture surface of a single-crystal specimen of nearly stoichiometric UO_2 . The specimen was neutron activated to 1×10^{17} fissions per cm^3 and then annealed for 24 hr at 1700 C. No porosity identifiable as fission-gas bubbles could be detected. On the basis of these observations, an upper limit of $9 \times 10^{-13} \text{ cm}^2$ per sec was calculated for the fission-gas diffusion coefficient in UO_2 at 1700 C. This value is greater by more than a factor of 50 than that obtained by extrapolating Cornell's diffusion data⁽¹⁾ to 1700 C, and it is about 100 times smaller than the preliminary results for UO_2 reported in the preceding section of this report.

Summary of Research Carried Out

A number of UC specimens that had been neutron activated at temperatures below 200 C and to exposures ranging up to 4×10^{17} fissions per cm^3 were annealed out-of-pile to promote fission-gas precipitation and possibly to produce detectable bubbles. The specimens were small cylinders of arc-cast, slightly hyperstoichiometric UC (4.9 w/o carbon). The anneals were performed in a vacuum induction furnace at temperatures of 1400 or 1700 C for periods of 6 hr or more. Specimens of unirradiated UC were exposed to similar annealing treatments for comparison. Following each anneal the specimens were fractured into two or more pieces and mounted for examination of exposed bubble populations by scanning electron microscopy. In some instances the fracturing procedure was carried out within a sealed chamber so that the fission gas evolved during fracture could be collected and analyzed.

Fracture pieces of some specimens were metallographically polished, and the polished surfaces were examined by optical microscopy as well as by scanning electron microscopy. Finally, certain specimens, after examination by SEM, were reirradiated at ambient temperature, refractured, and then examined again by SEM to determine the effect of irradiation on gas-bubble distributions.

Results of SEM and OM Examinations of UC. The microscopic examination of fractured and polished UC surfaces produced three general observations. First, no pores could be detected in unheated samples of either irradiated or unirradiated UC. Second, pores were observed in all annealed samples of UC, whether irradiated or not. Thus, heat treatment of the UC is crucial to development of detectable porosity by these examination techniques. Finally, it was observed that fracture characteristics of the UC varied somewhat but appeared to be independent of irradiation or annealing conditions. With one or two exceptions, the fracture patterns were predominantly transgranular rather than intergranular.

Pore counts in fracture specimens were recorded during SEM examinations from traverses across the surfaces, or from photographs of typical surface areas. Pore surface concentrations were computed from the results. Pore size distribution analyses were obtained, where possible, from the photographs also. For polished specimens an optical particle size analyzer was used to determine the pore size distribution and pore surface concentrations. Pore volumetric concentrations were calculated using the simple relationship, $C = (S)^{3/2}$, where C is the volumetric concentration and S is the surface concentration. A summary of these analyses is presented in Table B-16.

Inspection of Table B-16 suggests several general observations, but also indicates some anomalies in the results. Pore concentrations for the unirradiated UC seem to be about 10^5 cm^{-3} , while for irradiated material having exposures in excess of 10^{15} fissions per cm^3 , apparent pore concentrations range from about 10^6 to 10^9 cm^{-3} . Therefore, irradiation seems to result in the formation of more pores, which is to be expected if the pores are, indeed, fission-gas bubbles. The pore concentration also tends to increase with irradiation exposure, but variations in the data do not allow derivation of a functional relationship. Average pore radii appear to decrease as pore concentrations increase, and neither the concentration nor the size of pores appears to be a strong function of the annealing conditions used. These observations are consistent with the behavior expected of a precipitation process that has neared completion. Such behavior should be considered a necessary but not a sufficient condition for proof that the majority of the pores are fission-gas bubbles. Finally, it may be noted that at higher concentrations the pore distributions were not randomly dispersed but rather localized either in the form of stringers, along grain boundaries, or perhaps in clumps. This implies that the mechanism of growth of bubbles is primarily heterogeneous rather than homogeneous.

Since the reported pore distributions are relatively stable, which suggests that no new bubbles are forming and, hence, that precipitation is nearing completion, it is of interest to assume that the pores contain all the fission gas in the specimens and to

TABLE B-16. RESULTS OF SEM AND OM PORE ANALYSIS STUDY FOR UC

Specimen	Irradiation Exposure, fissions per cm ³	Annealing Conditions		Pore Concentration ^(a) , cm ⁻³	Average Pore Radius, μ	Specimen Type	Examination Method	Notes
		Temperature, C	Time, hr					
1	None	1700	25	(10 ⁴)	~1	Fracture	SEM	Pores randomly dispersed
2	None	1700	24	3 x 10 ⁴	--	Polished	SEM	Pores randomly dispersed
3	None	1700	24	5 x 10 ⁵	0.7	Polished	OM	Pores randomly dispersed
4	6 x 10 ¹³	1700	30	(10 ⁴)	0.5	Fracture	SEM	Pores randomly dispersed
5	4 x 10 ¹⁵	1700	25	10 ⁶ to 10 ⁷	0.3	Fracture	SEM	Pores aligned in stringers
6	4 x 10 ¹⁵	1700	9	10 ⁶ to 10 ⁷	0.1	Fracture	SEM	Pores aligned in stringers
7	1 x 10 ¹⁶	1700	24	2 x 10 ⁵	1.4	Fracture	SEM	Pores randomly dispersed
8	1 x 10 ¹⁶	1700	24	2 x 10 ⁶	0.9	Polished	OM	Pores aligned in stringers
9	1 x 10 ¹⁶	1700	24	7 x 10 ⁵	--	Polished	SEM	Pores aligned in stringers
10	4 x 10 ¹⁷	1700	29	10 ⁷ to 10 ⁸	0.27	Fracture	SEM	Pores aligned in stringers
11	4 x 10 ¹⁷	1700	29	5 x 10 ⁷	0.24	Polished	SEM	Pores aligned in stringers
12	4 x 10 ¹⁷	1700	29	6 x 10 ⁶	0.50	Polished	OM	Pores concentrated at grain boundaries
13	4 x 10 ¹⁷	1700	6	10 ⁹	0.41	Fracture	SEM	Pores concentrated at grain boundaries; high incidence of intergranular fracture
14	4 x 10 ¹⁷	1400	31	10 ⁹	0.2	Fracture	SEM	Pores aligned in stringers
15	4 x 10 ¹⁷	1400	15	10 ⁹	0.1	Fracture	SEM	Pores aligned in stringers
16	4 x 10 ¹⁵	1400	25	10 ⁷	0.5	Fracture	SEM	Pores localized in clumps
17	4 x 10 ¹⁵	1400	9	10 ⁷	0.5	Fracture	SEM	Pores localized in clumps

(a) Values in parentheses are estimates because data were limited.

compute the corresponding gas-bubble internal pressures. Such calculations were performed for Specimens 10, 11, 12, and 13 from Table B-16 using the listed pore concentrations and average radii in the ideal gas equation. The resulting gas-pressure estimates are compared in Table B-17 with gas pressures that are predicted from the equilibrium surface tension relationship: $P = 2\gamma/r$, where γ is the surface tension of UC (estimated at 1000 dynes per cm) and r is the gas-bubble radius. Except for Specimen 13, the assumption that all fission gas is contained in the observed pores leads to internal gas pressures much greater than can be accounted for by simple surface-tension restraint. For Specimen 13, the apparent agreement is considered fortuitous because the pore concentration used is believed to be erroneously high. The high incidence of intergranular fracture in this specimen combined with the observed predominance of pores at the exposed grain-boundary faces caused a gross overestimate of the volumetric pore concentration. This conclusion is supported by the lower pore counts obtained from the other specimens of the set for two reasons. First, although the annealing time for these samples was greater, no pore digestion or agglomeration apparently occurred because the measured pore sizes were either the same or smaller in Specimens 10, 11, and 12 than in Specimen 13. Second, the microscopic examination of these samples was performed on polished or fracture surfaces that were predominantly transgranular in cross section, thus giving a more representative record of the bulk pore concentration.

TABLE B-17. CALCULATED GAS-BUBBLE PRESSURES

Specimen	Gas Pressure Predicted Using Indicated Equation, atm	
	Ideal Gas Equation	Surface-Tension Equation
10	3×10^4 to 3×10^3	7×10^1
11	9×10^3	8×10^1
12	8×10^3	4×10^1
13	9×10^1	5×10^1

Clearly, the results shown in Table B-17 require some explanation. Two possible explanations can be advanced. The first involves the assumption that the observed pores contain nearly all the fission gas in the specimen. If so, then a restraining force much greater than the estimated surface-tension force must be operating to prevent bubble growth. Since it is doubtful that the uncertainty in the surface-tension value used is sufficient to account for the necessary force, the extra restraint would have to be supplied by the strength of the UC matrix. Creep data for UC at 1700 C show that it does not possess the required strength to support such pressures for long times(2).

The second explanation for the anomaly makes the usual assumption that surface tension constitutes the primary restraining force on gas bubbles that have grown to their equilibrium size. This assumption then requires that the observed pores not contain all the fission gas and that most of the gas be really contained in bubbles that were too small to be detected by the examination techniques used. Since the SEM technique had a resolution limit of about 500 A, this explanation would require a large population of bubbles having diameters below 500 A. The most probable location for this "invisible" bubble distribution would be within the UC grains themselves since the examination already detected the bubble distribution that forms at grain boundaries. The bubbles in grain boundaries should be larger as a result of the expected greater mobility of gas atoms and the greater availability of vacancies in the boundaries relative to the grain lattice.

The number of bubbles formed at UC₂ platelets within UC grains as opposed to the number of bubbles formed elsewhere within UC grains is believed to depend upon the

presence of UC_2 , which is a strong function of composition and temperature. For the specimens used in this study, the uranium-carbon phase diagram shows that UC and UC_2 begin to form a solid solution and have appreciable mutual solubility at temperatures above about 1500 C⁽³⁾. Therefore, much less UC_2 should have been present during the anneals at 1700 C than during the anneals at 1400 C, and less heterogeneous growth of bubbles (observed as bubble stringers) would be expected in these specimens. The indication of lower pore concentrations (resolvable bubbles) in specimens annealed at 1700 C relative to those annealed at 1400 C (at equivalent fission exposures) tends to confirm this prediction. Thus, in the specimens annealed at 1700 C, the bulk of the fission-gas inventory should be precipitated as tiny, unresolved bubbles in the UC.

Reirradiation Effects on Bubbles in UC. Several of the specimens listed in Table B-16 (specifically, Specimens 5, 10, 13, 14, and 16) were encapsulated and irradiated a second time to investigate the effects of fission events on the observed pore distributions. An exposure of 6×10^{15} fissions per cm^3 was selected, since earlier work⁽⁴⁾ (based on gas-release experiments) had indicated that this exposure should cause re-resolution of over 90 percent of the precipitated fission gases. However, when these specimens were recovered and examined by SEM again, no change in pore size, shape, or number was detectable. Therefore, by inference, the reirradiation apparently had no effect on the fission-gas precipitate phase and the new results seemed to contradict the earlier re-resolution measurements. However, the earlier measurements had incorporated annealing temperatures of 1600 and 1700 C to induce fission-gas precipitation prior to reirradiation, and it was postulated above that at these temperatures most of the fission gas does not collect in the large pores but rather in tiny homogeneously dispersed bubbles. If so, then reirradiation would not necessarily have much effect on the large pores but could cause extensive re-resolution of the tiny bubbles.

To evaluate this hypothesis, six specimens of UC were irradiated to 6×10^{15} fissions per cm^3 . These were separated into two groups of three, and one specimen from each group was then fractured in a sealed chamber so that liberated fission gas could be collected for analysis. The other two unfractured specimens from each group were annealed for 24 hr at 1600 C to produce fission-gas bubbles, whereupon one of the two annealed specimens from each group was also fractured in the sealed chamber. The sole remaining annealed and unfractured specimen from each group was reirradiated, again to 6×10^{15} fissions per cm^3 , and the fission gas liberated during subsequent fracture was also measured. After the fission-gas analyses obtained from fracturing were normalized for variations in fracture surface area and after appropriate corrections were made for radioactive decay, the results revealed that roughly 100 times more gas was liberated by fracture of the annealed specimens than from the unannealed specimens following the first irradiation. This result is considered to be confirmation that annealing caused precipitation of fission gas into some macroscopic bubbles (probably no larger than 20 Å in radius). That is, fractures in the annealed specimens intersected small fission-gas bubbles, and release from these bubbles was 100 times greater than the release that occurred from the unannealed specimens containing an equivalent concentration of more finely dispersed fission-gas atoms. It was further observed that reirradiation caused a definite reduction in the quantity of gas liberated during fracturing of previously annealed specimens. The degree of reduction corresponded to a fission re-resolution fraction of 0.1 to 0.5. This result, while showing less apparent re-resolution than expected, tends to support the re-resolution measurements, and thus supports the suggestion that most of the fission gas in UC may be contained in very small bubbles.

In summary, the experiments and results described above lead to the conclusion that at least two distinct fission-gas-bubble distributions are generated when neutron-activated UC is annealed at sufficiently high temperatures. One distribution has a mean bubble size much larger than the other and these larger bubbles seem to be most frequently located along grain boundaries. They are also apparently not affected by further

neutron activation. While not directly observed, it is postulated that the second distribution, which involves a much greater number of bubbles, is mainly homogeneously dispersed within the grains. This distribution may be severely affected by further neutron activation. Also, under certain annealing and material-composition conditions, it is suggested that fission-gas precipitation may occur preferentially at the UC_2 platelets in hyperstoichiometric UC.

Results of UO_2 Studies. Limited studies of bubble precipitation during postirradiation annealing were also conducted for UO_2 . These were deemed necessary in light of the gas-diffusion data obtained by Cornell⁽¹⁾, which predict low rates of fission-gas diffusion relative, for example, to UC at comparable temperatures⁽⁵⁾. In this experiment, a single crystal of nearly stoichiometric UO_2 (provided by Battelle-Northwest) was neutron activated to 1×10^{17} fissions per cm^3 and subsequently annealed for 24 hr at 1700 C. An unactivated control specimen (cut from the same crystal as the one that was subsequently activated) was given an identical heat treatment. Both heat treatments were conducted in a helium atmosphere (1 atm pressure) in order to retard vaporization from the specimen surface.

Following heat treatment, both specimens were fractured, and the fracture surfaces were examined by means of SEM. Some photomicrographs characteristic of a fracture surface of the control specimen are shown in Figure B-50. The white "specks" distributed over the surface are believed to be simply debris. The interesting morphological features are the collections of faceted voids found on the fracture surfaces. Each collection appears to be made up of one large void surrounded closely by a system of smaller voids. There were roughly 10^5 to 10^6 such collections per cm^3 . The regions between the collections were free of voids, at least at the SEM magnifications. It can be seen from Figure B-50 that the voids influenced the fracture behavior in their vicinity.

One tentative explanation that has been put forth⁽⁶⁾ to explain the presence of these voids follows. Purification work on the single crystals included a heat treatment in moist hydrogen at 1750 C in order to eliminate small inclusions, assure stoichiometry, and make the material less brittle. Combination of hydrogen with carbon, present as an impurity (the latter is assumed to be a chemical constituent of the small inclusions), could have left pores filled with methane at the inclusion sites. Hence, each collection of pores may represent the former site of one second-phase precipitate particle. The spatial configuration of the pores within each collection would have been determined by the rate of size reduction of the associated inclusion and the nucleation and growth kinetics of the porosity.

Sample photomicrographs of a fracture surface of the activated specimen are shown in Figure B-51. A detailed examination of the specimen surface revealed no new pores that could be positively identified as fission-gas bubbles, although the same kinds of collections of voids present in the control specimen were also found in the activated specimen, as illustrated in Figure B-51. Assuming that the smallest bubbles that could possibly have been seen at the highest magnification (20,000X) employed would have been about 200 Å in diameter (probably 500 Å is a more realistic assessment of the resolution that was actually obtained), it is concluded that any fission-gas bubbles present in the activated specimen had to have been quite small, with radii less than or equal to about 100 Å. Observations of defects this small would require a more refined method of examination, such as a replication technique, or transmission electron microscopy.

One piece of information that can be gleaned from this limited work is an estimate for the upper limit of the fission-gas diffusion coefficient in UO_2 at 1700 C. This was calculated from the fact that the maximum possible radius of any precipitated bubble was about 100 Å (just beyond the resolution limit of the scanning electron microscope), and by assuming that only a very small fraction of the total amount of fission gas had precipitated into bubbles during the anneal. This assumption removes all dependence of

1000X

S2725

a. Lower Magnification

10,000X

S2724

b. High Magnification

FIGURE B-50. SEM VIEWS OF FRACTURE SURFACE OF CONTROL UO_2 SPECIMEN
AFTER ANNEALING FOR 24 HR AT 1700 C

1,000X

S2737

a. Lower Magnification

10,000X

S2736

b. High Magnification

FIGURE B-51. SEM VIEWS OF FRACTURE SURFACE OF ACTIVATED UO_2 SPECIMEN AFTER ANNEALING FOR 24 HR AT 1700 C

bubble growth rate, during the heat treatment, upon the overall bubble concentration, since the effects of bubble "competition" for the dissolved gas are evidenced only as the amount of unprecipitated gas becomes reduced. An approximate expression for the rate of growth of a gas bubble, assuming gas-diffusion-controlled conditions, quasistationary gas diffusion, and a modified van der Waals equation of state for the gas within the bubble, has been developed⁽⁷⁾ and it was used in this calculation. On the basis of these assumptions, it was calculated that, under the given conditions of gas concentration and heat-treatment time and temperature, a diffusion coefficient of roughly $9 \times 10^{-13} \text{ cm}^2$ per sec would be required to precipitate bubbles of 100 Å radius. This may be compared, for example, with the value $1.7 \times 10^{-14} \text{ cm}^2$ per sec obtained by extrapolating Cornell's diffusion data⁽¹⁾ to 1700 C.

Plans for Future Work

During the next year a limited study will be directed at producing fission-gas bubbles that are observable by SEM techniques in postirradiation heated UO_2 . Samples of single-crystal UO_2 will be irradiated to near 10^{18} fissions per cm^3 and then heated out-of-pile for extended times to generate larger gas bubbles than have been produced previously. Results of SEM examination of these samples will be combined with bubble growth theory to obtain fission-gas diffusivity estimates. These diffusivities will be compared with values obtained from postactivation release studies.

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Gas-Bubble Nucleation and Growth

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Objective of Program

To describe the growth of fission-gas bubbles in nuclear fuels in terms of atomic diffusion processes, and thereby to predict the swelling and gas-release behavior of the fuels.

Approach Being Used

The growth of inert-gas bubbles resulting from the coupled influx of gas atoms and lattice vacancies is being investigated in solids. Analytical and numerical models, which take into account such parameters as nonuniformity of bubble size, gas diffusivity and solubility in the fuel, and the self-diffusivity of the fuel, are being developed for both the postirradiation and in-pile cases. The validity of the models is tested by comparison with bubble-growth and fuel-swelling data accumulated as another part of the program.

Significant Accomplishments During Fiscal Year 1970

Computer simulations of bubble precipitation in lightly irradiated UC, during postirradiation annealing at 1400 and 1700 C, have been analyzed in the light of experimental data gathered under comparable conditions⁽¹⁾. The most favorable comparison

with experimental data was found using, in combination, the gas diffusion data of Ritzman, et al. (2), and the self-diffusion data (for uranium in UC) of Lee and Barrett(3). The simulations showed that the restraint to bubble growth offered by the UC matrix could be an important, and at times the dominant, factor.

Analogous simulations of bubble precipitation in UO_2 , under similar conditions, have predicted much lower rates of bubble growth, due to correspondingly lower rates assumed for gas diffusion. These predictions are consistent with preliminary experimental studies of lightly irradiated and annealed UO_2 (1).

An analytical model(4), which describes the in-pile precipitation of fission-gas bubbles under conditions where precipitation might be assumed to be controlled by the diffusion of fission gas and which assumes a uniform size distribution of bubbles, was used to simulate bubble precipitation in UO_2 . It was shown that, because of the assumed low rates of gas diffusion in the UO_2 matrix, the UO_2 could become extensively supersaturated with fission gas during irradiation. In addition, swelling was found to be highly sensitive to temperature, primarily as a result of a large activation energy for fission-gas diffusion.

A computer program developed during the fiscal year simulates in-pile bubble precipitation under a relatively general set of conditions. The initial application of this program was to evaluate parametrically the effect of self-diffusion upon UO_2 swelling kinetics. It was found that self-diffusion plays an important role; thus, a need exists for experimental studies to more clearly define self-diffusion rates and, by inference, the kinetics of vacancy transport to the sites of gas bubbles in UO_2 .

Summary of Research Carried Out

Out-of-Pile Bubble Growth in UC. As part of another program(1), experiments were carried out in which gas-bubble distributions in lightly irradiated and annealed UC were analyzed by means of scanning-electron and optical microscopy. Computer simulations of bubble precipitation during several of these anneals were carried out using the computer program(5) developed to describe the out-of-pile growth of stationary gas bubbles resulting from the coupled volume diffusion of gas atoms and lattice vacancies.

All the simulations of out-of-pile growth were characterized by the following set of initial conditions: (1) a given size distribution of bubbles, ranging between 60 and 400 Å in radius; (2) the gas pressure in all the bubbles assumed to be equal to the surface-tension restraint. (This choice of initial conditions did not control the precipitation kinetics after significant further precipitation had occurred.) The temperature, bubble concentration, and total gas concentration were taken to correspond to values employed or measured on the above-mentioned experimental program(1). Obviously, these simulations bypass the bubble nucleation stage and consider only the growth of existing small bubbles by the precipitation of gas from solution in the UC. In addition, the equilibrium solubility of the fission gases in the fuel was taken to be zero.

In Figure B-52, the results are shown for three trial simulations of bubble growth in UC. These simulations assume a bubble concentration of 10^8 per cm^3 , a gas concentration of 10^{17} atoms per cm^3 , and three sets of gas-diffusion and self-diffusion data (the latter being for uranium in UC). The three trial sets of diffusion data used, at the assumed temperature of 1700 C, are tabulated below in units of cm^2 per sec:

Set	Xenon Diffusion in UC	Uranium Self-Diffusion in UC
I	8.2×10^{-10} , Reference (2)	2.5×10^{-11} , Reference (3)
II	8.2×10^{-10} , Reference (2)	1.9×10^{-14} , Reference (6)
III	9.5×10^{-13} , Reference (7)	2.5×10^{-11} , Reference (3)

FIGURE B-52. COMPUTER SIMULATION OF BUBBLE PRECIPITATION IN LIGHTLY IRRADIATED UC DURING HEAT TREATMENT AT 1700 C

All curves were drawn assuming a gas-atom concentration of $1 \times 10^{17} \text{ cm}^{-3}$, a bubble concentration of $1 \times 10^8 \text{ cm}^{-3}$, and diffusion data for the set indicated. The open circle and triangle represent data on bubble radii for the specimens indicated⁽¹⁾.

The triangular data point in Figure B-52, the observed mean radius of bubbles in Specimen 13⁽¹⁾, is related to bubbles observed principally on grain boundaries and hence cannot be strictly interpreted in terms of volume diffusion processes. Since the radius of bubbles in Specimen 10, represented by the open circle in Figure B-52, is related principally to bubbles growing within grains, this data point serves as a better basis for comparison with the model. It is evident from the figure that the data on bubble radii corresponding to Set I predict growth much faster than that actually observed, whereas those corresponding to Set III predict growth that is much too slow. On the other hand, those corresponding to Set II appear to give an excellent correlation with the observed mean radius. However, a closer examination of the latter trial simulation shows that the apparently good agreement actually does not exist. For example, it can be seen from the above tabulation that gas diffusion for Set II is greater than self-diffusion (as measured by the respective diffusion coefficients at 1700 C) by more than four orders of magnitude. Therefore, it might be suspected that very large gas pressures would be established within the bubbles during the heat treatment. Indeed, an analysis of the computer output for Set II showed that physically unrealistic pressures would have been established within the fuel matrix at 1700 C (in excess of 2000 atm) as a result of the sluggish response of the fuel to gas buildup within bubbles. Thus, the preliminary conclusion is forced that none of the three trial sets of diffusion data gives an acceptable description of the observed growth kinetics. A logical explanation for this apparent anomaly is given below following the discussion of further trial simulations. This explanation favors the diffusion data of Set I.

Consider next the trial simulations and the experimental data on Specimen 14 illustrated in Figure B-53. The gas diffusion data of Ritzman, et al.⁽²⁾, and the self-diffusion data of Lee and Barrett⁽³⁾ were used in these calculations. (These correspond to Set I of the above table, except for changing the diffusion rates to correspond to a temperature of 1400 C rather than 1700 C.) Obviously, the correlation between the trial simulations and the experimental data is quite good. The effect of an order-of-magnitude variation in the assumed bubble concentration is also illustrated in the figure.

Figure B-54 shows the variation with time at 1400 C of the gas pressure within a given bubble in one of the trial simulations of Figure B-53 (i.e., that for which the bubble concentration was $1 \times 10^9 \text{ cm}^{-3}$). The variation of the Laplace pressure (i.e., that resulting from surface-tension restraint) is also shown. The restraint to bubble growth offered by the UC matrix is equal to the total pressure minus the Laplace pressure and is seen to be significant, and the pressures that are established within the matrix are considered to be physically reasonable. It thus appears that this trial set of diffusion data does, indeed, provide an adequate simulation of experimental conditions. Had the data corresponding to Sets II or III (extrapolated to 1400 C), been used, bubble growth would have been much too slow.

The question remains as to why the combined data (Set I) of Ritzman, et al.⁽²⁾, and Lee and Barrett⁽³⁾, which provide a physically acceptable simulation of bubble precipitation at 1400 C, and also one that agrees with the experimental data, do not agree with the experimental data at 1700 C shown in Figure B-52. Since the model does not appear faulty, the answer probably lies with the experimental data; in particular, with the bubble concentration associated with Specimen 10, which appears to have been underestimated and was subsequently used in calculating the curves shown in Figure B-52. This conclusion is consistent with Table 2 of Reference (1), from which it can be found that, for Specimen 10, the calculated number of gas atoms per bubble and, hence, bubble pressures are unreasonably high for the observed bubble sizes. If a significantly larger number of bubbles than 10^8 per cm^3 had been observed in Specimen 10 and if this larger bubble concentration had been used in calculating the curves shown in Figure B-52, then all the curves would be displaced downward (see Figure B-53, for example). As a result of such displacement, the curves of Set I would show improved

FIGURE B-53. COMPUTER SIMULATION OF BUBBLE PRECIPITATION IN LIGHTLY IRRADIATED UC DURING HEAT TREATMENT AT 1400 C

All curves were drawn assuming a gas-atom concentration of $1 \times 10^{17} \text{ cm}^{-3}$, gas diffusion coefficient via Ritzman, et al. (2), and self-diffusion coefficient via Lee and Barrett (3). The shaded circle represents data on bubble radii for Specimen 14 (1).

agreement with the bubble radius measurements obtained on Specimen 10. This is consistent with a conclusion of the preceding section⁽¹⁾ to the effect that the bulk of the gas is precipitated as unresolved bubbles in the UC at 1700 C at these burnups.

FIGURE B-54. VARIATION WITH TIME OF THE RADIUS, TOTAL PRESSURE, AND LAPLACE PRESSURE ASSOCIATED WITH A GIVEN BUBBLE AT 1400 C

The bubble is from the distribution corresponding to the solid curves in Figure B-53.

To illustrate the strong effect of temperature upon bubble precipitation kinetics, two trial simulations are shown in Figure B-55 that differ only with respect to the assumed temperature (1400 and 1700 C). As it should, the model predicts that bubbles grow much more rapidly at 1700 C than at 1400 C.

On the basis of these studies, a number of observations can be made. Bubble precipitation in lightly irradiated UC during postirradiation heat treatment at 1400 and 1700 C can be adequately accounted for by the diffusive influx of gas atoms and lattice vacancies into stationary bubbles. Physically acceptable simulations which give closest agreement with experimental data are found using, in combination, the gas diffusion data of Ritzman, et al.⁽²⁾, and the self-diffusion data of Lee and Barrett⁽³⁾. The UC matrix offers considerable restraint to bubble growth, so that precipitation cannot, in general, be assumed to be controlled by gas diffusion.

Out-of-Pile Bubble Growth in UO₂. Some of the most recent data for fission-gas diffusion in UO₂ have been obtained by Cornell⁽⁸⁾. Trial simulations of bubble precipitation in lightly irradiated UO₂ have been carried out using the computer program⁽⁵⁾ and Cornell's data, and assuming conditions of gas concentration, bubble concentration, and temperature corresponding to those used in the UC simulations. Data for the self-diffusion of uranium in UO₂ were taken from the literature. As a result of the relatively low rates of gas diffusion predicted by Cornell's data, the precipitation of bubbles in UO₂ was found, correspondingly, to occur very slowly. This agrees qualitatively with the results of preliminary experimental studies⁽¹⁾ of bubble precipitation in lightly irradiated UO₂. Plans have been made for the continuation of both the experimental studies and the simulations.

FIGURE B-55. EFFECT OF TEMPERATURE ON BUBBLE PRECIPITATION KINETICS IN LIGHTLY IRRADIATED UC

All curves were drawn assuming a gas-atom concentration of $1 \times 10^{17} \text{ cm}^{-3}$, a bubble concentration of $1 \times 10^9 \text{ cm}^{-3}$, a gas-diffusion coefficient via Ritzman, et al. (2), and a self-diffusion coefficient via Lee and Barrett(3).

In-Pile Bubble Growth. A simplified analytical model for in-pile bubble growth has been developed and reported in the literature⁽⁴⁾. This model assumes conditions such that bubble precipitation is controlled by fission-gas diffusion to bubbles of a uniform size distribution. The model has been successfully used to predict the general temperature dependence of swelling of UC and, in particular, the abrupt onset of fission-gas swelling at roughly one-half the absolute melting temperature (at a given burnup). In this fiscal year, the model was used to simulate the in-pile swelling of UO_2 , at various temperatures, using Cornell's gas diffusion data; the results are shown in Figure B-56. A strong dependence upon temperature was found, mainly due to the large activation energy for fission-gas diffusion in UO_2 (i.e., 91 kcal per mole). As a result of the relatively low rates of fission-gas diffusion predicted by Cornell's data, the model shows little swelling of UO_2 (for the conditions indicated in Figure B-56), at burnups below about 3×10^{20} fissions per cm^3 at temperatures of 1400 C or lower. Consequently, it is possible for the UO_2 matrix to become highly supersaturated with fission gas. For example, for the curve shown in Figure B-56 corresponding to 1400 C, the concentration of dissolved gas attains a maximum value of about $0.9 \times 10^{20} \text{ cm}^{-3}$ at 1.28×10^7 sec into the irradiation. Of course, this calculation does not take into account any nucleation of new bubbles over and above 10^{12} bubbles per cm^3 that may actually occur as these large concentrations of gas are generated. The calculation also does not take into account the increasing matrix restraint to swelling that takes place as temperature decreases below 1700 C.

FIGURE B-56. SIMULATED IN-PILE SWELLING OF UO_2

The curves are based on an analytical treatment⁽⁴⁾ of gas-diffusion-controlled growth kinetics, together with the following parameters: bubble concentration = $1 \times 10^{12} \text{ cm}^{-3}$, fission rate = 4×10^{13} fissions/(cm^3)(sec), UO_2 surface tension = 10^3 dyne per cm, and fission-gas diffusion data via Cornell⁽⁸⁾.

In order to more closely simulate the actual in-pile growth kinetics of fission-gas bubbles, a computer program was developed during FY 1970 which, at present, is analogous to the program already in use describing out-of-pile growth kinetics. The principal difference is that the total fission-gas concentration remains constant in time

for the out-of-pile case and increases linearly with time for the in-pile case (neglecting any effects of gas release, for the present).

This program was used to simulate bubble precipitation in UO_2 at 1700 C. The bubble concentration was taken to be 10^{12} cm^{-3} , and the bubbles were assumed to range in radius from 10 to 30 A initially. The gas concentration in the fuel plus that in the bubbles was assumed initially to be $1 \times 10^{17} \text{ cm}^{-3}$, so that on the basis of the assumed gas generation rate of $1 \times 10^{13} \text{ atoms}/(\text{cm}^3)(\text{sec})$, i. e., a fission rate of $4 \times 10^{13} \text{ fissions}/(\text{cm}^3)(\text{sec})$, the trial simulation was caused to begin 10^4 sec into the irradiation.

Two trial simulations were carried out, both using the gas diffusion data of Cornell extrapolated to 1700 C ($D_{\text{Xe}} = 1.7 \times 10^{-14} \text{ cm}^2 \text{ per sec}$). One of these trials used the self-diffusion data of Auskern and Belle⁽⁹⁾ ($7.6 \times 10^{-14} \text{ cm}^2 \text{ per sec}$ at 1700 C) and the other used the self-diffusion data of Reimann and Lundy⁽¹⁰⁾ for uranium in UO_2 ($8.6 \times 10^{-16} \text{ cm}^2 \text{ per sec}$ at 1700 C). Hereafter, the former simulation will be termed "A", and the latter, "B". The results are shown in Figure B-57, from which a number of general deductions can be made: (1) as expected, the swelling, at any given instant, is greater for the larger self-diffusion coefficient; (2) decreasing the self-diffusion coefficient has the effect of retarding the precipitation of gas into bubbles; and (3) as precipitation proceeds, the supersaturation of gas (the saturation level assumed here to be zero) increases to a maximum value, and then decreases with time. The latter observation is in accord with other studies^(4, 11) and also is analogous to behavior observed in chemical reactions in which precipitation occurs in the presence of a generating process⁽¹²⁾.

Also shown in Figure B-57, for purposes of comparison, is the swelling curve that would be obtained under the assumed conditions of temperature, bubble concentration, and gas generation rate plus the assumptions that: (1) the bubble size distribution is uniform; (2) the gas pressure is maintained equal to the surface tension restraint; and (3) gas diffusion occurs "infinitely" fast. Under these conditions, bubble precipitation is controlled solely by the rate of gas generation. Thus, the assumption of finite, realistic rates of gas diffusion and self-diffusion leads to significantly reduced swelling even at 1700 C.

The most important knowledge to be drawn from Figure B-57 is the fact that the self-diffusion rate selected has a pronounced effect upon bubble growth in UO_2 under irradiation. For example, it is found that at $t = 5 \times 10^6 \text{ sec}$ (burnup $\approx 2 \times 10^{20} \text{ fissions per cm}^3$), the swelling is about 20 v/o for Simulation A, and less than 4 v/o for Simulation B. Correspondingly, for most of the irradiation, the restraint offered by the matrix was significantly greater for Simulation B than for Simulation A. In fact, for Simulation A, the predominant restraint to bubble growth was provided by the UO_2 surface tension (assumed here to be $1000 \text{ erg per cm}^2$), whereas for Simulation B, the matrix restraint was greater than the surface tension restraint for most of the irradiation.

It is interesting to note, from Figure B-57, that at times of the order of $2.5 \times 10^6 \text{ sec}$ (burnup $\approx 1 \times 10^{20} \text{ fissions per cm}^3$) the predicted swelling is about 7 v/o for Simulation A and about 1 v/o for Simulation B. When these results are compared with UO_2 swelling data at 1700 C⁽¹³⁾ it is found that the former simulation appears generally to correlate better with experiment than the latter. Of course, all the simulations were based on an assumed bubble concentration of $1 \times 10^{12} \text{ cm}^{-3}$, and any alteration of this assumption would affect the predicted swelling correspondingly.

What these in-pile simulations demonstrate most vividly is that, in order for bubble growth in UO_2 (or any other fuel, for that matter) to be properly understood and evaluated, the manner in which vacancies are transported to bubbles must be pinpointed more precisely. The existing data obviously predict widely differing rates of transport; what is needed now is an understanding of the possible mechanism of vacancy transport within the matrix and of the respective contributions of these mechanisms to bubble growth.

FIGURE B-57. COMPUTER SIMULATION OF IN-PILE SWELLING OF UO_2 AT 1700 C

These curves were drawn assuming a bubble concentration of $1 \times 10^{12} \text{ cm}^{-3}$, a gas generation rate of $1 \times 10^{13} \text{ atoms/(cm}^3 \text{ sec)}$, and an initial gas-atom concentration of $1 \times 10^{17} \text{ cm}^{-3}$. Gas-diffusion data via Cornell⁽⁸⁾ were used for both simulations. The hatched curve illustrates the hypothetical case in which gas generation is the rate-limiting process.

Plans for Future Work

Computer simulations of bubble growth in lightly irradiated UO_2 , during postirradiation heat treatment, will be continued in support of experimental work in this area⁽¹⁾. These combined studies are aimed toward increased understanding of the kinetics of bubble growth in UO_2 .

The computer program describing the in-pile growth of gas bubbles will be expanded in a number of directions. First, it is well known that vacancy concentrations within a fuel under irradiation can be well in excess of those characterizing thermal equilibrium. This essentially gives rise to a mechanism for irradiation-enhanced creep, and the program will be extended in an attempt to include this phenomenon. Second, the behavior of very small bubbles can be more realistically described by a van der Waals equation of state than by the perfect gas law, and the program will be correspondingly modified.

To more realistically account for the in-pile behavior of oxide fuels, the effect upon bubble-precipitation kinetics of periodic sweeping of bubbles by moving lenticular pores will be evaluated. Results obtained from another program⁽¹⁴⁾ will be of value here.

At every stage of expansion, the model will be tested, via parameter studies, regarding its predictions for fuel swelling under various sets of conditions. The model proposed here should provide a physically realistic simulation of the in-pile behavior of fission-gas bubbles in nuclear fuels, and will include a variety of irradiation parameters. The gap in understanding between macroscopically observed fuel swelling and the atomistic processes responsible for this swelling will thereby be considerably reduced.

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- (13) Hilbert, R. F., Storhok, V. W., and Chubb, W., *Trans. Am. Nucl. Soc.*, 13, 132 (1970). Also see Figure B-5 of the section of this report entitled "Irradiation Behavior of Oxide Fuels at High Temperatures".
- (14) See the following section of this report entitled "Mechanisms of Bubble Migration".

Mechanisms of Bubble Migration

J. B. Brown, Jr., W. Oldfield, and R. A. Wullaert

Objective of Program

To replicate, out-of-pile, the major qualitative and quantitative features of lenticular voids and columnar grains which characterize the response of certain fuels to irradiation.

Approach Being Used

A temperature gradient will be produced in ceramic fuels by laser-beam heating one surface of the specimen and cooling the opposite surface. Temperatures are to be defined or measured in at least three positions: (1) at a solid-liquid interface position near the point where power is applied to the specimen; (2) at an intermediate position near the point where power is applied to the specimen; and (3) at the cooled surface where temperatures are fixed in the present apparatus by the water temperature. The temperature profile will then be calculated using a one-dimensional heat flow code calibrated by the temperature measurements. Containment of the specimen will be provided by a stainless steel vessel.

Oxide fuels doped with various impurities and impurity concentrations will be heated in this apparatus, and an attempt will be made to cause bubbles to move. The velocity of any bubbles that move will be measured, the distribution of impurities in the grains that form will be determined, and the observations will be compared with the predictions of a computer simulation of the process of bubble migration.

Significant Accomplishments During Fiscal Year 1970

A theoretical model of bubble migration has been developed incorporating interface kinetic terms, surface energy, and impurity partitioning in addition to bulk diffusion. This model has been incorporated into a computer simulation designed to reproduce bubble shape. Although the simulation can model the interaction of the system of processes, it can also be used to highlight the influence of individual processes. The most striking effects noted were due to attachment kinetics and impurity segregation. When interface kinetic terms were included in the model, the bubble became flat and lens-shaped. When impurity effects were incorporated, the tips dropped backwards (in the direction of lower temperatures). These features are characteristic of the real shape of migrating bubbles, and they were ignored in previous theoretical studies of bubble shape.

The theoretical work has been backed by an experimental study. A laser image furnace has been developed to produce large temperature gradients and high surface temperatures in ceramic specimens. This apparatus has been used to study migration rates and bubble shapes. The results support the theoretical model. It was found that only a small part of the driving force for migration (provided by the temperature gradient) was utilized in driving diffusion. Other phenomena, such as facet formation, proved to be much more important.

Summary of Research Carried Out

A computer simulation of a migrating bubble was developed. This model describes a succession of closely spaced points in space at which there is a balance between the various thermodynamic components. Free energy is required to drive atomic attachment (this is dependent upon the crystal index of the surface), to overcome curvature effects, to drive diffusion, and to overcome segregation effects. This free energy is equal to that provided by the temperature gradient at each point.

One forecast of bubble shape made by the simulation is shown in Figure B-58. The surface curvature is mainly a consequence of kinetic factors related to the crystallographic index of the surface. The drooping "tails" of the bubble result from partitioning of impurities; the bubble migration can be seen as analogous to cellular solidification. Facets have been drawn on the lower surface. These were not included in the computer treatment, but were added on the basis of simple theory applied to layer nucleation on close-packed crystal planes.

FIGURE B-58. BUBBLE SHAPE PREDICTED BY A SIMPLE COMPUTER SIMULATION OF A MIGRATING BUBBLE

The predictions of the simulation and the observations made in-pile were related by out-of-pile experiments. An apparatus was constructed in which a beam of light from a continuous CO₂ laser was focused on the surface of a UO₂ specimen. By this means, high temperatures and temperature gradients could be obtained without restrictions with regard to the sample environment. In addition, calculations showed that steady state was achieved within seconds, permitting precise timing of migration times.

A comparison of measured migration velocities with those forecast by simple theory (assuming bulk diffusion in the vapor phase to be rate controlling) is shown in Figure B-59. The driving force can be shown to be distributed as follows:

$$\Delta T_{\text{total}} = \Delta T_{\text{facet formation}} + \Delta T_{\text{diffusion}} + \Delta T_{\text{(other kinetic terms)}}$$

$$8.6 \text{ C} = 5.8 \text{ C} \quad + 0.27 \text{ C} \quad + 2.6 \text{ C} , \quad (\text{B-1})$$

where ΔT_{total} is the temperature difference between the hot and cold surfaces at the bubble axis.

The observation has practical significance. Layer nucleation depends upon the cube of interfacial energy. Consequently, small changes in interfacial energy can exercise immense leverage upon restructuring and gas release. Surface active agents can enhance these phenomena. Removal of surface active agents (e.g., by incorporating trace additions which sink them out) can greatly slow restructuring and gas release.

We believe that the kinetic mechanism by which atoms attach at the cool surface may constitute a major difference between in-pile and out-of-pile behavior. Under irradiation, the continuous generation of defects may provide sources of new crystal layers and avoid the difficult process of layer nucleation. The present approach allows this possibility to be studied through the conjunction of the computer simulation (omitting layer nucleation) and the out-of-pile work which generates data for all the remaining processes.

Plans for Future Work

The computer model will be developed to better simulate the macroscopic effects of transfer of matter from hotter regions of fuel to colder regions, via the migration of lenticular voids up the thermal gradient. The computer simulations of the morphology of lenticular voids as a function of the subdivision of driving force will also be continued.

FIGURE B-59. MEASURED AND THEORETICAL VELOCITIES OF LENTICULAR VOIDS
Both velocities are referenced to a gradient of 1 C per micron.

The laser image furnace will be used to study lenticular void behavior in unirradiated UO_2 . This will include the following studies. Successive traversals of lenticular voids will be induced by producing void migration at a given laser power, then increasing the laser power to extend the region in which voids are generated. The newly generated voids will move into regions already traversed, and their behavior within these regions will be examined. Void behavior will be studied in specimens in which impurities (such as samarium) have been introduced. Void morphology and migrational behavior should be a function of both type and concentration of impurity. The partitioning of impurities at the boundaries of columnar grains produced by moving voids will be examined by taking microprobe traces across the grains. The effect of "poisons" (impurities which reduce surface energy) and "antipoisons" (impurities which increase surface energy) will be evaluated. Poisons should reduce the tendency for facet formation and thus lead to faster rates of migration; antipoisons should have the reverse effect. Experimentation of this nature could ultimately enable the migration rates of lenticular voids in fuels under irradiation to be controlled.

Mechanical Model of Swelling of Nuclear Fuels

S. K. Batra and R. L. Jentgen

Objective of Program

To develop a mathematical model for the external dimensional change of nuclear fuels whose mechanical behavior is representative of that believed to be occurring in-pile.

Approach Being Used

The model is to be applicable to both high-temperature irradiations and LMFBR conditions so that it can be used both as a vehicle for interpreting data obtained under each of the above conditions and for relating high-temperature irradiation data to LMFBR behavior.

A purely mechanistic approach is adopted in meeting this objective. A quantitative analysis of an idealized model of a clad fuel element is used to provide further insight into the radial swelling problem and to suggest ways in which such dimensional changes can be retarded.

Significant Accomplishments During Fiscal Year 1970

A mathematical model called SWLTHR was developed to describe the external dimensional changes of clad UO_2 fuel elements operating in-pile under steady-state conditions. The model determines the temperature profile in the fuel, and then determines the mechanical response of the materials at each point by creep induced by gas pressure from fission gases appearing in fine pores distributed uniformly throughout the fuel.

Summary of Research Carried Out

During FY 1970, some additional parametric studies were carried out, with the single-region isothermal model, to predict the external dimensional change of clad UC at temperatures closer to those characteristic of LMFBR operation.

Figure B-60 shows the predicted external swelling at 1200 C of a UC fuel element clad in 0.2-in. -ID tungsten-26 w/o rhenium. The creep strength of the cladding at 1200 C was extrapolated from creep data taken between 1500 and 1800 C and it corresponded to a value of 1750 psi for a strain rate of 10^{-6} per hr; the creep exponent was very near 1. The creep properties of the fuel were taken from the data of Stellrecht, et al. (1), which indicated a creep strength of 2325 psi and a creep exponent of 3. The fuel was assumed to be 99 percent dense and the fission rate was taken to be 10^{13} fissions/(cm³)(sec).

FIGURE B-60. FISSION-GAS SWELLING AT 1200 C OF A UC FUEL ELEMENT CLAD IN TUNGSTEN-26 w/o RHENIUM

It was observed that a thicker tungsten-26 w/o rhenium cladding resulted in a lower percentage of radial swelling; however, inspection of the results indicated that the strength of the cladding had little effect on the predicted growth of the fuel at 1200 C. The absolute radial growth of the fuel was, in fact, predicted to be almost the same for 20- and 60-mil cladding thicknesses and the significantly lower external swelling of the fuel with the 60-mil cladding arose primarily from the fact that a given increase in fuel volume produces a lower percentage change on the larger-diameter fuel element. Similar results were found to occur when the creep properties for niobium-1 w/o zirconium, which is much weaker than tungsten-26 w/o rhenium, were used.

In addition to the above parametric studies, effort was devoted to setting up an anisothermal model that would be capable of accounting for the temperature dependence of creep properties in different regions of the fuel. Initially, an elementary, four-region model was developed to study the significance of such an approach. Results indicated the desirability of developing a more comprehensive model that would not only treat the temperature dependence of creep properties in a continuous manner, but also predict the temperature at any time and at any location in the fuel.

Such a model was developed. The fundamental assumptions governing this model are as follows:

- (1) Thermal conductivity of the fuel is a cubic function of the porosity, i. e., $k = k_0 (1 - \theta)^3$, where θ is porosity and k_0 is the thermal conductivity of the fully dense material. This assumption accounts for the inability of voids to conduct heat. Thus, higher porosity results in reduced conductivity.
- (2) Porosity is a function of radius, i. e., $\theta = \theta(r)$. Thus, varying temperatures along the radius will tend to generate varying gas pressures and creep strengths, which in turn will affect the rate of growth of porosity. The initial porosity can be designated to be either uniform or nonuniform as a function of radius to correspond to real conditions.
- (3) The intrinsic density of the fully dense material remains unchanged, which manifests the incompressibility of the solid fuel, and no new pores are generated.

- (4) The cladding is assumed to be at a constant temperature because the temperature gradient across its small thickness is expected to be small.
- (5) The fuel is allowed an axial hole, where the released gases and swollen fuel may accumulate; however, in the analysis, zero gas release is assumed.
- (6) The heat flux at the hole surface is assumed to be zero.
- (7) The material spheroid is subjected to a hydrostatic pressure which is a function of the radial position of the spheroid. These material spheroids are the idealization of the dodecahedron (with a central hole) unit cells of the fuel material. The functional dependence of the hydrostatic pressure on radius is another manifestation of the temperature-dependent material properties.
- (8) Heat generation rates in the fuel are uniform, although this assumption can be relaxed.
- (9) The fuel material obeys the nonlinear creep law of steady-state secondary creep, which is temperature dependent.
- (10) The swelling of the fuel and cladding is a quasi-stationary process.

On the basis of these assumptions the analysis was performed to yield the external dimensional change of the fuel-cladding system as a function of burnup. Analysis requires iterative solutions of two coupled algebraic equations. A numerical scheme to perform the iterations was developed and has been programmed for the GE time-sharing system (Mark II). A sample case was run using the following input parameters in the new program called SWLTHR:

Thermal conductivity of $\text{UO}_2 = 0.028 \text{ cal}/(\text{sec})(\text{cm})(\text{C})$

Initial porosity = 1 percent

Creep strength of fuel = 800 psi

Creep strength of cladding = 1750 psi

Activation energy of fuel = 90 kcal per mole

Fuel base temperature (for creep strength) = 1573 K

Creep exponent of fuel = 1.5

Creep exponent of cladding = 1.0

Temperature of cladding = 1773 K

Outer radius of cladding = 0.125 in.

Inner radius of cladding = 0.105 in.

Inner radius of fuel = 0.0275 in.

Fission rate = 1.2×10^{13} fissions/ $(\text{cm}^3)(\text{sec})$.

Over a burnup period of 1×10^{20} fissions per cm^3 , essentially no external dimensional change was predicted by the model. In its present form, the computation time of the model is quite large. Efforts will be made to reduce this.

Plans for Future Work

The SWLTHR program will be employed to analyze the influence of several parameters, such as creep strengths of the fuel and cladding, thicknesses of the annular fuel and cladding, thermal conductivity and initial porosity of the fuel, etc., on the external dimensional changes of the UO_2 rods.

(1) Stellrecht, D. E., Farkas, M. S., and Moak, D. P., "Compressive Creep of Uranium Carbide", J. Am. Ceram. Soc., 51 (8) (1968).

Creep Rupture of High-Temperature Fuels

D. E. Stellrecht and D. P. Moak

Objective of Program

To determine the toughness, ductility before fracture, and the creep rates of UN in tension.

Approach Being Used

Since the state of stress around bubbles in a swelling fuel is predominantly tensile, compressive creep data may not be entirely satisfactory for explaining irradiation behavior or for input into mathematical models. Tensile creep-rupture tests may produce results that are more comparable to stress conditions in a real fuel at high temperatures.

Tensile creep tests will be performed in vacuum at temperatures of 1400 and 1700 C and at two stresses in the range of 1000 to 5000 psi. Strain will be measured mechanically with an extensometer. The creep tests will be made at two temperatures: (1) typical of recent irradiations (1700 C) and (2) comparable to those used previously in compressive creep tests (1400 C). Two stresses (1000 to 5000 psi) will be used to determine the stress dependency.

Significant Accomplishments During Fiscal Year 1970

Tensile creep tests performed on UN showed that UN has significantly less ductility than UC. After creep testing, intergranular cracks or porosity are present in UN. These cracks may provide channels for fission-gas release during irradiation of UN and permit UN to release gas more rapidly than UC. The creep rates of UN were found to depend on stress to the third power. The composition as varied by nitrogen pressure over UN may also affect the creep rates.

Summary of Research Carried Out

Three tensile creep tests were performed on high-density, polycrystalline, stoichiometric UN. The specimens were machined to have gage sections 0.100 in. in diameter by 0.65 in. long with hemispherical ends. The ends were held by graphite grips with a tantalum diffusion barrier between the specimen and the grip. The creep tests were performed in a flowing atmosphere of high-purity argon mixed with nitrogen. The nitrogen pressures selected were slightly above the logarithmic center of the range of nitrogen pressure over UN. At 1400 C, UN is stable at 5×10^{-10} to 1.3 atm of nitrogen; consequently, a nitrogen pressure of 10^{-4} atm was used. At 1700 C, UN is stable at 3×10^{-7} to 6 atm of nitrogen, so a pressure of 4×10^{-3} atm was used. The selected pressures were expected to keep the composition of the UN near the center of the composition range for UN.

Specimen UN-1 was creep tested at 1400 C and 5000 psi in argon-100 ppm nitrogen. The deformation curve given in Figure B-61 shows that UN exhibits a minimum of primary creep, secondary creep up to about 9 percent deformation, and a very short period of tertiary creep before failure at 11 percent deformation and 344 hr. The minimum creep rate was $2.5 \times 10^{-4} \text{ hr}^{-1}$. The specimen deformed by uniform elongation with practically no necking and had no cracks along the gage section, as shown in Figure B-62.

Specimen UN-2 was creep tested at 1400 C and 2500 psi in argon-100 ppm nitrogen. The deformation curve given in Figure B-61 shows about 1 percent deformation in 330 hr with no primary creep and a minimum creep rate of $3 \times 10^{-5} \text{ hr}^{-1}$. This specimen did not fail, so the stress was lowered to 1700 psi, the gas was changed to argon-4000 ppm nitrogen, and the temperature was raised to 1700 C. Figure B-63 gives the

FIGURE B-61. TENSILE CREEP OF UN AT 1400 C

Note the lack of primary creep.
Also note the small amount of
tertiary creep in the test at 5000
psi.

3.5X

40

FIGURE B-62. APPEARANCE OF SPECIMEN UN-1 AFTER TESTING

Note the absence of cracks in the reduced section or
necking at the fracture as compared with the be-
havior of UC (BMI-1870).

FIGURE B-63. TENSILE CREEP OF UN AT 1700 C AND 1700 PSI

Note the absence of primary creep and the small amount of tertiary creep.

FIGURE B-64. CREEP RATES OF UN AT 1400 C AND 5000 PSI

The creep rates are lower near the center of the range of nitrogen pressure over UN.

creep curve of Specimen UN-2 at 1700 C and 1700 psi. The deformation curve shows no primary creep and a secondary creep rate of $2.5 \times 10^{-3} \text{ hr}^{-1}$. The specimen failed in 10 hr after 4 percent deformation. Examination of the specimen showed no necking or cracks along the reduced section.

The ductility observed in UN is 11 percent at 1400 C. Although this is significant ductility, it is much less than that determined for UC, as described in BMI-1870. At 1400 C, UC had 37 percent elongation but, more significantly, 61 percent reduction of area occurred at the necked section. In addition, partially developed cracks which had not propagated through the specimen were observed along the reduced section. The UN specimens probably formed one crack which propagated through the specimen, resulting in the short period of tertiary creep.

The creep rates of UN at 1400 C are proportional to stress to the third power, based on the difference between the creep rates at 2500 and 5000 psi. This is a lower stress dependency than the values of 5.3 determined by Vandervoort, et al. (1), and 4.15 determined by Fassler, et al. (2).

The creep rates of UN at 1400 C and 5000 psi as a function of nitrogen pressure are given in Figure B-64. The creep rates of other investigators were extrapolated to 1400 C and 5000 psi. As shown, the creep rates of UN determined by Fassler, et al. (2), in vacuum (near the uranium + UN phase boundary) are about as high as those determined by Vandervoort, et al. (1), in 0.26 atm of nitrogen (near the UN + U_2N_3 phase boundary). The creep rate determined in 10^{-4} atm of nitrogen is nearly two orders of magnitude lower. These results suggest that as nitrogen pressure is changed, the composition of UN is changed such that a more creep-resistant and defect-free structure is obtained near the center of the phase field than is obtained near the ends. This conclusion is tentative because the UN specimens were fabricated and tested by different procedures and the variations caused by these differences could have led to the difference in creep rates.

FIGURE B-65. FRACTURE ZONE OF SPECIMEN UN-2 CREEP TESTED AT 1700 C

Horizontal cracks or grain-boundary separations are visible. The high temperature resulted in some grain growth in this specimen. The UO_2 (gray) in the lighter band of UN solid solution (probably with oxygen) formed after the specimen fractured but while it was still at temperature.

Metallographic examination of the UN specimens after creep testing generally revealed intergranular cracking or grain-boundary porosity, as shown in Figure B-65. Such cracking did not occur in UC and local deformation was accommodated by subgrain formation, as described in BMI-1870 (pp 164-173). Metallographic examination of the UN specimens also revealed differences in the phases formed at the surfaces of the specimens at the different test temperatures. These phases probably were caused by impurities in the argon-nitrogen gas mixture.

The intergranular cracking found in the UN creep specimens (Figure B-65) appears to be similar to the grain-boundary parting observed in a UN specimen with an axial centerline hole irradiated at 1450 C (Specimen J, BMI-1884, Figure 7; also this report, Figure B-41). The grain-boundary parting in irradiation was associated with deformation in the radial direction.

Plans for Future Work

No additional tensile creep tests of nuclear fuels are planned at this time.

- (1) Vandervoort, R. R., Barmore, W. L., and Cline, C. F., "Compressive Creep of Polycrystalline Uranium Mononitride", Trans. Soc. AIME, 242, 1466-7 (July, 1968).
- (2) Fassler, M. H., Huegel, F. J., and DeCrescente, M. A., "Compressive Creep of UC and UN", PWAC-482 (October 20, 1965).

Creep Properties of Cladding Alloys

D. E. Stellrecht and D. P. Moak

Objective of Program

To determine the creep properties of tungsten and tungsten-26 w/o rhenium under a continuously increasing load, a load sequence believed to be similar to that experienced by the cladding of a fuel under high-temperature irradiation conditions.

Approach Being Used

A cladding being deformed by swelling fuel does not necessarily experience a constant load similar to that experienced in a typical creep test. Rather, if the fuel releases 100 percent of its gas, the gas pressure inside an unvented cladding will build up gradually, resulting in a continuously increasing load. The deformation rates determined under a continuously increasing load will be of value to mathematical models of fuel swelling.

Tensile creep tests will be performed on tungsten and tungsten-26 w/o rhenium in a high-temperature vacuum furnace at a temperature of 1760 C and under conditions of an increasing stress as well as conditions of a constant stress. The increasing-stress tests will be similar to irradiation swelling conditions where fission gas is generated during the irradiation, and the constant-stress tests will serve as controls. In order to closely simulate irradiation conditions, the tests will have a duration of 1500 hr and a maximum stress of 2000 psi. This will mean an increase of 32 psi per day for the increasing-stress condition. Deformation will be measured optically during these tests.

Significant Accomplishments During Fiscal Year 1970

Increasing-stress creep tests were performed at 1760 C on tungsten-26 w/o rhenium and unalloyed tungsten to simulate the stress generated by fission gas being continuously released into an unvented cladding during irradiation. Tungsten-26 w/o rhenium was found to deform much more rapidly than unalloyed tungsten under low

stresses. At 1760 C and relatively low stresses, the creep rates of tungsten-26 w/o rhenium were found to depend on stress to the first power and to vary as the reciprocal of grain size.

Summary of Research Carried Out

Tungsten-26 w/o rhenium was creep tested in tension at 1760 C under a continuously increasing load. The deformation curve given in Figure B-66 has a roughly parabolic shape, as would be expected under an increasing load. During this test, the stress was

FIGURE B-66. DEFORMATION OF TUNGSTEN-26 w/o RHENIUM AND TUNGSTEN AT 1760 C

For the alloy, the increasing-stress creep test has a parabolic shape, as would be expected; also, the slope of the 1000-psi constant-stress creep test is nearly equal to the tangent to the increasing-stress creep test at 1000 psi. Note that the tungsten is deforming much more slowly than tungsten-26 w/o rhenium during identical increasing-stress creep tests.

usually increased by 32 psi each day. The overall shape of the creep curve was not sensitive to loading rate, since no change was observed when the load increases were 16 psi every 12 hr, or 64 psi every 2 days. Creep rates were obtained from the deformation curve by taking tangents to the curve at different stresses. Figure B-67 is a graph of creep rate as a function of stress which shows that the creep rate is nearly proportional to stress. A stress dependency to the first power was also found by Vandervoort and Barmore⁽¹⁾, as shown in Figure B-67. Sawyer and Steigerwald⁽²⁾ found a higher stress dependency on tungsten-rhenium with a larger grain size. Differences in the values of the creep rates determined at or extrapolated to 1760 C and 1500 psi can be explained by the grain-size variation shown in Figure B-68. Here, the creep rates are found to vary approximately as the reciprocal of grain size.

A constant-stress creep test on tungsten-26 w/o rhenium at 1000 psi and 1760 C is also included in Figure B-66. No primary creep was observed in this test, which is in agreement with the results of Vandervoort and Barmore⁽¹⁾. The creep rate of $7.5 \times 10^{-5} \text{ hr}^{-1}$ falls nearly on the same plot as the creep rates obtained from the slope of the tangent to the increasing-stress creep test. A creep test at 1700 C and 1000 psi was also performed on this specimen; it resulted in a creep rate of $2.5 \times 10^{-5} \text{ hr}^{-1}$.

FIGURE B-67. CREEP RATES OF TUNGSTEN-26 w/o RHENIUM AT 1760 C AS A FUNCTION OF STRESS

Except as noted, the points above were obtained by taking the tangents to the increasing-stress creep test curve. The constant-stress creep test is in good agreement with the creep rates obtained from the tangents. The creep rates were found to be nearly proportional to stress, as found by Vandervoort and Barmore⁽¹⁾.

FIGURE B-68. CREEP RATES OF TUNGSTEN-26 w/o RHENIUM AS A FUNCTION OF GRAIN SIZE

The current data combined with those of other investigators(1,2) show that the creep rates of tungsten-26 w/o rhenium vary approximately as the reciprocal of grain size.

Unalloyed tungsten plate was prepared by the hydrogen reduction of WF_6 at $\approx 600^\circ\text{C}$ using chemical vapor-deposition techniques and a stainless steel mandrel. A sheet-type creep specimen machined from this material was creep tested in tension at 1760°C with a continuously increasing load identical to the load used for the tungsten-26 w/o rhenium specimen. The deformation curve given in Figure B-66 shows that the unalloyed tungsten deforms much less than tungsten-26 w/o rhenium under low stresses at high temperatures. This is somewhat surprising since the mean grain diameter of the tungsten is smaller than that of the tungsten-26 w/o rhenium. The vapor-deposited tungsten grains are not equiaxed; they are columnar grains about $20\ \mu$ in diameter and about $400\ \mu$ long.

The deformations observed during these creep tests are comparable to, although somewhat greater than, diameter increases observed on fuel elements (a 10 to 15 percent correction would be made for biaxial stress conditions). Consequently, the rate of external dimensional increase would not be significantly reduced if a fuel that released all its fission gas without swelling itself were available. The pressure of released gas would deform the cladding as fast or faster than the same gas contained in the fuel unless the cladding was thicker or fabricated from a stronger material, such as unalloyed tungsten.

Plans for Future Work

No additional work in this area is planned.

- (1) Vandervoort, R. R., and Barmore, W. L., "Elevated Temperature Deformation and Electron Microscope Studies of Polycrystalline Tungsten and Tungsten-Rhenium Alloys", Proceedings of the 6th Plansee Seminar, Springer-Verlag/Wein, New York (1969), pp 108-137.
- (2) Sawyer, J. C., and Steigerwald, E. A., "Creep Properties of Refractory Metal Alloys in Ultrahigh Vacuum", J. Mater., 2, 341-361 (1967).

Thermodynamics and Kinetics of Subliming Fuels

C. A. Alexander, J. S. Ogden, and W. M. Pardue

Objective of Program

To perform a combined theoretical and experimental effort to define chemical activities and to establish sublimation-condensation mechanisms for candidate uranium-plutonium fuels in order to provide guidance for selection of fuel compositions and fuel-cladding combinations that might or might not release gas more readily during irradiation.

Approach Being Used

Gas release from fuels at high temperature can be governed by a bubble migration mechanism whose movement is controlled by sublimation-condensation within the fuel. The thermal gradient in the fuel provides a driving force for such migration. Temperature, temperature gradient, stoichiometry, and composition of the fuel govern the rate of migration.

For this evaluation, use will be made of data generated at other laboratories as well as the results of other programs at Battelle-Columbus. Experiments to establish the effect of stoichiometry on the vaporization characteristics of mixed carbides and oxides will be generated for use during the course of this program. The experiments will be performed on a vacuum thermobalance and with a high-temperature sector-type mass spectrometer.

Significant Accomplishments During Fiscal Year 1970

Vaporization characteristics in the uranium carbide-plutonium carbide system were determined and, in addition, oxygen potentials as a function of composition for PuO_{2-x} were established.

Summary of Research Carried Out

A series of determinations of vapor pressures of plutonium over $(\text{U}_{0.8}\text{Pu}_{0.2})\text{C}$ was performed. The charge employed was arc-cast $(\text{U}_{0.8}\text{Pu}_{0.2})\text{C}$ with a metal/carbon ratio of unity. A photomicrograph of the starting material is shown in Figure B-69. There is some evidence at the grain boundaries of a higher-carbide second phase that appears to have precipitated on cooling. Vapor pressure measurements on pure $\text{PuC}^{(1)}$ indicated that the volatility of plutonium would be several orders of magnitude higher than that of either carbon or uranium, or of any gaseous carbide species; hence, the effusion thermobalance was employed rather than the mass spectrometer. The charge utilized in the studies consisted of 2.00 g of carbide maintained in a tungsten effusion cell. Determinations were performed over a temperature range from 1810 to 1530 C. The initial determinations were quite close to the values reported for pure $\text{PuC}^{(1)}$ in equilibrium with Pu_2C_3 ; however, after a loss of plutonium amounting to about 0.5 w/o of the total charge, a state was reached where the effusion rate did not vary with time over the period of the experiments. This may imply that condensed phases of two components were present in the charge at temperature. Certainly the observations would suggest this. The values of vapor pressure of plutonium over carbon-rich $(\text{U}, \text{Pu})\text{C}$ are given in Table B-18. These data can be fitted to the equation,

$$\log p = 19,200/T + 5.02 \quad . \quad (\text{B-2})$$

From fuel transport considerations a more meaningful value is the flux rate Z , expressed in $\text{g}/(\text{sec})(\text{cm}^2)$. This value is

$$\log Z = -19,200/T + 6.22 \quad . \quad (\text{B-3})$$

(U_{0.8}Pu_{0.2})C_{1.01} and (U_{0.8}Pu_{0.2})C_{1.05}. This observation strongly suggests that this composition consists of two condensed phases at temperature. The (U_{0.8}Pu_{0.2})C_{0.95} also reached a constant vaporization rate. However, in reaching the composition a significant amount of plutonium was lost; hence, the slight lowering of the partial pressure of plutonium is considered to be caused by the depletion of plutonium. The carbon/metal ratio again was near 1.01 when the steady state was reached. Based on a more complete analysis of the data, activities of uranium and plutonium have been computed and are shown in Table B-19. The activities show a slight temperature dependence and indicate that at lower temperatures the composition would exhibit less tendency toward reactions with cladding materials. It is rather interesting to observe that at temperatures somewhat above 2000 K the activity of plutonium in (U_{0.8}Pu_{0.2})C_{1.01} would be about the same as the activity of plutonium in metallic uranium-20 w/o plutonium, which indicates that the presence of carbon has almost no effect on the bonding of plutonium in (U_{0.8}Pu_{0.2})C.

TABLE B-19. VAPORIZATION OF (U_{0.8}Pu_{0.2})C_{1.01}

Temperature, K	Vapor Pressure, atm		Uranium Activity	Plutonium Activity
	Plutonium	Uranium		
2083	6.61×10^{-5}	1.0×10^{-7}	0.61	0.17
2025	3.70×10^{-5}	6.1×10^{-8}	0.57	0.16
1975	2.08×10^{-5}	2.4×10^{-8}	0.53	0.16
1950	1.76×10^{-5}	1.5×10^{-8}	0.51	0.17
1930	1.30×10^{-5}	9.4×10^{-9}	0.49	0.15
1880	6.61×10^{-6}	5.6×10^{-9}	0.48	0.14
1835	2.83×10^{-6}	10^{-9}	0.44	0.10
1803	2.55×10^{-6}	10^{-9}	0.42	0.13

In an effort to determine whether a unique composition of (U_{0.8}Pu_{0.2})O_{2-x} exists such that the composition of the gas phase is the same as that of the condensed phase, a thermodynamic analysis of the system has been made. Some conclusions that were reached are:

- (1) At O/M ratios of ~2.00 or above, UO₃ is the principal gaseous species.
- (2) The partial pressures of neither gaseous UO₂ nor PuO₂ vary appreciably with modest changes in the O/M ratio.
- (3) UO₂ is more volatile by about an order of magnitude than PuO₂ in the solid solution.
- (4) Gaseous PuO is considerably more stable than gaseous UO.

On the basis of Items (1), (2), and (3) above, it could be concluded that U_{0.8}Pu_{0.2}O_{2-x} would preferentially lose uranium as either UO₃ or UO₂ certainly under oxidizing conditions. Item (4) above, however, would indicate that possibly some condition exists where the plutonium and uranium might be balanced. The overall reaction might be

If the molar rate of vaporization of UO₂ were four times the rate for PuO, then the specimen would become neither richer nor poorer in uranium. Considering a reference temperature of 2000 K, the vapor pressure of UO₂ is 10^{-7} atm. When the above conditions are satisfied, then

$$Z \text{UO}_2 = 4Z \text{PuO} \quad (\text{B-5})$$

where Z is the molar evaporation rate per unit area, and

$$Z = 44.3p/\sqrt{MT} \quad , \quad (B-6)$$

where p is the vapor pressure in atmospheres, M the molecular weight, and T the absolute temperature. Then

$$\frac{p_{\text{UO}_2}}{\sqrt{267}} = \frac{4p_{\text{PuO}}}{\sqrt{255}} \quad , \quad (B-7)$$

or

$$p_{\text{UO}_2} = 4.1p_{\text{PuO}} \quad ; \quad (B-8)$$

hence,

$$p_{\text{PuO}} = 2.4 \times 10^{-8} \text{ atm} \quad . \quad (B-9)$$

As a first approximation, it can be considered that the integral free energy of the PuO_{2-x} does not differ from that of $\text{PuO}_{2.00}$; then

$$\text{PuO}_2 = \text{PuO(g)} + 1/2\text{O}_2 \quad , \quad (B-10)$$

and if PuO_2 is present at 0.2 activity

$$K = \frac{p_{\text{PuO}}(p_{\text{O}_2})^{1/2}}{0.2} = 2 \times 10^{-13} \quad . \quad (B-11)$$

Thus

$$p_{\text{O}_2} = 2.5 \times 10^{-12} \text{ atm} \quad . \quad (B-12)$$

A relationship between p_{O_2} and the composition of PuO_{2-x} has been experimentally established(2). The values would indicate that a composition of $\text{PuO}_{1.72}$ in solid solution would have an oxygen pressure of about 2×10^{-12} atm. Iterating further by considering that the composition of the PuO_{2-x} is $\text{PuO}_{1.70}$, then

$$K = \frac{p_{\text{PuO}}(p_{\text{O}_2})^{0.35}}{0.2} = 5.6 \times 10^{-12} \quad . \quad (B-13)$$

Thus

$$p_{\text{O}_2} = 1.2 \times 10^{-13} \text{ atm} \quad . \quad (B-14)$$

The composition of PuO_{2-x} , then, is $\text{PuO}_{1.69}$ in solid solution.

Thus, when the integral free energy is taken into consideration, the O/Pu ratio changes from 1.72 to 1.69; hence, it is apparent that this O/M ratio is not very sensitive to possible errors in the literature values of the integral free energy. It is then concluded that at 2000 K a composition near $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_{1.94}$ should vaporize in such a manner that the U/Pu ratio in the solid remains unchanged. The vaporization reaction is

The residual oxygen shown in Equation (B-15) might tend to shift the O/M ratio of the condensed phase to a higher O/M ratio if appreciable amounts of $\text{PuO}(\text{g})$ were lost from the system without similar oxygen losses. This would eventually lead to changes in rates of volatilization of the plutonium- and uranium-bearing species. The presence of gaseous PuO_2 would help somewhat in preventing the solid sample from becoming oxygen-rich; however, the thermodynamic data are not sufficiently reliable to carry the analysis past its present state and it is considered that further laboratory experiments, or irradiation experiments, need to be performed to establish the precision of the above analytical evaluation.

Plans for Future Work

It is planned to investigate the variation at the O/M ratio of oxide fuels when in contact with certain metals which might be used to fix the O/M ratio near a particular value for long periods of time.

- (1) Olson and Mulford, "Thermodynamics of Nuclear Materials 1967", Paper SM-98/40, International Atomic Energy Agency, Vienna (1968).
- (2) Alexander, C. A., unpublished data on the partial pressure of oxygen over PuO_{2-x} (1968).

Solid Bond Studies

J. M. Fackelmann, D. P. Moak, and W. H. Pfeifer

Objective of Program

To study the mechanical and chemical effects of a solid bonding agent between refractory fuels and a tungsten-26 w/o rhenium cladding.

Approach Being Used

One potential way of reducing the external swelling of fuel elements is to separate the fuel from a strong cladding with a solid, soft bonding material that will deform readily, while providing good thermal contact. The ideal bonding material is nonreactive to both fuel and cladding. With a solid bonding agent, there is no possibility of local heat excursions related to gas-bubble formation, as might occur with a liquid bond.

Two groups of metals are potentially useful as solid bonding materials at service temperatures of 1400 to 1800 C. The first group involves nonrefractory metals having melting points of 1800 to 2200 C. With service temperatures so near their melting points, metals in this group are likely to be soft and pliable. However, only two potentially useful elements exist in this group, namely vanadium and chromium. The second group involves weak refractory metals, such as unalloyed niobium, tantalum, and molybdenum. Tantalum and molybdenum are excluded because they are somewhat similar to, but more refractory than, niobium. Thus, the metals to be considered are chromium and vanadium from the first group and niobium from the second group, since appropriate combinations involving these metals, fuels, and claddings should be compatible.

Significant Accomplishments During Fiscal Year 1970

Hot-hardness and compression tests were performed on vanadium, chromium, and niobium to obtain an indication of the relative resistance of these materials to deformation and to evaluate the usefulness of these materials as solid bonding agents at the fuel-cladding interface. The hot-hardness values at 1400 C were 3, 6, and 15 kg per mm^2 for vanadium, chromium, and niobium, respectively. The proportional limit of vanadium, in compression by tungsten platens at 1400 C, varied inversely with specimen thickness from a value of 2000 psi for an 80-mil-thick specimen to more than 5100 psi for a 20-mil specimen. The results suggest that a material softer than vanadium at 1400 C would be required to serve as a useful solid bonding agent between refractory fuels and a tungsten cladding.

Summary of Research Carried Out

Hot-hardness and compression properties of vanadium, chromium, and niobium were determined in order to evaluate the potential usefulness of these materials as a solid bonding agent between refractory fuels and a tungsten-alloy cladding. Analyses of these materials and the UN fuel are listed in Table B-20. The metals were vacuum annealed prior to testing.

TABLE B-20. ANALYSES OF MATERIALS USED IN HOT-HARDNESS AND COMPRESSION SPECIMENS

Element	Impurity Content of Indicated Test Specimen, w/o				
	Hot-Pressed UN	Niobium Rod	Vanadium Rod	Arc-Cast Electrolytic Chromium(a)	Tungsten Rod(a)
Carbon	0.023	--	--	--	0.0003
Oxygen	0.0240 to 0.0620	--	0.0770	0.5	0.0044
Silicon	0.0400	<0.0030	0.0300	--	--
All other metals	<0.1	<0.01	<0.05	--	<0.01

(a) Typical values.

Hot-hardness measurements were obtained with a sapphire indenter of Vickers shape and a load of approximately 1 kg. These tests were performed in a cold-wall, tantalum-heater furnace under a vacuum of $<10^{-3}$ torr. The variance of hardness with temperature from room temperature to 1600 C is plotted in Figure B-70. These results indicate that vanadium has the least resistance to plastic flow in the temperature range studied. The lowest value was 2.7 kg per mm² (3800 psi) for vanadium at 1400 C.

Compressions tests were performed at elevated temperatures in order to determine flow stress information that might be useful in fuel-element concepts involving a solid bond to separate a ceramic fuel from tungsten-26 w/o rhenium or tungsten claddings. Initially, an effort was made to identify the appropriate combinations of specimens and methods for obtaining useful information. The different test apparatus utilized are identified in Table B-21. In these experiments, 20-mil-thick vanadium wafers were compressed between UN and tungsten platens at 1400 C, in various compression cages or dies. The diameters of the vanadium wafers were generally larger than the diameters of the UN and tungsten platens. The contact areas corresponded to about one-tenth of those involved in a typical fuel element. Results of these tests are given in Table B-22.

TABLE B-21. COMPARISON OF HIGH-TEMPERATURE COMPRESSION TEST APPARATUS

Designation	Apparatus A	Apparatus B
Load application	Hot-press unit	Instron testing machine
Compression "cage"	Graphite; load applied by punch and die	"TZM"; load applied by hemispherical rod-socket arrangement, self-aligning in all directions
Atmosphere	$\approx 10^{-4}$ torr vacuum	$\approx 10^{-5}$ torr vacuum
Accuracy of load-strain data(a)	Fair	Very good
Temperature limitation	>2000 C	1500 C

(a) Strain data were obtained from crosshead movement.

In Test 151 (see Table B-22) sufficient gaseous contaminants were present in the system to slightly carburize the vanadium. This carburizing effect was eliminated by wrapping the specimen assembly with tungsten foil. The room-temperature Vickers hardness of the undeformed part of the vanadium in Test 151 was 320 DPH, compared with 130 DPH for the vanadium in Test 170. As noted for Test 170 in Table B-22, a maximum stress of about 9.7 ksi resulted in significant deformation of both the vanadium and the UN. All subsequent tests have been performed on an Instron machine because the hot-pressing apparatus was not designed for obtaining precise load-strain data.

FIGURE B-70. HOT HARDNESS OF VANADIUM, CHROMIUM, AND NIOBIUM
A sapphire indenter and a 1-kg load were used.

TABLE B-22 CONDITIONS AND RESULTS OF COMPRESSION TESTS AT 1400 C ON TUNGSTEN-VANADIUM-UN SPECIMENS^(a)

Test Designation	Apparatus (See Table B-21)	Maximum Load, ksi	Proportional Limit, ksi	Vanadium Compression		UN Compression		UN Type	Formation of Uranium-Rich Liquid With Associated Extrusion of Vanadium Plus Liquid Into UN
				Mils	Percent	Mils	Percent		
151	A	12 3	--	10	50	15	8	Powder metallurgy	No
170	A	9 7	<3 0	12	60	30	15	Arc cast	No
165	B	4 3	2 7	3	15	7	3	Arc cast	Yes
166	B	5 7	3 1	8	40	30	15	Arc cast	Yes
169	B	5 2	<3 0	1 5	8	2 5	1	Powder metallurgy	No

(a) Tungsten and UN platens were 0.295 in. in diameter; vanadium wafers were 0.4 in. in diameter by 0.020 in. thick. The strain rate was 0.002 in. per min.

Tests 165, 166, and 169 were then performed, with the results indicated in Table B-22. In each case there was significant compression of both the UN and the vanadium. Metallographic examination indicated that in some cases the deformation was accompanied by localized chemical reactions. These reactions, as observed metallographically, are illustrated in Figure B-71. The liquid formed (see Figure B-71b) was always associated with extensive extrusion of "fingers" of vanadium into cracks in the UN for distances up to 0.3 in. In the sections examined, only two or three such isolated areas were noted along the vanadium-UN interface. It seems possible that at 1400 C, where the equilibrium vapor pressure of UN is about 10^{-7} torr, some decomposition of UN could occur locally in the presence of the tensile stresses associated with cracking while most of the system is under a pressure of 10^{-5} torr.

In the next five tests, another tungsten platen was substituted for the UN platen to eliminate deformation of the UN. The results are summarized in Table B-23. No plastic deformation of vanadium wafers 20 mils thick was observed at stresses up to 5100 psi at 1400 C. However, significant plastic deformation of vanadium occurred at 1400 C when the thickness of the vanadium wafer was increased to 40 mils or greater. The results of tests with 40- and 80-mil-thick vanadium (Specimens 177 and 185) are summarized in Table B-23. The proportional limit, as listed in Tables B-22 and B-23, evidently indicates the onset of plastic flow of the test specimens.

TABLE B-23 CONDITIONS AND RESULTS OF COMPRESSION TESTS ON TUNGSTEN-VANADIUM-TUNGSTEN SPECIMENS^(a)

Test Designation	Test Temperature, C	Thickness of Vanadium, in	Diameter of Tungsten Platen, in	Maximum Load, ksi	Proportional Limit, ksi	Vanadium Compression	
						Mils	Percent
176	1400	0.020	0.295	5.1	>5.1	0	0
178	1400	0.022	0.418	2.9	>2.9	0	0
177	1400	0.041	0.295	5.9	3.2	11.5	29
185	1400	0.081	0.295	3.1	2.0	14	17
179	1500	0.021	0.295	4.5	>4.5	1	5

(a) The diameter of each vanadium wafer was about 0.1 in. greater than that of a tungsten platen. Apparatus B (Table B-21) was used, and a strain rate of 0.002 in. per min.

120X

Etched

pdc166

a. Typical Section of Tungsten-Vanadium-UN

100X

pdb166

b. Localized Section of Tungsten-Vanadium-UN

Extrusion of vanadium "fingers" into cracks in the UN was accompanied by formation of a uranium-rich liquid, the lightest phase.

FIGURE B-71. TUNGSTEN-VANADIUM-UN SPECIMEN 166 AFTER COMPRESSION TESTING AT 1400 C

In Test 179, the temperature was increased to 1500 C (the only test at a temperature other than 1400 C). As indicated in Table B-23, deformation was small at a maximum stress of 4500 psi.

Since hot-hardness measurements had shown that vanadium came closest to the hardness (0.1 to 1 kg per mm²) estimated to be adequate for an extrudable bonding layer, all compression tests utilized vanadium. Plastic flow of vanadium between tungsten platens at 1400 C was found to be proportional to the thickness of the vanadium, varying from 2000 psi for an 80-mil thickness to >5100 psi for a 20-mil thickness. The thickest wafer of vanadium was compressed 17 percent by a 3100-psi load. Apparently, plastic flow of 20-mil-thick pieces is controlled by frictional effects between the tungsten and the vanadium, whereas with greater thicknesses a relatively large amount of metal in the center is free to deform. A desirable upper limit of acceptable stress in a fuel element clad with tungsten-26 w/o rhenium corresponds to the stress that causes 1 percent deformation in 1000 hr. The hydrostatic pressure causing this deformation on a 1/4-in. -diameter pin possessing a 20-mil-thick tungsten-rhenium cladding is on the order of 1000 psi at 1400 C. Thus, in such fuel elements, vanadium thicknesses greater than 80 mils are required to avoid cladding deformation. For thicknesses of less than 80 mils, temperatures in excess of 1400 C are necessary for sufficient softening of the materials tested. Based on an extrapolation of the hot-hardness data, the hardness of vanadium and chromium would be reduced to 1 kg per mm² at about 1700 and 1850 C, respectively. Since vanadium melts at 1900 C and chromium melts at 1875 C, it would appear likely that at temperatures above 1400 C vanadium or chromium would soften more rapidly than tungsten-26 w/o rhenium, which melts at about 3100 C; therefore, vanadium thicknesses of less than 80 mils might be suitable at these temperatures.

Plans for Future Work

No further work on the mechanical properties of potential solid bonding agents is planned.

Fission-Gas Pressure-Transducer Development

L. L. Yarger, N. E. Miller, and J. W. Ray

Objective of Program

To better understand the observed changes in gas pressure within the cladding of a typical HT-BRR specimen during irradiation.

Approach Being Used

A series of laboratory experiments is being conducted to aid in understanding the changes in gas pressure that have been observed in fuel claddings during irradiation. Also, modifications are being made in the present pressure-transducer design for measuring lower pressures for use with the laboratory experiments and in future irradiation capsules.

Significant Accomplishments During Fiscal Year 1970

In Capsule HT-BRR-9 and subsequent capsules the changes in the gas pressure inside the cladding of the top specimen were monitored during the irradiation with a null-balance pressure transducer. Upon initial startup in some experiments an anomalous pressure decrease was observed after the initial thermally induced pressure increase. The laboratory experiments conducted to study this anomalous change were unsuccessful in producing the pressure decrease. It was concluded that during the start of the irradiation there is a radiation-induced outgassing from some types of fuels which occurs

concurrently with the thermally induced pressure increase. These gases are subsequently removed by some reaction and do not escape through the cladding.

The design of the null-balance pressure transducer was modified to improve its reproducibility and to extend its capability to pressures as low as 0.5 psi.

Summary of Research Carried Out

In the first two irradiation experiments in which the null-balance pressure-transducer system was used to measure the gas pressure inside a cladding during irradiation, the pressure was observed to increase rapidly during initial heating, then decrease rapidly for several hours, and eventually increase more slowly as the irradiation progressed. The initial pressure increase occurred in a fashion that would be predicted from heating the gas sealed in the cladding, and the final gradual increase would be expected from fission-gas release. However, the significant pressure decrease early in the irradiation is not well understood. In order to correlate fission-gas release from the fuel with system pressure with confidence, it is necessary to better understand the mechanism by which this loss in pressure occurs.

If the pressure decrease was caused by permeation of the helium cover gas through the tungsten-rhenium cladding, this fact must be taken into account in interpreting the release data. Also, if helium was lost by permeation, the degree of loss of xenon by permeation should be determined. On the other hand, the fluctuations in pressure may have been caused by the absorption or desorption of gases by the fuel, and this possibility must be evaluated.

A series of laboratory experiments was planned to study the above effects. A nominally 2-in.-long tungsten-26 w/o rhenium cladding with a thin tungsten-26 w/o rhenium tube integral with the cladding end cap was fabricated for the experiments; the diameters of the cladding and the tube and the length of the tube were fabricated to the same dimensions as those of the specimens used in the HT-BRR experiments. The cladding and its integral tungsten-26 w/o rhenium tube were joined to a stainless steel capillary tube. The stainless steel tube terminated in the null-balance pressure transducer. The entire system was identical in size to the systems used to monitor fission-gas-pressure release in irradiation capsules. The system was backfilled with approximately 1 atm of helium, and sealed. Eight thermocouples were attached to the cladding and along the tungsten-26 w/o rhenium and stainless steel tubes so that thermal profiles could be obtained for the system at various cladding surface temperatures. The system was placed in a glass vacuum system and the cladding was heated by an induction heater. The cladding surface temperature was increased in increments of 100 C from 1000 to 1700 C, with temperature data being obtained after each incremental change. The helium in the system behaved as an ideal gas and the relative changes in pressure could be accurately correlated with changes in temperature. However, the absolute pressure could not be accurately predicted because of uncertainties in the initial filling pressure. (The heating of the transducer system during the final sealing operation causes the expulsion of some gas and results in the system having a lower final pressure than the measured glove-box pressure in which it is sealed.)

Following the above portion of the experiment, the cladding surface temperature was maintained near 1700 C for approximately 16 hr. There was no loss in system pressure. The temperature of the cladding was then increased to 1900 C and allowed to remain there for several hours. Again, no loss in pressure occurred, indicating that the losses of pressure seen during in-pile irradiation of fuel specimens are not caused by helium permeation of the cladding. The cladding was then thermally cycled a number of times to determine the reproducibility of the results. The thermal cycles were performed in such a manner as to simulate the conditions that would occur in an irradiation test with a reactor scram. The induction heater was abruptly turned off, allowing the specimen to cool rapidly. The heater power was then increased slowly, causing the

specimen to be gradually brought to temperature. Excellent reproducibility was found in the pressure measurements.

The series of experiments was continued following loading of the empty cladding with a 95 percent dense UN specimen. The system was again heated to a cladding surface temperature of 1700 C for 16 hr and the effects noted. After the pressure increased from the temperature change, no increase or decrease in system pressure occurred. It was thought that the 95 percent dense specimen did not have enough interconnected porosity to allow a postulated release and subsequent absorption of trapped gases, so the 95 percent dense UN specimen was replaced by a 75 percent dense UN specimen. Again, the pressure remained stable after heating to 1700 C. Losses in cladding pressure similar to those observed during in-pile irradiation of fuel specimens have not occurred in these laboratory tests.

In these experiments there was no measurable loss of helium by permeation of the tungsten-26 w/o rhenium cladding at temperatures to 1900 C. This provides some assurance that the xenon and krypton released by the fuel during irradiation, as well as the initial helium charge, will not diffuse through the claddings, thus making it possible to measure gas release by measuring the pressure inside the cladding. There were no changes in the pressure measured in specimens containing dense or porous UN out-of-pile, showing that there was no net thermally induced adsorption or desorption of gases from that fuel. The inability to reproduce in laboratory tests the decrease in pressure observed in the capsule experiments lends support to the proposition that the pressure decrease is radiation dependent. A proposed mechanism is that upon initial startup there is a radiation-induced desorption of gases from the fuel. The increase in pressure from these gases is added to, and partially masked by, the increase in pressure caused by the large temperature change. The subsequent decrease in pressure which has been observed results from reaction of these gases with the fuel or cladding. In addition, it may be necessary that the released gaseous products be decomposed prior to their removal by the radiation-induced reaction. The pressure decrease has now been observed in three experiments ranging in temperature from 1500 to 1900 C, and the rate of decrease has been observed to increase rapidly with temperature.

In the first two in-pile experiments incorporating the null-balance pressure transducer, no pressure data were obtained during reactor shutdown because the minimum detectable pressure was too high. It is quite important to be able to measure gas pressure at shutdown in order to fully characterize the fission-gas-release behavior of the fuel. Therefore, it was desirable to create a more sensitive transducer and also to improve its reproducibility. These were accomplished by:

- (1) Improving the shape of the cavity that houses the diaphragm
- (2) Redesigning the electrical contact to prevent the possibility of local deformation of the diaphragm.

The cavity housing the diaphragm in the redesigned transducer has been made very shallow so that a very small deflection in one direction causes the diaphragm to contact the chamber wall; no deflection is permitted in the other direction. These limitations minimize the stresses in the diaphragm. The cavity in the first two in-pile experiments was conical in shape (see Figure B-72a). The disadvantage of this shape is that as the diaphragm deforms to conform to this shape, the outer portion of the diaphragm contacts the conical surface, thereby decreasing the effective diameter of the diaphragm. This, in turn, increases the pressure required to displace the diaphragm against the electrical contact.

In order to increase the pressure sensitivity and reliability of the transducer, use of a step cavity shape and a redesigned electrical contact have been investigated. Instead of the electrical contact being a pin protruding into the cavity as in the first transducers, the redesigned contact is machined even with the top of the cavity and is insulated from

FIGURE B-72. SCHEMATIC DIAGRAM OF NULL-BALANCE PRESSURE TRANSDUCER

the chamber housing by a ceramic material (see Figure B-72b). This makes a smooth cavity wall and eliminates the possibility of local deformation of the diaphragm. The diameter of the step cavity is essentially the same as the diaphragm diameter (0.5 in.) and the sharp edges associated with the step are rounded to reduce stresses in the edge of the diaphragm. Also, the depth of the cavity housing the diaphragm has been reduced from 0.005 to 0.003 in. to shorten the distance the diaphragm must deform before touching the electrical contact. The combination of the step cavity and the redesigned contact has resulted in a transducer that has better sensitivity than the original devices. Laboratory tests indicate that the redesigned transducer is capable of having a minimum detectable pressure as low as 0.5 psi, as compared to 6 to 12 psi for the previous transducers.

A redesigned transducer was installed in Capsule HT-BRR-11 and subsequent capsules; shortly after startup, a leak occurred in the specimen cladding or in the connecting tube. In Capsule HT-BRR-12, the pressure measured in the cladding of a UO₂ specimen showed that there were no bursts of gas from the fuel upon heating or cooling; rather, a more continuous release occurred during operation at a nominal cladding temperature of 1500 C.

Plans for Future Work

No further work is planned on the pressure transducer.

Control of Neutron Radiograph Quality

A. M. Plummer and J. W. Ray

Objective of Program

To provide uniform, high-quality neutron radiographs of irradiation capsules before, during, and after irradiation.

Approach Being Used

The transfer neutron radiography technique is used in making neutron radiographs of irradiation capsules. Use of the neutron radiographs in determining dimensional changes of fuel specimens requires that the radiographs be of high quality and uniform contrast. The achievement of uniformity and quality is dependent on the transfer medium and control of exposure parameters, since the geometrical parameters are fixed by the configuration of existing collimators and of the capsules themselves. Improvement of resolution and contrast are being sought through the control of neutron exposure and transfer foil-to-film exposure.

Significant Accomplishments During Fiscal Year 1970

Significant improvements in the quality and uniformity of neutron radiographs of the HT-BRR capsule series have been achieved. Existing facilities were modified to permit neutron exposures to be made with the capsules in a dry condition and to permit the full length of the capsules to be radiographed at one time. These modifications also made it possible for dimensional standards to be included in the radiograph for use as measurement references.

Summary of Research Carried Out

Neutron radiography of irradiation capsules has previously been accomplished by passing the capsule and an indium transfer foil simultaneously through the 1-1/4-in. - square neutron beam from the parallel-wall collimator at the Battelle Research Reactor (BRR). This procedure leads to an activity gradient along the length of the indium transfer foil at the time it is exposed to the film and results in a nonuniform film density

along the length of the capsule image in the neutron radiograph. This, in turn, makes it difficult to achieve consistent quality in the neutron radiographs produced by this method. To circumvent this problem, the possibility of performing capsule neutron radiography in the BRR conical collimator was investigated. This collimator has a 14 by 17-in. neutron beam at the collimator outlet and, hence, can be used to obtain a simultaneous neutron exposure of the entire capsule length.

The underwater conical collimator facility is equipped with a gas-filled bell jar in which specimens are located during neutron radiography. Capsules are therefore in a gas (rather than water) environment while being radiographed and will tend to heat up as a result of the decay heat from the irradiated fuel specimens. Estimates indicate that capsule temperatures of approximately 400 F may be reached. This is above the melting point of indium; accordingly, dysprosium has been used for capsule radiography in this facility. Dysprosium has the added advantage of a higher thermal neutron cross section than indium, which permits the use of a thinner transfer foil with accompanying improvements in resolution on the resulting radiographs.

Neutron radiography of instrumented capsules in the conical collimator facility requires that the capsule lead tube penetrate a watertight seal at the top of the bell jar. A special inflatable seal was designed to accommodate HT-BRR capsules and has been installed and used for this purpose.

Neutron radiographs of capsules of the HT-BRR series made in the conical collimator showed definite improvements over those made in the scanning facility, but some variations in quality were observed. Some of these variations were identified with scattered neutrons incident on the back side of the transfer foil. Test exposures with mock-up specimens showed that a backup foil of cadmium significantly reduces the exposure by scattered neutrons.

Dimensional standards of tungsten-rhenium are now included in all radiographs of this capsule series; these standards have the approximate dimensions of the fuel specimens and are used as measurement references on the radiographs.

Plans for Future Work

No further modifications of facilities are planned; improvements in techniques will continue to be applied to this program as they become available through other programs.

✓ CREEP OF REACTOR FUEL MATERIALS
—(AEC-DRDT AND ANL)—

J. S. Perrin

Substantial fuel-element dimensional changes can occur in-pile during reactor operation. A major portion of the dimensional changes can be caused by fuel swelling from the accumulation of fission-product atoms. The gaseous atoms will agglomerate or flow into bubbles, the fuel matrix is stressed, and deformation or growth occurs in a manner thought to be analogous to creep deformation. As the fuel swells, both from the gaseous and solid fission products, growth is restrained by the fuel-element cladding and the cooler, outer region of fuel. Fuel porosity is introduced to accommodate part of this swelling, thus reducing the total strain on the cladding. This fuel swelling accommodation factor will depend primarily on the relative creep strength of the fuel and cladding. These considerations require that the influence of the fission process on the creep strength of ceramic fuels be determined before the most meaningful fuel design studies can be made.

In recognition of these factors, a program was set up to study the in-pile and out-of-pile creep of ceramic fuels. The program is being conducted for the AEC Division of Reactor Development and Technology and Argonne National Laboratory. Initial emphasis is on UO_2 and $\text{UO}_2\text{-PuO}_2$, since $\text{UO}_2\text{-PuO}_2$ is the reference fuel for the Fast Flux Test Facility. Later studies will include UN-PuN .

The in-pile creep experiments will be conducted in compression and a constant load will be maintained during testing. In order to reduce the radial temperature gradient, specimens will be hollow cylinders. Capsules will be operated in both the Battelle Research Reactor (BRR) and in a higher flux reactor.

Preirradiation creep tests will be conducted on UO_2 and $\text{UO}_2\text{-PuO}_2$ to determine to what extent out-of-pile behavior can be used to predict in-pile behavior, and to help provide information on basic creep mechanisms which can be used in the design of fuels of increased creep strength. The obtained data will be used in the selection of stresses and temperatures for the in-pile creep tests and will later be compared with the in-pile data to determine the effect of the fission process on the creep rate. In the case of UO_2 , tests will be run on solid cylindrical as well as hollow cylindrical specimens to determine whether specimen geometry affects creep behavior.

During the in-pile creep tests, specimens will be under a temperature gradient. In order to determine whether there is an effect of the fission process on the creep behavior, it will be necessary to compare isothermal preirradiation creep behavior with anisothermal in-pile creep behavior. An analysis will be developed for making this comparison and will include a thermal analysis to predict the temperature distribution of in-pile test specimens.

In order to predict the results of the fission process on the creep behavior of UO_2 and $\text{UO}_2\text{-PuO}_2$, the known effects of the fission process on those properties of UO_2 and $\text{UO}_2\text{-PuO}_2$ that may influence the creep behavior will be considered. This will be combined with additional creep experiments on UO_2 to determine the effect of variables such as stoichiometry, grain structure, and porosity. Etch pitting and transmission-electron microscopy will be used to determine structural changes.

Design, Fabrication, and Operation of In-Pile Creep Capsules

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Objective of Program

To design, fabricate, and operate capsules for determining the in-pile compressive creep behavior of UO_2 - PuO_2 fuels as affected by fission rate, stress, temperature, and burnup.

Approach Being Used

A series of irradiation capsules is planned for creep studies of UO_2 - PuO_2 during in-pile exposure. Environmental conditions include specimen surface temperatures up to 1300 C with compressive stresses up to 13,000 psi. The experimental variables will include temperature, stress, burnup, and fission rate.

A stepwise procedure has been developed which involves the following series of experiments:

- (1) Capsules operated in the BRR to determine the creep behavior of UO_2 and UO_2 - PuO_2 at fission rates of $\sim 1.2 \times 10^{13}$ fissions/(cm³)(sec)
- (2) A capsule containing a UO_2 - PuO_2 specimen operated in the BRR in a special core position to obtain an intermediate fission rate approaching 2×10^{13} fissions/(cm³)(sec)
- (3) A capsule operated in the BRR to obtain the creep behavior of UN-PuN at a fission rate of approximately 1.5×10^{13} fissions/(cm³)(sec)
- (4) Capsules with high heat-removal capability operated in a high-flux facility to obtain the creep behavior of UN-PuN at high fission rates, $\sim 5 \times 10^{13}$ fissions/(cm³)(sec)
- (5) Capsules operated in both the BRR and the high-flux facility to further study the in-pile creep behavior of UO_2 - PuO_2 and UN-PuN.

Significant Accomplishments During Fiscal Year 1970

Irradiation of the second capsule in this program was completed, a third capsule was irradiated, and the fourth capsule was assembled. Results of each irradiation have been used to guide the improvement of subsequent experiments. Specimen electrical heater designs were revised after further evaluation of these components in laboratory heater mock-up experiments. Hot-cell examination of terminated experiments showed that capsule components were substantially unaffected by irradiation.

Summary of Research Carried Out

The initial effort on this program was reported in BMI-1851. A feasible concept for the in-pile capsule at the BRR was developed. It incorporated electrical heating, a hollow-cylinder specimen, a gas-flow transducer for specimen deformation measurement, and bellows-sealed, gas-actuated specimen loading.

Both computer analyses and laboratory heater mock-up experiments were used to aid in materials selections for the capsule components. A prototype of the in-pile capsule was assembled and operated in the laboratory. A series of creep tests was conducted with a UO_2 sample. During these tests the helium load gas, nitrogen-gas transducer, and temperature control systems performed satisfactorily.

After the successful performance of the heater mock-up and capsule prototype experiments, two in-pile creep capsules were assembled and operated in the BRR. Ten creep tests were performed with a UO_2 specimen in Creep Capsule BRR-1 at various levels of temperature, stress, fission rate, and burnup. The first three of a series of creep tests were performed in Creep Capsule BRR-2. The above items were presented in detail in BMI-1868.

Creep Capsule BRR-2 Operation. All creep tests performed in Creep Capsule BRR-2 are summarized in Table C-1. After the initial series of creep tests was performed with the capsule located out-of-pile, the capsule was inserted into a test cell at the BRR. On the basis of earlier dosimetry work, the capsule was located in a position that would produce a fission rate of about 1.7×10^{12} fissions/(cm³)(sec) in the UO₂ specimen. A nominal load was applied to the specimen (stress $\approx$ 100 psi), and power to the electrical heaters was adjusted to maintain the specimen at a nominal temperature of 1180 C. The nominal temperature is monitored at the axial midpoint of the specimen outer wall. As mentioned in BMI-1868, length changes recorded over the initial period of the in-pile operation of Creep Capsule BRR-1 indicated that the UO₂ specimen grew about 0.0036 in. To verify that the growth effect was real and to accentuate the anticipated growth, the first in-pile experiment in Capsule BRR-2 (Test 2E) was planned as a nominal-load test (stress $\leq$ 100 psi). A reactor scram occurred 54 hr after the start of the test and the main heater open-circuited at 97 hr. There was no apparent interruption in the overall continuity of the measurements as a result of these short time perturbations on the specimen temperature. The experiment was terminated at the end of 142 hr by a scheduled reactor shutdown. The transducer system had indicated an apparent specimen growth of 0.0098 in. over the test period.

After a neutron radiograph was obtained the capsule was reinserted into the BRR core at a position that would provide a specimen fission rate of about 1.2×10^{13} fissions/(cm³)(sec). The reactor was brought to full power in steps and the electrical power input to the two guard heaters was adjusted to maintain the fuel at a nominal temperature of 1180 C. The load pressure was increased at the beginning of Test 2F from 100 to 200 psi to ensure that the load mechanism was in solid contact with the specimen and creep-sensing probes. The transducer system indicated a specimen deformation during the initial part of the test, followed by specimen growth.

The apparent specimen growth under nominal loading was not believed to be a reliable indication of specimen performance, since a nominal stress of 100 to 200 psi was found to be too low to keep specimen, load train, and extensometer all in good mechanical contact. The nominal-load tests performed in Capsule BRR-2 indicated that the minimum specimen stress should be set $\geq$ 500 psi for future nominal-load experiments. This minimum load would insure that all load-carrying components were fully seated. All future in-pile tests were to be started with an initial nominal load applied, this load being less than that necessary to cause any appreciable creep, with the purpose being to allow any possible specimen growth that may occur to take place before the actual creep tests are started.

In order to resolve the uncertainty in the performance of the apparatus, it was decided to terminate the nominal-load experimentation and proceed to Test 2G at a stress level of 1500 psi. Test 2G was operated for 138 hr up to the scheduled shutdown date for BRR Cycle 253. During the test, a loss of electrical power and a resultant reactor scram occurred 90 hr into the test. The specimen temperature dropped from 1185 C to about 50 C as a result of the complete loss of electrical and fission heating. After this rather severe thermal shock to the strain-measuring system, heater elements, and fuel specimen, the reactor was returned to full power in a number of steps and electrical power was supplied to the guard heaters to bring the nominal specimen temperature back to 1185 C.

The transducer system indicated that an apparent stepwise change in specimen length of about 2 mils (deformation) had occurred during the power excursion in Test 2G. This abrupt shift in the transducer output is not surprising since the severe thermal shock on the apparatus could have caused one of the ceramic probes to crack or shift position. This type of movement of the strain-measuring system would show up as an indicated stepwise change in specimen length. Also, the specimen could have cracked

TABLE C-1. SUMMARY OF CREEP EXPERIMENTS PERFORMED IN CREEP CAPSULE BRR-2

Test	Fission Rate, fissions/(cm ³)(sec)	Measured Specimen Temperature ^(a) , C	Effective Specimen Temperature ^(b) , C	Stress, psi	Steady-State Creep Rate, hr ⁻¹	Indicated Cumulative Deformation, mils	Objective of Test and Comments
2A	Out of capsule	1300 ^(c)	1300	3500	6.79×10^{-5}	6.4	To establish out-of-pile creep rate
2B	0	1360	1360	3500	1.37×10^{-3}	46.6	To approximate Test 2A in-capsule; questionable data due to controller malfunction; neutron radiograph taken at completion of test
2C	0	1110	1110	3500	4.90×10^{-6}	47.0	To establish in-capsule creep rate out- of-pile; test terminated by power failure; neutron radiographed at end of test
2D	0	1180	1180	3500	1.71×10^{-5}	48.6	To establish in-capsule creep rate out- of-pile
2E	1.7×10^{12}	1180	--	100	--	38.8	To determine effect of flux under low load; main heater failed; neutron radiograph taken after completion of test
2F	1.2×10^{13}	1180	1155	200	--	44.2	To check low-load behavior at higher fission rate than Test 2E
2G	1.2×10^{13}	1185	1160	1500	4.8×10^{-5} and 7.6×10^{-5}	50.3	To determine behavior at lower stress than that of Test 2D; neutron radio- graphed at end of test
2H	0	1180	1180	1500	1.05×10^{-5}	51.9	To compare out-of-pile behavior with in-pile Test 2G; bottom guard heater failed; neutron radiographed at end of test
2I	1.2×10^{13}	1100	1075	2500	--	--	Experiment concluded; neutron radio- graph taken at end of test; capsule transferred to hot cell

(a) Temperature measured at axial midpoint of specimen outer wall.

(b) Effective temperature is the temperature at which an isothermal specimen would have the same overall measured creep rate, assuming no in-pile enhancement of creep rate.

(c) Direct measurement out of capsule.

during the thermal cycle; however, the neutron radiograph taken at the end of the test did not show any cracks or chips.

Test 2H was conducted at 1180 C and 1500 psi during the maintenance period between reactor cycles. The purpose of this test was to measure the creep behavior of the specimen under a zero fission rate for comparison with the in-pile behavior of Test 2G. The bottom guard heater open-circuited 115 hr into the test and caused a premature termination of the experiment. The capsule was neutron radiographed at the end of the test, and the specimen appeared to be sound.

An unusually large amount of scatter was observed in the data obtained during the second day of operation of Test 2H. An investigation of the transducer-system pressure output indicated that an oscillatory drift of the pressure drop across the fixed orifice had been encountered. During this period of unstable pressure output, the transducer sensitivity had decreased from ± 0.1 mil to about ± 0.4 mil. This instability was not evident during calibration of the device in the laboratory. Consultations with the vendor indicated that this behavior had been observed in some transducers and could be eliminated by increasing the exhaust pressure.

Although only one of the three electrical heaters was functional in the capsule at the end of Test 2H, it was possible to perform creep tests in-pile at the fission rate of 1.2×10^{13} fissions/(cm³)(sec), since fission heating contributed a significant portion of the total capsule power output. Accordingly, Creep Test 2I was initiated with the remaining guard heater. A malfunction in the temperature-recorder unit of the temperature control system occurred 10 hr into the test and caused the specimen temperature to increase from 1100 C to about 1400 C. During the time period of the temperature excursion (~2 hr), the transducer system indicated an additional specimen deformation of at least 42 mils (the end of the transducer sensing range was reached at that point). The capsule was removed from the reactor core and a neutron radiograph was taken to examine the condition of the fuel specimen. The radiograph indicated that the fuel had, indeed, deformed about 1/16 in. The overall barreled shape of the annular fuel indicated that the deformation had occurred uniformly over the entire specimen length. The capsule was transferred to the Battelle-Columbus Hot-Cell Facility for postirradiation examination.

Temperature Control of Creep Capsule BRR-2. During the first 3 days of operation of the first in-pile experiment (Test 2E) difficulty was experienced with the control-thermocouple recorder in the electrical heater control system. There was very little temperature control afforded by the available automatic settings on the controller. The control unit supplied heat to the capsule in a pulsing on-off mode for specimen temperature control. The same problem was observed in Test 2B, as discussed in BMI-1868. However, the thermal fluctuations were substantially greater for Test 2B than for any subsequent test in the capsule. When the main heater failed during Test 2E, the guard heaters were manually operated to hold the specimen at 1180 C and the recorder-controller was removed for inspection. Extensive testing of the unit disclosed an intermittent electrical shorting malfunction in the slide-wire circuit. After the malfunction was repaired and the recorder was recalibrated, the unit was returned to service. Subsequent operation of the unit showed that the temperature-control problem was corrected and that power to the guard heaters was being controlled in a proportioning-band mode so as to minimize severe temperature cycling of the heater windings.

It is believed that the initial on-off power control action of the electrical heaters may have resulted in many small but rapid thermal cycles in the heater windings and lead-in connections. Since the main heater was drawing much more current than were the guard heaters, the thermal cycles in the main heater elements were much more severe and led to the eventual open-circuit failure. It was planned to examine the recorder unit at the end of Test 2E rather than cause a severe temperature cycle on the specimen during the test by removing the controller. Previous operating experience

indicated that the specimen temperature could drop 400 to 600 C during the time required to switch to manual electrical control and remove the temperature recorder-controller unit.

The temperature recorder that had malfunctioned for a short period of time and caused the specimen temperature excursion in Test 2I was examined to determine the cause of the failure. It was not possible to tell whether the trouble arose from the millivolt input signal from the thermocouple or from the amplifier-recorder circuitry. To protect against unnecessary power cycling of heaters in future experiments, it was decided to replace the recorder unit and recheck the operational performance of the entire temperature control system by operating a heater with a control thermocouple for a period of 2 to 3 weeks in a manner identical to the in-pile capsule system.

Postirradiation Examination of Creep Capsule BRR-2. The capsule was disassembled in the Battelle-Columbus Hot-Cell Facility. The connectors that joined the nickel lead-in wires to the tungsten-26 w/o rhenium heater elements were found to be in excellent physical condition, eliminating one potential point of open-circuiting of the main and lower guard heaters. Inspection of the heater windings revealed that the apparent cause of heater failure was a melted region of heater wire in the lower section of the main heater. The guard-heater windings appeared to be slightly oxidized but in relatively good physical condition. The cause of the electrical open-circuiting of the bottom guard heater could not be determined since the heater shells were broken during disassembly.

The general appearance of the surface finishes of the molybdenum radiation baffles, heater windings, and various stainless steel components indicated that the helium atmosphere in the primary-containment region had remained relatively free of contamination during the life of the experiment. The alumina creep-sensing probes were recovered in two pieces. It is believed that the breakage occurred during disassembly, in view of the condition of other components after disassembly. The individual pieces retained good strength and did not appear to be otherwise damaged. The UO_2 specimen was recovered in about 10 pieces and therefore could not be measured for length and diameter changes. A neutron radiograph taken before disassembly of the capsule showed the specimen was apparently in one piece at that time; presumably it was broken during the difficult disassembly procedure. The alumina load columns and insulating disks appeared to be unaffected by the exposure.

On the basis of visual and metallographic examination, there was no evidence of reaction of the UO_2 with the thoriated tungsten platens located at each end of the specimen. Oriented angular porosity or cracks were observed at specimen grain boundaries. The pores were aligned approximately parallel with the principal stress direction. Similar porosity has been observed in specimens tested out-of-pile, as discussed in BMI-1857. This porosity is believed to be caused by development of grain-boundary separation; the separation occurs as the specimen starts barreling during creep testing.

The thoriated tungsten platens at each end of the UO_2 specimen were measured. The thickness did not change during irradiation. The transducer needle used in the extensometer was also unaffected during irradiation. These key components of the strain-measuring system were examined for dimensional changes since an error would be introduced into the deformation measurements if changes had occurred during operation of the experiment.

On the basis of the postirradiation examination, no incompatibilities of materials or of the capsule design which would affect performance were found. The only problem observed was the failure of the heater wire, which was known to have occurred during operation of the capsule.

Creep Capsule BRR-3 Fabrication. The assembly process for Creep Capsule BRR-3 was reevaluated in light of the difficulties encountered with the operation of Creep Capsule BRR-2. In particular, several steps were added to the assembly procedure to

increase electric heater life and reliability in the capsules. These included the following:

- (1) A longer pumpdown time was used before the capsule primary-containment region was backfilled and sealed. Experience had shown that a 48-hr minimum pumping time (with the capsule components heated to about 300 C) was required to maintain a pressure of 10^{-3} torr in the primary containment (with the diffusion pump isolated from the chamber).
- (2) The pumping and backfilling procedures were reviewed and modified to insure that the gas-tank valve and lines were thoroughly purged and free of gaseous and volatile impurities prior to and during this step in the assembly.
- (3) Ultrahigh-purity helium with certified analyses of impurities (e. g., oxygen ≤ 0.5 ppm and $H_2O \leq 0.15$ ppm) was used for backfilling.
- (4) Modification of the procedure used to achieve the final seal on the primary-containment region was made. A hydraulic sealing clamp was developed to crimp and mechanically seal the evacuation/backfill line while the line was being severed and seal-welded. In addition, an electropneumatic pressure transducer was installed to continuously monitor the primary-system pressure in the capsule during the sealing process, and in subsequent testing.

Creep Capsule BRR-3 was assembled and transported to the BRR in the middle of November, 1969. The final assembly of the lead tube and connection of the capsule leads to the auxiliary support systems at the BRR were routine.

Creep Capsule BRR-3 Operation. Five creep tests that were performed in Creep Capsule BRR-3 are summarized in Table C-2 along with the out-of-capsule test that was used to characterize the specimen before loading into the creep capsule.

The first creep test in the capsule, Test 3B, was performed out-of-pile at a temperature of 1100 C and stress of 4000 psi. A neutron radiograph of the UO_2 specimen was obtained at the beginning of the test to ensure that the fuel specimen was intact and well centered between the loading columns. There were no problems encountered with either the temperature control system or the strain-measuring system during the test. The test was terminated at the end of 260 hr by reducing the specimen stress to 1700 psi for the next run. After the load pressure was reduced, the capsule was placed into a BRR test-cell position that would provide a fission rate of about 1.2×10^{13} fissions/(cm^3)(sec) in the UO_2 specimen. Power to the electrical heaters was reduced to maintain the specimen at a nominal temperature of 1125 C as the reactor was brought slowly to full power. The operation of all the auxiliary support systems was excellent.

At the conclusion of Test 3C the load pressure was increased to raise the specimen stress to 4000 psi to initiate Test 3D. The nominal specimen temperature was held at 1125 C with the same fission rate as in Test 3C. The load pressure was reduced to drop the specimen stress to about 1000 psi at the end of 150 hr because of an apparent increase in the specimen creep rate (a factor of 2 to 3). The 1000-psi stress level was continued for an additional 113 hr to the end of the BRR operating cycle and there was no indicated deformation during this period (as expected). Thus, the increase in specimen creep rate appeared to be real and not a transducer malfunction.

The capsule was removed from the BRR test cell at the end of the cycle and a neutron radiograph was obtained of the fuel specimen to determine its physical state. The specimen appeared to be well centered, intact, and did not contain any observable cracks or chipped areas.

Test 3E was then conducted out-of-pile at 1100 C and 4000 psi. The creep rate was $3.63 \times 10^{-6} hr^{-1}$, which compares well with the value of $3.57 \times 10^{-6} hr^{-1}$ measured in Test 3B for the same test conditions.

The capsule was reinserted in the BRR test cell at the conclusion of Test 3E for continued in-pile operation. Test 3F was initiated at a nominal specimen temperature of

TABLE C-2. SUMMARY OF CREEP EXPERIMENTS PERFORMED IN CREEP CAPSULE BRR-3

Test	Fission Rate, fissions/(cm ³)(sec)	Measured Specimen Temperature ^(a) , C	Effective Specimen Temperature ^(b) , C	Stress, psi	Steady-State Creep Rate, hr ⁻¹	Indicated Cumulative Deformation, mils	Objective of Test and Comments
3A	Out of capsule	1300 ^(c)	1300	3500	9.49×10^{-5}	8.9	To establish out-of-pile creep rate
3B	0	1100	1100	4000	3.57×10^{-6}	9.8	To establish in-capsule creep rate out-of-pile; neutron radiograph taken at beginning of test
3C	1.2×10^{13}	1125	1100	1700	9.93×10^{-6}	12.6	To determine effect of flux under low stress at temperature comparable to Test 3B
3D	1.2×10^{13}	1125	1100	4000	2.75×10^{-5}	15.8	To determine effect of flux at higher stress; neutron radiograph taken at end of test
3E	0	1100	1100	4000	3.63×10^{-6}	16.5	To determine creep rate out-of-pile to compare with Test 3B
3F	1.2×10^{13}	1125	1100	4000	--	--	To determine creep rate to compare with Test 3D; specimen failed; neutron radiographed; capsule transferred to hot cell

(a) Temperature measured at axial midpoint of specimen outer wall.

(b) Effective temperature is the temperature at which an isothermal specimen would have the same overall measured creep rate, assuming no in-pile enhancement of creep rate.

(c) Direct measurement out of capsule.

1125 C, a compressive stress of 4000 psi, and a fission rate in the fuel of about 1.2×10^{13} fissions/(cm³)(sec). The transducer system indicated that the specimen collapsed after 1 hr of exposure. The reactor was shut down and a neutron radiograph was obtained of the fuel to enable observation of its physical appearance. The radiograph showed the specimen had a horizontal crack across its midplane surface and some chips were observed on the lower platen. Since the specimen was no longer in a suitable test condition, the capsule was transported to the Battelle-Columbus Hot-Cell Facility for postirradiation examination.

Postirradiation Examination of Creep Capsule BRR-3. Creep Capsule BRR-3 was disassembled and examined in the Battelle-Columbus Hot-Cell Facility. The transducer needle appeared unaffected by the in-pile operation. The inner probe was recovered in three pieces, and the outer probe in two pieces. It is believed that the probes were broken during disassembly. They did not appear to be otherwise damaged.

The thoriated tungsten platens at each end of the UO₂ specimen were measured. The thickness of the lower platen was unchanged. The upper platen showed slight depressions on each side, totaling less than 1 mil. There was no reaction of the platens with the specimen. The alumina load columns appeared to be in excellent condition.

The UO₂ specimen was recovered in about eight pieces, so that length and diameter measurements could not be made. The specimen fractured during the last creep test. Metallographic examination showed that no significant grain growth had occurred during irradiation and creep testing.

The microstructure near the end of the specimen had porosity that was generally randomly distributed with little, if any, pore distribution. Microstructures of an area away from the ends of the specimen showed some oriented angular porosity at the grain boundaries; the pores were aligned parallel with the compressive stress direction. Similar porosity was observed in the specimen from Creep Capsule BRR-2 and in specimens tested out-of-pile, as discussed in BMI-1857.

Review of Heater Design. To better assure the integrity of the standard tungsten-26 w/o rhenium wire that was used to form the resistance element of the heaters, each of the seven strands of wire was examined microscopically (30X) for defects, and individual wire resistances were measured prior to the stranding operation. After the wires were stranded the elements were again examined for physical and electrical defects. The addition of these steps in the assembly procedure insured that the resistance elements were free of defects arising from the fabrication operations. This procedure was initiated for Capsule BRR-3 and will be used in the fabrication of all future capsules.

Since electrical heater failures occurred during the operation of Creep Capsule BRR-2, the basic design of this key component of the device was reevaluated. The hypothesis that the cause of the failures could be traced to the malfunctioning controller in the temperature control system was investigated by operating a typical heater unit in the laboratory in a pulsing on-off power mode similar to that observed during the operation of Creep Capsule BRR-2. The unit was operated for about 300 hr when the heater element open-circuited.

An optical pyrometer was used to monitor the heater-wire temperatures. The temperature ranges and times are given in the tabulation that follows:

Approximate Wire Temperature, C	Duration, hr	Remarks
1300	150	No alumina specimen
1400	70	Dummy alumina specimen at 1300 C
1530	80	Dummy alumina specimen at 1360 C

It should be noted that the ratios of heater winding temperature to specimen temperature were probably not the same as the ratios in an actual capsule since the mock-up was not an exact duplicate in terms of overall system heat transfer. Molybdenum radiation baffles surrounded the heater in the mock-up as in a creep capsule, but there were no massive alumina end pieces in the mock-up. Therefore, end losses of heat were different from the creep-capsule situation. The significant data are the wire temperatures. These were difficult to determine with precision owing to the pulsing mode of power input, but were probably accurate to within ± 30 C.

Posttest examination of the heater winding showed that it had failed in a manner identical to the failure of the main heater winding from Capsule BRR-2 (observed during hot-cell examination): a localized melting of the heater wire. During the latter stages of operation (winding temperature > 1500 C) particles were observed depositing on the alumina shell next to the windings. Analyses of heater windings (from the mock-up and prototype heater windings) have shown the material to be tungsten.

It was suggested that this deposition is a result of the presence of water vapor which permits the reaction

With a temperature gradient between a hot tungsten-rhenium wire and a cold alumina shell, in the presence of water vapor in a sealed system, a transfer of tungsten occurs. The reaction rate increases with temperature gradient and with the concentration of water vapor. These findings suggested several things about heater life:

- (1) Any mode of operation that results in very high wire temperatures in the presence of water vapor is extremely detrimental to extended life.
- (2) The wire temperatures associated with peak specimen temperatures of 1300 C or less (with steady-state operation) probably do not result in heater failure in times of interest to this program. The original mock-up heater experiment operated for 2000 hr and appeared to be in good condition (i. e., very little reaction) at the end of the test.
- (3) The faulty temperature recorder-controller probably contributed to the failure of the heater in Creep Capsule BRR-2 owing to the very high wire temperatures associated with the pulsating mode of operation.
- (4) Increased care in cleanup of components and the gas environment to remove water vapor, in particular, should increase heater life.

In light of the experience with operation of heater mock-ups, an analysis of water vapor in the alumina heater shells, and the proposed use of a sintered nickel-NiO body for control of oxygen partial pressure in later capsules, several points concerning capsule fabrication were established. These included:

- (1) The original technique of cleaning and baking ceramic parts appeared to be adequate.
- (2) Long pumpdown times with the primary system heated to 300 C were required to thoroughly outgas all surfaces.
- (3) Use of a control system for oxygen partial pressure permitted the use of tantalum heaters to be considered again, in the event that the changed oxygen partial pressure would improve the possibility of using tantalum.
- (4) Long life for tungsten heaters required considerable effort to obtain an environment free of water vapor.
- (5) Experience with tantalum heaters in other irradiation programs had not indicated that such extreme care is needed for long heater lifetimes. (In the creep program tantalum heaters were removed from consideration because of their possible effect on the mixed-oxide stoichiometry.)

To obtain heater-lifetime data to corroborate the information obtained on heater performance, several additional heater mock-ups were constructed. They were:

- (1) A tungsten-rhenium heater in a system without a nickel-NiO body
- (2) A tungsten-rhenium heater in a system with a nickel-NiO body
- (3) A tantalum heater in a system with a nickel-NiO body.

In general, tantalum is an excellent material for a high-temperature heater. Even though thermodynamics studies predicted that tantalum heaters might not be stable in the new controlled atmosphere, they were tested in the event that the kinetics of any harmful reaction with the atmosphere would be slow. All of the units were constructed using techniques to minimize water vapor. The atmosphere was the same high-purity helium as used in capsules. The nickel-NiO bodies were sintered compacts. All units were designed to be operated with dummy Al_2O_3 specimens at temperatures of about 1300 C and nickel-NiO temperatures of about 700 C. These tests were planned to be long-term life tests at steady-state conditions.

The operation of the three heater lifetime/compatibility mock-ups was begun in early December, 1969. The mock-up that contained the nickel-NiO atmosphere control system with the tantalum-element electric heaters failed during the first day of operation. The unit was opened and examined. The cause of the open-circuit failure appeared to be the result of a severe oxidation reaction between the nickel-NiO mixture and the tantalum heater element. The heater winding nearest the nickel-NiO mixture had deteriorated badly, causing a local high-resistance path and an eventual melting and open circuit of the tantalum element. This experiment showed that tantalum could not be used in this atmosphere.

The two mock-ups that contained tungsten-rhenium heater elements were continuously operated for about 2100 hr, shut down, and examined for materials compatibility of the various components. The primary-containment pressure gages indicated that the containment seals and/or pressure vessel may have developed a leak during the operation. For this reason the mock-up heaters were shut down before failure and examined for materials compatibility of the various components. The 2100-hr lifetime exceeds the specified in-pile service lifetime of about 1700 hr.

Micrographic examination of the tungsten-rhenium heater elements in the posttest and as-received conditions showed very little attack by the environment. Since the radiation baffles were found to be heavily corroded by the atmosphere in both tests, the hypothesis that a leak had developed during the test seemed to be substantiated.

In order to determine the source of the gas leaks, the epoxy-sealed connectors were examined with a helium leak detector. Three of the four tungsten-rhenium thermocouple seals were found to have gas leaks. These seals were made using a procedure that is identical to the one used on the epoxy seals of the in-pile creep capsules. In order to prevent this type of leak from occurring in the capsules, it is planned to perform a double seal on all eight of the epoxy connectors that are used as containment seals on the primary-containment system. In addition to the double seal, the handling of this step in the assembly has been modified to ensure that epoxy compounding and cleanliness of components are carefully controlled.

The leaks in this case appear to be an isolated case; i. e., they have not been encountered before in this program. A small leak (diffusion path) in an epoxy seal would not necessarily cause an in-pile experiment to be terminated and these seals have been used successfully for in-pile experiments for a number of years. However, detection of three leaks in this type of seal calls for increased precautions in the assembly operation to prevent the possible recurrence of this problem.

Investigation of the compatibility of the nickel-NiO atmosphere control system with heater windings led to a number of conclusions:

- (1) The tantalum heater elements were not compatible with the nickel-NiO system.
- (2) The tungsten-rhenium heater elements were compatible with the nickel-NiO system and showed no adverse effects even in the presence of a large source of oxygen.

- (3) The exclusion of water vapor in the atmosphere surrounding the tungsten-rhenium heater elements is important for long lifetime (~3000 hr).
- (4) There appear to be no materials compatibility problems associated with using the nickel-NiO mixture as a stoichiometry control system in the mixed-oxide capsules.

Creep Capsule BRR-4 Operation. Creep Capsule BRR-4 (containing a bare $\text{UO}_2\text{-PuO}_2$ specimen) was fabricated utilizing the techniques established in the development and operation of Creep Capsules BRR-1, BRR-2, and BRR-3. The capsule was shipped to the BRR in mid-May, 1970, and the first planned creep test (Test 4B, out-of-pile, at 1200 C and 4000 psi) was begun. A neutron radiograph was made that showed the specimen to be well centered and intact prior to application of the full load. One hour after the start of the test the transducer system indicated an abrupt failure of the specimen. A neutron radiograph was then made, and it confirmed the hypothesis of a specimen failure. The radiograph showed that the specimen had experienced a brittle fracture in the lower third of its length.

The capsule was removed from the BRR pool and decontaminated for possible salvage. The lead tube was severed and the lower 7 ft of the assembly was shipped back to the Battelle-Columbus Capsule Laboratory. Since it was found possible to salvage a major portion of the capsule components, the capsule was reassembled with a UO_2 specimen and designated Creep Capsule BRR-4A. The alumina components were cleaned, three new tungsten-rhenium thermocouples were installed, new heaters were fabricated, and the creep probes, displacement transducer, and platens were replaced.

High-Flux Creep-Capsule Design. Design studies are currently in progress on the development of a high-fission-rate creep apparatus. The final product will necessarily differ from the design of the BRR low-flux creep capsule because of the requirement for dissipation of gamma and fission heat generation which is greater by an order of magnitude than that for the low-flux design.

Visits were made to various test reactor facilities during the year to select a suitable test location for a high-flux creep capsule. The thermal-neutron flux requirements were dictated by the criteria of attaining a maximum of 5×10^{13} fissions/(cm^3)(sec) in the LMFBR reference mixed-oxide fuel and a maximum of 1×10^{14} fissions/(cm^3)(sec) in a 20 percent enriched mixed-nitride fuel. In addition to the fission-rate criteria, it was also considered important for the facility to provide a relatively large (2 to 3-in. diameter) test location where the neutron flux was held constant for long periods of time (1 to 2 weeks). Of the eight reactor facilities investigated, three were immediately rejected as the result of a lack of sufficient thermal-neutron flux to achieve the required fission-rate densities. These facilities were the BRR, CP-5, and B&W test reactor.

The ETR, ATR, GETR, and ORR test reactor facilities all meet the neutron-flux criteria for the reference fuel material. The required fission rates can also be attained at the EBR-II facility by increasing the enrichment of the fissile fuel in the reference material. Of all the facilities that were investigated, the ORR facility appeared to be best suited for conducting a high-fission-rate creep experiment. Thus, it was decided to use neutronics data from the operation of the ORR in the design of the experiment.

Requirements for the experiment which had a major influence on the design included the following items:

- (1) Temperature: It is necessary to maintain the fuel temperature relatively constant during the irradiation to aid in data interpretation. Also, relatively isothermal conditions make the creep data easier to analyze. Temperatures in the range from 600 to 1300 C were anticipated.
- (2) Stress: Compressive loading should be employed since ceramic materials will be used. Stress levels up to 10,000 psi were planned.
- (3) Fission Rate: LMFBR fission rates of about 5×10^{13} fissions/(cm^3)(sec) were anticipated for the reference fuels.
- (4) Specimen Material: $\text{UO}_2\text{-PuO}_2$ and UN-PuN were considered.

Analyses were made with selected fission and gamma heat-generation rates to establish the temperature distribution in the fuel material. A series of calculations was made to determine the temperature profile for a particular specimen geometry with a purely radial or axial mode of heat rejection. Six typical cases are presented in Table C-3 for mixed-oxide and mixed-nitride specimens. The first three cases were calculated for pure radial heat loss from the hollow-cylinder fuel specimens. The last three cases show radial and axial temperature differentials in the fuel specimens that were designed for predominately axial heat losses. Temperature gradients for UN-PuN are substantially smaller than for $\text{UO}_2\text{-PuO}_2$ as a result of the large differences in thermal conductivity.

TABLE C-3. SUMMARY OF TEMPERATURE DISTRIBUTION FOR SELECTED SPECIMEN CONFIGURATIONS

Material	Fission Rate, fissions/(cm^3)(sec)	Specimen Geometry ^(a)	L/D Ratio ^(b)	Temperature Differen- tial (ΔT), C	
				Radial	Axial
$\text{UO}_2\text{-PuO}_2$	5×10^{13}	Hollow cylinder	∞	450 ^(c)	0
UN-PuN	5×10^{13}	Hollow cylinder	∞	65 ^(c)	0
UN-PuN	1×10^{14}	Hollow cylinder	∞	110 ^(c)	0
$\text{UO}_2\text{-PuO}_2$	5×10^{13}	Hollow cylinder	0.28	30	245
$\text{UO}_2\text{-PuO}_2$	5×10^{13}	Hollow cylinder	0.20	25	125
UN-PuN	1×10^{14}	Hollow cylinder	0.5	20	215

(a) The hollow, cylindrical specimens have a 0.25-in. OD and a 0.15-in. ID.

(b) D is taken as the outer diameter.

(c) Calculated for the boundary conditions that $dT/dr = 0$ at the inner radius and T (at the outer radius) = 900 C.

A temperature map of a typical fuel specimen and surrounding components is shown in Figure C-1. The two-dimensional solution of this problem was used to obtain the radial and axial temperature differentials that are shown for the last three cases in Table C-3.

$\text{UO}_2\text{-PuO}_2$ specimens in the low-flux capsules have an L/D ratio of 3.0. In order to consider $\text{UO}_2\text{-PuO}_2$ specimens in a high-flux capsule, it will be necessary to use much lower L/D ratios in order to have realistic radial temperature gradients. If the radial temperature gradient gets very large, a majority of the load on a given cross section is supported by a very small part of the specimen. Therefore, calculations of $\text{UO}_2\text{-PuO}_2$ were made for the low L/D ratios of the 0.28 and 0.20.

The $\text{UO}_2\text{-PuO}_2$ region of the temperature map that is shown in Figure C-1 depicts half of a creep specimen. In order to increase the effective height of a $\text{UO}_2\text{-PuO}_2$ creep specimen a series of these washer-shaped disks can be stacked in a long column. Thus, the effective L/D ratio of the specimen can be easily increased from 0.28 to 2.

A schematic representation of the high-flux creep capsule showing a stacked-disk specimen is given in Figure C-2. The finned tungsten load platens shown in the figure between the fuel disks are used to form a smooth, hard, load-bearing surface for the ends of the specimen and to provide an axial heat sink so that the heat generated in the specimen flows out the end surfaces. This mode of heat flow is provided to minimize the radial temperature gradients in the fuel since a radial temperature gradient in excess of about 50 C will cause an order-of-magnitude change in the stress across the wall of the hollow cylindrical specimen. This load concentration occurs because the inner zones of the fuel are hotter than the outer surfaces, with the result that the stronger (cooler) zones support most of the imposed load.

FIGURE C-2. SCHEMATIC REPRESENTATION OF CONCEPTUAL DESIGN FOR HIGH-FLUX CREEP CAPSULE

The axial variation of specimen temperature will be minimized by employing a constant-temperature heat sink along the entire length of fuel. The magnitude of specimen temperature is regulated by passing a variable-conductivity gas through a gas gap that is located between the heat sink and the coolant water of the reactor. The axial movement of the fuel stack is detected by a pneumatic transducer similar to the one used in the low-flux capsules. Uniaxial compressive loading is used to apply a compressive stress to the column of fuel. A bellows-sealed, pressurized chamber is used to apply the required loads.

A number of support systems are required for operation of the capsule. The major units are:

- (1) Pneumatic-transducer gas supply and pressure-monitoring system
- (2) Gas system for specimen loading
- (3) Sweep-gas system for monitoring for fission-product gases
- (4) Gas-mixing system for control of specimen temperature
- (5) Temperature recording system.

Items (1), (2), (3), and (5) will be essentially the same as those systems designed for the low-flux capsule. Item (4), the gas-mixing system, has been specified as a part of other capsule designs for AEC programs at Battelle-Columbus and is thus readily available.

The UN-PuN fuel material has a thermal conductivity that is greater than that of the UO_2 - PuO_2 material by about a factor of eight, which results in a high-flux creep experiment with a more nearly isothermal fuel. In addition, the larger value of thermal conductivity permits selection of a specimen geometry that lends itself to more meaningful creep data. Thus, it was decided to abandon the mixed-oxide, stacked-disk approach and proceed with a mixed-nitride specimen in a standard hollow-cylinder geometry.

The capsule design for the mixed nitride will be identical to the one shown in Figure C-2 except for the fuel-specimen geometry and associated components that are used for heat removal. The detailed design of this section of the capsule is in progress and will not affect the design of the previously specified support systems.

Plans for Future Work

Operation of Creep Capsule BRR-4A will begin, with completion of the operation scheduled during the first quarter of Fiscal Year 1971.

To accomplish the goals for the program during Fiscal Year 1971, the following tasks will be undertaken:

- (1) Additional creep capsules will be fabricated.
- (2) In-pile creep data will be obtained from the operation of Creep Capsule BRR-4A and following capsules.
- (3) The design of the high-flux creep capsule will be completed.
- (4) Laboratory experiments will be initiated to aid in the final design of the high-flux capsule.

In-Pile Creep Experiments

J. S. Perrin, R. A. Robinson, and S. J. Basham

Objective of Program

To generate and analyze creep data obtained from in-pile creep capsules.

Approach Being Used

In-pile creep data will be generated for UO_2 and UO_2 - PuO_2 . The in-pile creep data will be analyzed both with respect to all in-pile tests and out-of-pile reference creep tests on both UO_2 and UO_2 - PuO_2 .

Significant Accomplishments During Fiscal Year 1970

The creep data from Capsules BRR-2 and BRR-3 were analyzed. At a fission rate of approximately 1.2×10^{13} fissions/(cm³)(sec), a stress range of 1500 to 4000 psi, and a nominal temperature range of 1100 to 1200 C, an in-pile enhancement of creep rate of a factor of eight to ten was observed.

Summary of Research Carried Out

The creep data generated in Capsules BRR-2 and BRR-3 were given in the preceding section of this report in Tables C-1 and C-2, respectively. Figure C-3 is a plot of creep rate as a function of stress showing data from Capsules BRR-2 and BRR-3. Both actual test results and extrapolated results are given. In-pile Test 2G was run at a fission rate of 1.2×10^{13} fissions/(cm³)(sec), an effective temperature of 1160 C, and a stress of 1500 psi; the resultant steady-state creep rate was 6.2×10^{-5} hr⁻¹. Out-of-pile Test 2D was run at 3500 psi and 1180 C, and had a steady-state creep rate of 1.71×10^{-5} hr⁻¹. To compare the two tests, the out-of-pile test was first corrected for temperature using an activation energy of 90 kcal per mole, and then extrapolated from 3500 psi to 1500 psi. This extrapolation is indicated by the dashed lines. The upper dashed line is for the case where the stress dependency of the creep rate is 1, and the lower dashed line is for a stress dependency of 4. The steady-state creep rate is proportional to stress to a power that ranges from 1 to approximately 4, depending on the creep mechanism. Even assuming a stress dependency of only 1, the most conservative case, the creep rate in-pile can be seen to be enhanced by an order of magnitude as compared to the out-of-pile creep rate.

A similar comparison can be made for in-pile Test 3C and out-of-pile Test 3B. The in-pile test was run at a fission rate of 1.2×10^{13} fissions/(cm³)(sec), a stress of 1700 psi, and an effective temperature of 1100 C. The steady-state creep rate was 9.93×10^{-6} hr⁻¹. Out-of-pile Test 3B was run at 1100 C and a stress of 4000 psi, with a resultant steady-state creep rate of 3.57×10^{-6} hr⁻¹. Extrapolating the out-of-pile test from 4000 psi to 1700 psi using a stress dependency of 1, the figure shows that the creep rate under these conditions is also enhanced by close to one order of magnitude. Also shown in Figure C-3 is in-pile Test 3D, which was run at a stress of 4000 psi, a fission rate of 1.2×10^{13} fissions/(cm³)(sec), and an effective temperature of 1100 C. The resultant steady-state creep rate is 2.75×10^{-5} hr⁻¹. This can be directly compared to out-of-pile Test 3B, which had a steady-state creep rate of 3.57×10^{-6} hr⁻¹; therefore, the in-pile enhancement under these conditions is a factor of six. Thus, the results of creep tests in both Capsules BRR-2 and BRR-3 show substantial, consistent creep enhancement in UO₂ as a result of the fission process.

Plans for Future Work

The analysis of the in-pile creep data and out-of-pile reference creep data will continue.

Mechanical and Thermal Analyses

W.R.D. Wilson

Objective of Program

To provide the analytical means for determining compressive creep properties of UO₂ and UO₂-PuO₂ from the anisothermal in-pile experiments so that they can be compared to the properties of the fuels obtained in isothermal out-of-pile tests, and therefore the effect of the fission process on creep can be determined.

FIGURE C-3. COMPARISON OF OUT-OF-PILE AND IN-PILE CREEP TESTS SHOWING CREEP ENHANCEMENT DUE TO FISSIONING

Approach Being Used

An analysis for predicting creep behavior under anisothermal conditions with arbitrary creep properties and specimen temperature distributions has been developed. A heat-transfer code is used to predict the temperature distributions in the test specimens under in-pile conditions. By using these analytical tools, the effect of anisothermal conditions on the creep rate of the in-pile specimen may be estimated and appropriate corrections made.

Significant Accomplishments During Fiscal Year 1970

A parametric study of the influence of the form of creep model and temperature distribution on the magnitude of the effect of anisothermal conditions on the creep of the in-pile specimen was conducted. This revealed that over the range of practical interest the bulk specimen creep rate was very close to that of an isothermal specimen at a temperature 25 C lower than the nominal temperature of the in-pile specimen, which is measured on the outside diameter midway between the platens. Thus, the effects of anisothermal conditions in the in-pile tests could be allowed for by subtracting 25 C from the nominal specimen temperature. The application of this correction enabled a comparison of in-pile and out-of-pile data in order to establish the effect of the fission process on creep.

Summary of Research Carried Out

The basic objective of work this year has been to develop a method of correcting for the anisothermal conditions present in the in-pile creep tests. To this end the analytical tools developed during the previous fiscal year have been used. These include a heat-transfer code called TRAHT-2 which is used to estimate the specimen temperature distribution. The output temperature distribution is then used as input to a program called INPIC. INPIC calculates the stress and strain distributions in the in-pile specimen with arbitrary creep properties and temperature distribution. It also calculates the bulk strain rate for the specimen.

Figure C-4 shows typical calculated temperature, stress, and strain-rate distributions in the in-pile specimen. The calculations are based on a fission rate of 1×10^{13} fissions/(cm³)(sec) with a nominal specimen temperature, T_N (measured on the outside diameter midway between the platens), of 1200 C. The fuel is assumed to have a linear dependence between creep rate and applied stress, and an activation energy of 90 kcal per mole.

Figure C-4a is a plot of the isotherms within one quarter of the specimen. It can be seen that most of the heat flow is axial with a very sharp temperature gradient near the platens. The inside of the specimen is cooler than the outside because the gas surrounding the specimen is a very poor heat-transfer medium while the alumina rod inside the specimen provides a low-conductivity heat path to the platens.

Figure C-4b shows the distribution of axial stress across the specimen wall at six equally spaced planes in the lower half of the specimen. It can be seen that the stress is relatively uniform. The maximum stress level is only about 50 percent greater than the mean; this occurs because the heat flow is largely in the axial direction. Thus, the temperature is relatively uniform across the specimen wall. It can also be seen that on any given plane the stress is highest where the temperature is lowest; this is reasonable, for the increased rigidity of the fuel at low temperature allows it to carry a larger portion of the applied load.

A parametric study of the influence of the type of creep model and temperature distribution on the magnitude of the effect of anisothermal conditions on the creep of the in-pile specimen has been conducted. In discussing this work, it is useful to define an "effective specimen temperature", T_E . This is the temperature at which an isothermal specimen would have the same bulk creep rate as the anisothermal in-pile specimen under the same conditions of loading and for a given model of creep behavior. The difference

FIGURE C-4. TYPICAL CALCULATED TEMPERATURE, STRESS, AND STRAIN-RATE DISTRIBUTIONS FOR IN-PILE SPECIMENS

The calculations are based on a fission rate of 1×10^{13} fissions/(cm³)(sec) and a nominal specimen temperature of 1200 C. The fuel is assumed to have a linear dependence between creep rate and applied stress, and an activation energy of 90 kcal per mole.

between the effective specimen temperature, T_E , and the nominal temperature, T_N , is the temperature correction that must be applied to allow for anisothermal conditions.

For a given specimen temperature distribution, the temperature correction, $T_E - T_N$, will vary with the dependence of the creep of the fuel on stress and temperature. In investigating this effect, a creep model has been used of the form

$$\dot{\epsilon} = A e^{-B/T} \sigma^C,$$

where $\dot{\epsilon}$ is the creep rate at temperature, T , under a stress, σ ; A , B , and C are constants. Figure C-5 shows the variation of temperature correction ($T_E - T_N$) with B (~activation energy) for creep exponents (C) of 1 and 4. The correction is independent of A . The temperature distribution used was that shown in Figure C-4. It can be seen that the temperature correction increases with a decrease in activation energy or creep exponent but that the effect is relatively slight; therefore, for most practical purposes, a correction of about -25 C is sufficiently accurate.

After the effect of fuel creep properties on the temperature correction was shown to be relatively slight, attention was concentrated on the effect of different temperature distributions on the correction. Figure C-6 summarizes the results of this study. The temperature correction has been plotted on a base of nominal specimen temperature (T_N) for fission rates (ϕ) of 1×10^{13} and 2×10^{13} fissions/(cm³)(sec). The creep model used had a creep exponent of unity and an activation energy of 90 kcal per mole. It can be seen that the magnitude of the correction increases slightly with increase in nominal temperature or activation energy. However, the value of -25 C is conservative.

The use of the 25 C correction for anisothermal conditions allowed a direct comparison of in-pile and out-of-pile results. An enhancement of creep in-pile was indicated. This is best illustrated by reducing all the results to one effective temperature. Figure C-7 shows secondary creep rates plotted on a base of stress. All the data have been reduced to 1100 C by the use of an activation energy of 90 kcal per mole. It can be seen that the creep rates from Tests 2C, 2D, 2H, 3B, and 3E, which were conducted in a capsule but out-of-pile, all lie close to a line with a slope of unity. Thus, there is excellent agreement between the out-of-pile results from Capsules BRR-2 and BRR-3. The in-pile tests, 2G, 3C, and 3D, were conducted at a fission rate of approximately 1.2×10^{13} fissions/(cm³)(sec). They are all close to another line with a slope of unity lying at a creep rate about eight times higher than that of the out-of-pile tests, 2C, 2D, 2H, 3B, and 3E. The data presented in Figure C-7 are convincing evidence that a real in-pile effect exists.

Some effort has also been devoted to determining the stress distribution in candidate specimen geometries for the high-flux tests on mixed-oxide fuels. This is essential to insure that the stress distribution in the final geometry will be such that meaningful creep properties can be extracted from the test results.

Plans for Future Work

As in-pile data become available, the effects of temperature variations will be estimated and accounted for. The analytical technique developed for UO₂ will be applied to the anisothermal creep of UO₂-PuO₂ specimens. Further work will be conducted on the stress distributions in candidate high-flux specimen geometries.

Fabrication of UO₂-PuO₂ Preirradiation and In-Pile Compressive Creep Specimens

M. D. Houston, O. L. Kruger, and W. M. Pardue

Objective of Program

To fabricate and characterize UO₂-PuO₂ specimens for preirradiation and in-pile compressive creep experiments.

FIGURE C-5. EFFECT OF FUEL PROPERTIES ON TEMPERATURE CORRECTION

The temperature distribution used is that shown in Figure C-4.

FIGURE C-6. EFFECT OF TEMPERATURE DISTRIBUTION ON TEMPERATURE CORRECTION

The creep model used has a creep exponent of unity and an activation energy of 90 kcal per mole.

FIGURE C-7. COMPARISON OF THE IN-PILE AND OUT-OF-PILE TEST RESULTS

Approach Being Used

UO₂-22 w/o PuO₂ specimens will be fabricated at Battelle-Columbus in a manner consistent with fast-reactor fuel procedures. The process will utilize mechanically blended powders and coprecipitated powders with normal ceramic cold-pressing and sintering techniques. Powder compacts will be sintered in the range of 90 to 98 percent of theoretical density in a flowing atmosphere of argon-8 v/o hydrogen. The stoichiometry of the final specimens will be controlled by adjustment of the oxygen partial pressure during the sintering cycle or during an equilibration process performed at 900 to 1000 C after sintering. The stoichiometry of the mixed oxide will correspond to the stoichiometry expected in the fuel of the FTR which is operating in the same temperature range as the creep tests. Specimens will be characterized by measurements of the following properties in accordance with well-established procedures: stoichiometry, composition (uranium/plutonium ratio), homogeneity, metallic and nonmetallic impurity content, grain size, and density.

Significant Accomplishments During Fiscal Year 1970

Cold-pressing and sintering techniques were used to fabricate compressive creep specimens of UO₂-22 w/o PuO₂ from mechanically blended Eldorado UO₂ and Arhco PuO₂ (oxalate derivative) powders and from G.E. coprecipitated UO₂-PuO₂ powder. Three general types of specimens were produced: (1) mechanically blended, 90 ± 1 percent of theoretical density, 10 to 15-μ grain size; (2) mechanically blended, 94 ± 1 percent of theoretical density, 3 to 5-μ grain size; and (3) coprecipitated, 96 ± 1 percent of theoretical density, 33-μ average grain size. Sintering parameters varied in temperature from 1530 to 1760 C and in firing times from 4 to 18 hr. Solid cylindrical specimens were machined by ultrasonic cutting techniques and by standard abrasive processes to yield hollow cylinders for preirradiation and in-pile creep trials.

Summary of Research Carried Out

Compressive creep specimens of UO₂-22 w/o PuO₂ were fabricated from mechanically blended powders and coprecipitated powder by cold-pressing and sintering techniques. For mechanically blended compositions, the component oxides, Eldorado UO₂ and Arhco PuO₂, were wet ball milled in a rubber- or Viton-lined mill with uranium slugs and alcohol or oxalene, respectively, for a period of 6 hr. After milling, the liquid was evacuated and the semidry powder was then vacuum dried at 100 C for 20 hr. Coprecipitated UO₂-21.77 w/o PuO₂ powder for this program was obtained from General Electric and was utilized in the as-received state. Both types of powders were compacted in a tungsten carbide die at 20,000 psi and sintered using various time-temperature parameters in a flowing atmosphere of argon-8 v/o hydrogen. Solid cylindrical specimens, approximately 1 in. long by 0.335 in. in diameter, were produced. Hollow cylindrical specimens, 0.750 in. long and 0.150 in. in ID by 0.250 in. in OD, were machined from the solid cylinders by ultrasonic cutting techniques and by regular cutting and grinding techniques. Examples of the solid and hollow cylindrical specimens are shown in Figure C-8.

Details for the mechanical blending process were presented previously in BMI-1868. Further sintering studies with this type of powder were undertaken to prepare UO₂-22 w/o PuO₂ specimens with different grain sizes. The results of the sintering trials, given in Table C-4, show that grain sizes in the range from 1 to 15 μ were produced. Specimens with the larger grain sizes attained at sintering temperatures of 1700 to 1760 C were lower in density. Two types of sintered, mechanically blended materials were selected for compressive creep studies: (1) Batch A, 94 ± 1 percent of theoretical density, 3 to 5-μ grain size, and (2) Batch B, 90 ± 1 percent of theoretical density, 10 to 15-μ grain size. The typical microstructures for these two materials are shown in Figure C-9. Most of the porosity is observed to lie along the grain boundaries, while the oxide grains appear to be quite dense.

2.5X

PLM452

a. Solid Cylinders After Sintering

1.5X

PLM511

b. Hollow Specimen Machined From Solid Cylinder

FIGURE C-8. PHOTOGRAPHS OF TYPICAL UO₂-22 w/o PuO₂ CREEP SPECIMENS BEFORE AND AFTER MACHINING

500X

PL7116

a. Sintered at 1530 C

The grain size is 3 to 5 μ and the density is 94 ± 1 percent of theoretical.

500X

PL7702

b. Sintered at 1760 C

The grain size is 10 to 15 μ and the density is 90 ± 1 percent of theoretical.

FIGURE C-9. MICROSTRUCTURES OF MECHANICALLY BLENDED UO_2 -22 w/o PuO_2 AFTER SINTERING

TABLE C-4. SINTERING RESULTS FOR MECHANICALLY BLENDED UO_2 -22 w/o PuO_2 SPECIMENS
COMPACTED AT 20,000 PSI AND SINTERED IN ARGON-8 v/o HYDROGEN

Powder Batch(a)	Heatup Time, hr	Sintering Parameters		Cooling Time, hr	Density, percent of theoretical	Grain Size, μ
		Temperature, C	Time, hr			
A	1.8	1530	5	1.5	94.0	3-5
	4.0	1550	18	2.0	94.6	2-6
B	2.0	1550	4	1.5	89.6	3-5
	8.0	1550	18	2.5	94.8	1-3
	2.1	1625	4	1.5	89.9	5-8
	2.2	1700	4	1.5	87.3	7-12
	2.5	1760	4	1.5	88.3 ^(b)	10-15

(a) A = initial batch, mixed in rubber-lined mill with alcohol medium.

B = another batch, mixed in Viton-lined mill with oxalene medium.

(b) Density of larger specimens with same sintering parameters = 90 ± 1 percent of theoretical.

Coprecipitated UO_2 - PuO_2 powder was selected in anticipation of achieving high-density specimens of large grain size. A quantity of UO_2 -21.77 w/o PuO_2 was procured from G.E. Specimens were prepared from the as-received powder by cold pressing at 20,000 psi. Sintering trials were performed in the temperature range from 1475 to 1760 C, and results are shown in Table C-5. Specimens having densities in excess of 95 percent of theoretical were attainable only with a slow heatup cycle and a sintering temperature in the range from 1550 to 1700 C. The microstructure for the high-density oxide, as sintered at 1625 C, is shown in Figure C-10. Much of the porosity in this material is intragranular. Complete characterization of the as-received coprecipitated powder and the products sintered from it is in progress, and results will be presented in following reports.

TABLE C-5. SINTERING RESULTS FOR COPRECIPITATED UO_2 -21.77 w/o PuO_2 SPECIMENS
COMPACTED AT 20,000 PSI AND SINTERED IN ARGON-8 v/o HYDROGEN

Heatup Time, hr	Sintering Parameters		Cooling Time, hr	Density, percent of theoretical	Average Grain Size, μ
	Temperature, C	Time, hr			
8.0	1475	18	2.5	93.1	--
8.0	1550	18	2.5	96.2	--
2.1	1625	4	1.5	93.4	23
8.0	1625	18	2.5	96.3	33
8.0	1700	18	2.5	95.8	25
8.0	1760	6	1.5	93.0	28

FIGURE C-10. MICROSTRUCTURE OF SINTERED COPRECIPITATED UO_2 -21.77 w/o PuO_2

The specimen was sintered at 1625 C for 18 hr. A density of 96.3 percent of theoretical was achieved along with a 33- μ average grain size.

Plans for Future Work

Compressive creep specimens of UO_2 -22 w/o PuO_2 for both in-pile and out-of-pile creep experiments will be prepared as required. These will be fabricated from mechanically blended powders and from coprecipitated powder. Prior to testing, all specimens will be fully characterized with respect to stoichiometry, uranium/plutonium ratio, homogeneity, impurity content, grain size, and density.

Preirradiation Compressive Creep Testing of UO_2 - PuO_2

M. D. Houston, O. L. Kruger, and W. M. Pardue

Objective of Program

To determine the creep behavior of unirradiated UO_2 -22 w/o PuO_2 as a reference for the in-pile creep behavior of identical specimens.

Approach Being Used

Compressive creep tests at stresses of 1000 to 5000 psi and at temperatures of 900 to 1500 C will be performed in a vacuum furnace adapted for plutonium containment. The compressive load will be applied by a compression-cage creep-testing apparatus. Deformation will be measured continuously by a mechanical device in conjunction with an LVDT unit. The test specimens will have the same physical and chemical properties and dimensions as the in-pile creep specimens.

The generated data will be utilized in the selection of stresses and temperatures for the in-pile creep tests and will be used as reference data for the in-pile creep data on UO_2 - PuO_2 .

Significant Accomplishments During Fiscal Year 1970

The compressive creep behavior of various types of UO_2 -22 w/o PuO_2 was studied. The steady-state creep rates for mechanically blended specimens of high density (94 percent of theoretical) and fine grain size (3 to 5 μ) were determined in the temperature range from 1100 to 1330 C and at stresses of 1100 to 3200 psi. The steady-state creep rate was also determined for a lower density (90 percent of theoretical), coarser grained (10 to 15 μ) material at 1210 C and 2500 psi. Creep tests were initiated utilizing coprecipitated material which had higher densities (96 percent of theoretical) and larger grain sizes (25 to 35 μ).

The activation energy for creep of the fine-grained mechanically blended material was determined to be 77 kcal per mole. The stress exponent (n) at 1210 C for stresses from 1500 to 3200 psi was 1.4. No detectable differences in properties were found to be associated with specimen configuration, hollow or solid cylinders. Erratic behavior during the long-term creep test was experienced with this fine-grained material that resulted from thermal- and stress-induced grain growth. This phenomenon was minimized at low temperature and low stress (1100 C and 1500 psi). Coarser grained, mechanically blended material had a lower creep rate. This lower creep rate correlated well with the creep rates of the fine-grained material assuming that creep rate was proportional to the reciprocal of the grain size squared. This material proceeded into tertiary creep at a strain level of less than 1 percent. Preliminary results for the coprecipitated material indicate that at strain levels of approximately 2 percent the specimens fracture.

Summary of Research Carried Out

Compressive creep tests were performed with UO_2 and various types of UO_2 -22 w/o PuO_2 in the temperature range from 1030 to 1330 C and at stresses in the range from 1100 to 3765 psi. Initial creep tests to establish the performance of the creep cage and the LVDT recording unit were carried out with a UO_2 specimen that had been precharacterized and reported in the UO_2 creep results of BMI-1868. The succeeding creep tests were done using both hollow and solid cylindrical specimens which were fabricated from either mechanically blended or coprecipitated UO_2 -22 w/o PuO_2 . Variables in the mixed-oxide specimens, which will be discussed more in detail later, included density and grain size. All creep tests were performed in vacuum (approximately 5×10^{-6} torr) in a creep cage of TZM. Thoriated tungsten platens were in direct contact with the specimen. The results from these creep tests are shown in Table C-6. Typical creep curves are shown in Figure C-11.

Preliminary trials with a UO_2 hollow specimen indicated that the creep cage and LVDT recording unit were performing in a satisfactory manner. A minor problem related to nonparallel alignment of the platens was corrected after the first run. An attempt to reface this specimen appeared to be successful, but the creep curve obtained during the second test was not interpretable because of the formation of six symmetrical longitudinal cracks, approximately 1/4 in. long and positioned slightly above and below the specimen midplane.

Extensive tests were performed with mechanically blended UO_2 -22 w/o PuO_2 with a density of 94 ± 1 percent of theoretical and a uniform grain size of 3 to 5 μ . Both hollow and solid cylindrical specimens were tested. The oxygen/metal ratio of the specimens as fabricated was 1.98 ± 0.01 and the oxygen/metal ratio of specimens after creep trials at 1030 to 1175 C was found to be 1.99 ± 0.01 . The first two creep tests showed the specimens went almost immediately from primary to tertiary creep. The specimen in the third creep test (Specimen E73, Curve A of Figure C-11) showed normal behavior with a second-stage creep region for the first 72 hr. At that point, the creep rate abruptly increased by a factor of 2.5 and the deformation continued in a near-linear manner for the next 222 hr to a total strain of approximately 10 percent without any

TABLE C-6. RESULTS OF UO_2 AND UO_2 -22 w/o PuO_2 CREEP TESTS

Material	Specimen Identification	Type	Creep Test Parameters			Secondary Creep Rate, hr^{-1}	Final Oxygen/Metal Ratio
			Temperature, C	Stress, psi	Time, hr		
UO_2	G-1	Hollow	1100	2500	350	3.4×10^{-5}	--
	G-1	Hollow	1200	3765	42	1.05×10^{-4}	--
	G-1	Hollow	1200	3500	52	--	--
UO_2 -22 w/o PuO_2 (3-5 μ)	E58	Hollow	1030	3500	234	--	2.00
	E57	Hollow	1175	2500	45	--	1.99
	E73	Hollow	1175	2500	294	1.58×10^{-4}	1.98
	E64	Hollow	1100	1100	364	1.52×10^{-5}	--
	E64	Hollow	1100	1500	536	1.21×10^{-5}	--
	E52	Solid	1100	1500	234	1.37×10^{-5}	--
	E52	Solid	1210	1500	68	1.10×10^{-4}	--
	E52	Solid	1210	2500	29	2.29×10^{-4}	--
	E52	Solid	1210	3200	30	2.32×10^{-4}	--
	E52	Solid	1210	1500	22	8.15×10^{-5}	--
	E52	Solid	1330	1500	28	4.81×10^{-4}	--
UO_2 -22 w/o PuO_2 (10-15 μ)	H13	Hollow	1210	2500	197	2.09×10^{-5}	--
	H15	Hollow	1210	2500	120	2.08×10^{-5}	--
	H15	Hollow	1210	1500	190	6.48×10^{-5}	1.99
UO_2 -21.77 w/o PuO_2 (25-35 μ)	H37	Solid	1300	3500	23	--	--
	H50	Hollow	1300	2500	37	--	--

FIGURE C-11. COMPRESSIVE CREEP RESULTS FOR VARIOUS UO_2 -22 w/o PuO_2 SPECIMENS

definite indication of tertiary creep. In all of these mixed-oxide specimens, measurements after creep testing indicated that the hollow cylinders were expanding more at the ends than in the middle. The temperature profile along the longitudinal axis, which was determined by attaching thermocouples to a specimen, showed that the ends were slightly cooler than the middle and that the temperature gradient was approximately 15 C. Metallographic examination of specimens indicated that the erratic behavior was associated with thermal- and stress-induced grain growth in the triaxially stressed region near the platen. This is illustrated in Figures C-12 and C-13 with the photographic details for Specimen E73. The conical fracture or weakened plane shown in Figure C-13 extended into the wall at an angle of approximately 45 deg and traversed the entire cross section. This fracture most probably resulted from a strengthening effect due to the increased grain size of 20 to 40 μ in the region between the plane and the contact face. To overcome this erratic behavior, creep tests were performed at a lower temperature and a lower stress. The results obtained with Specimen E64 (Curve D of Figure C-11) in two successive tests indicated that the difficulties were eliminated at these lower test parameters. Grain growth was still observed in the triaxially stressed region but the grain size had only increased by a factor of two, 5 to 10 μ . This feature may contribute to the lower creep rate that was observed after the stress was increased from 1100 to 1500 psi. Other than the slight increase in grain size as described, the fine-grained $\text{UO}_2\text{-22 w/o PuO}_2$ appeared to maintain dimensional stability and physical integrity for an extended time period when tested at 1100 C with stresses in the range from 1100 to 1500 psi.

A series of creep tests was performed with a single solid cylindrical specimen (E52) over a temperature and stress range to establish the stress exponent (n) and the activation energy for creep of the fine-grained, mechanically blended mixed-oxide material. Tests at 1210 C were carried out first with various stresses which were applied in the order of 1500, 2500, 3200 and 1500 psi. A stress exponent of 1.4 was calculated from the plot shown in Figure C-14. The calculated stress exponent ($n = 1.4$) is about as expected in the low stress-low temperature region where diffusional mechanisms ($n = 1$) rather than dislocation movement ($n = 4.5$) predominate.

Following the creep tests at 1210 C, the solid cylindrical specimen (E52) was creep tested at a stress of 1500 psi, first at 1100 C and finally at 1330 C. A plot of the creep rates against the reciprocal of the absolute temperature for this specimen is shown in Figure C-15. From the slope of this line, the activation energy for creep was calculated to be 77 kcal per mole. This value is lower than the 90 to 110 kcal per mole reported in other $\text{UO}_2\text{-PuO}_2$ creep studies^(1,2). Creep results obtained in the earlier tests with hollow, fine-grained, mechanically blended specimens are also plotted in Figure C-15 and indicate that the specimen configuration has little effect upon the observed creep properties.

Mechanically blended mixed-oxide specimens were fabricated with a density of 90 ± 1 percent of theoretical, a grain size of 10 to 15 μ , and an oxygen/metal ratio of 1.95 ± 0.01 . The typical creep behavior for this material is shown in Figure C-11, Curve C (Specimens H13 and H15). These specimens have a lower creep rate than the fine-grained ones and proceed into accelerated creep at a strain level of less than 1 percent. The steady-state creep rate for the 10 to 15- μ material is approximately as expected based on the creep behavior of the 3 to 5- μ material and assuming a $1/D^2$ (D = grain diameter) dependence. This is shown in Figure C-15 where both the actual and calculated creep rates are plotted. The lower density of this material does not appear to make a significant contribution, but the distribution of the large porosity along the grain boundaries may have a weakening effect that leads to tertiary creep at the low strain level. The apparent discrepancy in the creep rates shown in Table C-6 for Specimen H15 when the stress was lowered from 2500 to 1500 psi is due to the strain level of the specimen at the time of the change in stress. It is assumed that the specimen at this strain level was on the threshold of accelerated creep. From the microstructures of the coarser grained specimens after creep, two details are apparent: (1) grain growth

FIGURE C-12. TYPICAL ETCHED MICROSTRUCTURES FOR SINTERED AND DEFORMED $\text{UO}_2\text{-22 w/o PuO}_2$ SPECIMENS

50X

PL7370

a. Inside Diameter

Creep Parameters:

2500 psi

1175 C

294 hr

9.3 percent strain

50X

PL7371

b. Outside Diameter

FIGURE C-13. PHOTOMACROGRAPHS OF CONTACT END ON DEFORMED UO_2 -22 w/o PuO_2 SPECIMEN

FIGURE C-14. CREEP RATES OF $\text{UO}_2\text{-22 w/o PuO}_2$ AT 1210°C AS A FUNCTION OF STRESS

FIGURE C-15. CREEP RATE VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE FOR MECHANICALLY BLENDED $\text{UO}_2\text{-22 w/o PuO}_2$ SPECIMENS

was negligible and (2) a slight amount of grain-boundary parting in the triaxially stressed region was observed. The oxygen/metal ratio of the material was found to be 1.99 ± 0.01 , which compares favorably with the final oxygen/metal ratio determined with the fine-grained specimens. This indicates that the mixed-oxide material, initially at an oxygen/metal ratio of 1.95, equilibrated to the higher oxygen level during the test. This equilibration, based on the kinetics of the process, should have been completed in the first hour or two at temperature.

High-density, large-grained creep specimens were next produced from coprecipitated UO_2 -21.77 w/o PuO_2 . These specimens had a density of 93 (Specimen H50) to 96 (Specimen H37) percent of theoretical and an average grain size in the range from 25 to 35 μ , respectively. Preliminary tests on two specimens, one hollow and one solid, have produced failure in a relatively short time at a strain level of 2 to 3 percent. A steady-state creep region was not observed with the solid specimen before fracture. The steady-state creep rate determined for the hollow specimen appears to be too high by one or two orders of magnitude. This high creep rate may be associated with the microstructural details peculiar to the lower density specimen, which showed elongated porosity aligned in such a manner that the longitudinal axis of the pore was parallel to the end face of the creep specimen. This porosity problem has since been overcome by use of a lower heatup rate during the sintering cycle. Numerous high-density specimens are in the machining stage, and creep tests with these specimens will be initiated as soon as dimensional finishing has been completed.

Plans for Future Work

Creep testing of UO_2 -22 w/o PuO_2 specimens from both mechanically blended and coprecipitated powders will continue. Tests will be run at temperatures of 1100 to 1300 C and stresses of 1500 to 5000 psi to determine the characteristic out-of-pile creep data for the mixed-oxide material and to aid in the selection of material and optimum test conditions for in-pile trials.

- (1) Sheely, W. F., "Reactor Fuels and Materials Development Programs For Fuels and Materials Branch, Quarterly Progress Report, July-September, 1969", BNWL-1223 (November, 1969).
- (2) Bohaboy, P. E., Asamoto, P. R., and Conti, A. E., "Compressive Creep Characteristics of Stoichiometric Uranium Dioxide", GEAP-10054 (May, 1969).

Mechanisms of Creep in UO_2 and UO_2 - PuO_2

M. S. Seltzer, A. H. Clauer, and B. A. Wilcox

Objective of Program

To provide a method for predicting the results of neutron irradiation on the compressive creep behavior of UO_2 and UO_2 - PuO_2 by combining a program of creep experiments on unirradiated materials with an analysis of the known effects of the fission process on the properties and microstructures of these materials.

Approach Being Used

The experimental phase of the program involves studies on the creep of unirradiated single-crystal and polycrystalline UO_2 as influenced by (1) temperature, (2) compressive stress, (3) stoichiometry, and (4) microstructure, including grain size and voids (porosity). Tests are being performed in compression in a controlled-atmosphere creep apparatus, using cylindrical specimens prepared by ultrasonic machining. Creep properties are being examined in light of structural changes as revealed by transmission-electron microscopy and etch pitting.

The theoretical analysis includes two phases: (1) an analysis of creep data gathered in this program to ascertain the modes and mechanisms of creep in UO_2 , and (2) a

collaborative effort with other task scientists to examine the known effects of the fission process on those properties of UO_2 and $\text{UO}_2\text{-PuO}_2$ which may influence creep rates in these materials, and from this survey to make predictions about the effects of neutron irradiation on the creep behavior of UO_2 and $\text{UO}_2\text{-PuO}_2$.

Significant Accomplishments During Fiscal Year 1970

Studies of the influence of stress, temperature, and stoichiometry on the creep behavior of single-crystal uranium dioxide have been completed. Values for creep rates of UO_{2+x} and the activation energies for high-temperature creep of this material have been found to be strongly dependent upon the oxygen/uranium ratio of the specimens tested. In the power-law stress regime (10,000 psi) the activation energy, Q , decreases from 135 kcal per mole to 57.5 kcal per mole as the oxygen/uranium ratio increases from 2.0001 to 2.062. Over this same range of compositions creep rates increase by some three to five orders of magnitude in the temperature range of 1100 to 1300 C. This dependence of creep rates on oxygen/uranium ratio can be expressed as $\dot{\epsilon} \propto x^2$ for values of x above 0.003.

At lower stresses, whose values depend on temperature and composition, creep rates for UO_{2+x} single crystals are found to decrease linearly with decreasing stress. At a typical stress in this linear stress region (3000 psi) creep rates appear to be nearly independent of stoichiometry and the creep activation energy has a value of approximately 130 kcal per mole, nearly identical to that found in the power-law stress region for "stoichiometric" uranium dioxide single crystals.

Some transmission-electron microscopy has been performed on nonstoichiometric UO_{2+x} specimens deformed some 10 percent in compression. Many features of these unirradiated specimens resemble features that have previously been attributed to neutron irradiation.

Work has been initiated to study the effects of temperature, stress, grain size, density, and stoichiometry on the creep of polycrystalline uranium dioxide. At 1100 C, creep rates have been found to increase with increasing stress and with increasing oxygen/uranium ratio and to increase with decreasing grain size. For specimens having a grain size of 6 to 7 μ and a density of 95 percent of theoretical, creep rates increase linearly with stress for low stresses ($\dot{\epsilon} \propto \sigma$) and follow a power-law dependence where $\dot{\epsilon} \propto \sigma^4$ at high stresses. Creep tests with specimens having a 4- μ grain size and a density of 92 percent of theoretical show only the linear stress dependence. In the linear stress region $\dot{\epsilon} \propto x$, while in the power-law stress region $\dot{\epsilon} \propto x^{1.75}$, approximately the same dependence on stoichiometry as was found for single-crystal creep. For the 6 to 7- μ specimens, the stress at which the transition in stress dependence occurs decreases from 20,000 psi to 5,500 psi as the oxygen/uranium ratio increases from 2.001 to 2.05.

Summary of Research Carried Out

The results obtained for UO_{2+x} single crystals in the region $0.0001 < x < 0.121$ at 1100 C are given in Figure C-16, which is a log-log plot of creep rate, $\dot{\epsilon}$, versus applied stress, σ . The results for each composition were obtained from a series of stress changes on a given specimen. Thus, the five compositions shown in Figure C-16 represent five different specimens. In order to demonstrate the reproducibility of the results, the oxygen/uranium ratio for the specimen used to obtain $\text{UO}_{2.0001}$ was changed, after the data for this composition had been obtained, to give a final composition of $\text{UO}_{2.01}$. This was done by removing the load, reequilibrating the specimen under a CO/CO_2 atmosphere to give the new oxygen/uranium ratio, then reapplying the load. Results obtained from this experiment are represented by the solid triangles for $\text{UO}_{2.01}$ at 12,000, 9,000, and 7,500 psi in Figure C-16. Excellent agreement is found between the data from the two different specimens of $\text{UO}_{2.01}$. Also included in the figure are results

FIGURE C-16. CREEP RATE AS A FUNCTION OF APPLIED STRESS FOR UO_2 SINGLE CRYSTALS TESTED IN COMPRESSION AT 1100 C

"Stoichiometric" UO_2 was tested in hydrogen while nonstoichiometric compositions were obtained under CO/CO_2 atmospheres.

obtained from a specimen equilibrated in hydrogen to give "stoichiometric" UO_2 . The composition of the specimen with an oxygen/uranium ratio of 2.121 was determined by chemical analysis, while the other compositions are those in equilibrium with the CO/CO_2 gas mixtures employed in the test.

For nonstoichiometric UO_2 the creep rate is seen to be a very sensitive function of the stress. If a power-law stress dependence is assumed where $\dot{\epsilon} \propto \sigma^n$, then $n \approx 17$ for oxygen/uranium ratios $\gtrsim 2.001$ according to results obtained in this study and from those obtained by Nadeau⁽¹⁾, while $n = 13$ for an oxygen/uranium ratio of 2.0001. For the case of stoichiometric UO_2 , $n \approx 7$. As shown in Figures C-17 and C-18, the creep curves for stoichiometric and nonstoichiometric UO_2 differed, with sigmoidal creep being observed in the latter case (see Figure C-17) while creep of stoichiometric UO_2 was of the classical form with a region of instantaneous deformation followed by primary and steady-state creep (Figure C-18). Although a high stress dependence was observed for all nonstoichiometric UO_2 tested, the tendency toward sigmoidal creep appeared to increase with increasing oxygen/uranium ratio, and was not observed for $\text{UO}_{2.001}$ or $\text{UO}_{2.0001}$. For the specimen in which the oxygen/uranium ratio was changed during the test, sigmoidal creep was observed at the $\text{UO}_{2.01}$ composition, but not when the oxygen/uranium ratio was 2.0001.

For the range of compositions $x = 0.001$ to 0.121, it is seen that $\dot{\epsilon} \propto x^2$ at a given stress. This is in accord with previous studies of the composition dependence for uranium diffusion⁽²⁻⁴⁾, and suggests that high-temperature creep is controlled by the diffusion of U^{4+} via uranium vacancies. The implications of an x^2 composition dependence are clear from examination of Figure C-16. Under a constant stress, for example, the creep rate of UO_2 can be expected to increase by four orders of magnitude if the oxygen/uranium ratio changes from 2.0001 to 2.01, which still represents only a small oxygen excess.

In addition to the considerable sensitivity of creep behavior to changes in stoichiometry, these experiments revealed a very high stress dependence for the creep rate, which apparently varies with stoichiometry for compositions below $\text{UO}_{2.001}$. The shape of the strain-time curves obtained from compression creep tests also varied from sigmoidal for compositions $\gtrsim \text{UO}_{2.01}$ to the typical primary and steady-state behavior for compositions $\lesssim \text{UO}_{2.001}$. These results suggest that a transition in creep behavior occurs as the UO_2 stoichiometry is varied. One possible interpretation of the observed behavior involves the interaction of charged dislocations with charged point defects. Yust and McHargue⁽⁵⁾ have shown that the dynamic compressive shear stress for UO_2 may be controlled by the force required to free charged dislocations from a surrounding charge cloud consisting of impurity atoms or charged vacancies.

In light of these findings it is suggested that the sigmoidal creep found for high oxygen/uranium ratios results from the pinning of dislocations by the high concentrations of charged point defects in these crystals. Once the dislocations break away from their charge clouds, the usual characteristics of accelerated creep followed by a steady-state region are observed. The very high apparent dependence of the creep rate on applied stress may then reflect large internal stress fields resulting from the point defect-dislocation interactions. The existence of high internal stresses has been postulated⁽⁶⁾ to account for apparent high stress dependencies found for creep of dispersion-strengthened metals such as thoriaed nickel (TD Nickel) where a creep exponent of 40 has been obtained⁽⁷⁾. In these cases it is expected that the dependence of creep rates on effective stress (applied stress minus internal stress) would be on the order of 4 to 5 predicted by various dislocation theories of creep. In complex alloys such as TD Nickel it is possible that the effective stress acting on dislocations may only be a small fraction of the applied stress.

Somewhat more limited data on the stress dependence for creep of nonstoichiometric UO_{2+x} have been obtained at 1300 and 1400 C and are presented in Figure C-19. At high

FIGURE C-17. STRAIN AS A FUNCTION OF TIME FOR SINGLE-CRYSTAL $\text{UO}_{2.01}$ TESTED AT 1100 C UNDER 10,000 PSI

FIGURE C-18. STRAIN AS A FUNCTION OF TIME FOR SINGLE-CRYSTAL $\text{UO}_{2.0000}$ TESTED AT 1300 C UNDER 10,000 PSI

stresses the creep rates follow a power-law dependence with n increasing from 7 to 10 with increasing oxygen/uranium ratio. Tests performed at low stresses reveal a sharp break in the strain rate-stress behavior, creep rates decreasing linearly with decreasing stress in the low-stress region. Furthermore, it is seen in Figure C-19 that creep rates are nearly independent of composition in the low-stress region, in contrast to the power-law regime where $\dot{\epsilon} \propto \sigma^2$. The significance of the data suggesting a low-stress region for UO_{2+x} single crystals will be discussed in detail below.

In order to determine the effects of temperature on creep of hyperstoichiometric uranium dioxide a series of tests was conducted at 10,000 psi in the temperature range of 1100 to 1400 C on specimens whose oxygen/uranium ratio was fixed by varying the oxygen partial pressure to the appropriate value as the testing temperature was changed. Results obtained are presented in Figure C-20 as creep rate versus reciprocal of absolute temperature. Also included in this figure are data for "stoichiometric" UO_2 . It is seen that creep rates increase with increasing oxygen/uranium ratio, and furthermore, that the activation energies for creep decrease with increasing oxygen excess. The dotted points shown at 1100 C for low oxygen/uranium ratios represent values obtained by extrapolating the data given in Figure C-16. The fact that they appear to be higher than expected reflects the lower stress dependence found for these compositions.

The effect of changing stoichiometry is greatest at 1100 C and decreases with increasing temperature. This is presumably the result of an increasing contribution of thermally created uranium vacancies to the total defect concentration with increasing temperature. At compositions above $\text{UO}_{2.05}$ the activation energy for creep appears to reach a plateau value of 57 kcal per mole. This may represent the enthalpy of migration for a uranium vacancy under conditions where the vacancy concentration is fixed, independent of temperature.

Activation energies for creep determined from the slopes of the lines in Figure C-20 are plotted in Figure C-21 as a function of $\log_{10}x$. The activation energies decrease from 134 to 57 kcal per mole with increasing oxygen/uranium ratio. Also included in this figure are creep activation energies determined in previous studies. The values reported all fall within the range found in this investigation.

The information presented in Figure C-21 perhaps most clearly points out the need to define the stoichiometry of uranium dioxide for which creep data are being reported. It is seen that the activation energies obtained in this study span the entire range of values previously reported to represent the correct energies for creep of stoichiometric uranium dioxide. In actuality, examination of Figure C-21 suggests that the compositions tested probably encompassed the range of $0.0001 < x < 0.007$. The question of applying a given composition to a particular activation energy is complicated, however, by the fact that some data have been obtained from fine-grained polycrystals in the linear-stress-dependence region, where grain-boundary-diffusion effects may contribute to the creep process.

The activation energies for creep of single-crystal UO_{2+x} in the low-stress-dependence region have been determined by testing at 3000 psi in the temperature range of 1250 to 1400 C. Results are included in Figure C-22 for tests performed in hydrogen to give "stoichiometric" uranium dioxide and in CO/CO_2 to give an oxygen/uranium ratio of 2.01. The activation energies are found to be 129.4 kcal per mole for "stoichiometric" UO_2 and 131.5 kcal per mole for $\text{UO}_{2.01}$, which are nearly the same as the values obtained in the high-stress region for "stoichiometric" UO_2 . In addition, over the temperature range studied, the creep rates are nearly independent of composition. These results are of course in marked contrast to those for creep at 10,000 psi, where activation energies are a sensitive function of composition and where creep rates increase markedly with oxygen/uranium ratio.

The low stress dependence for single-crystal creep, observed under conditions of low applied stress, is somewhat unexpected. This variation of creep rate with stress is

FIGURE C-19. CREEP RATE AS A FUNCTION OF APPLIED STRESS FOR UO_2 SINGLE CRYSTALS TESTED IN COMPRESSION AT 1300 AND 1400 C

FIGURE C-20. CREEP RATE AS A FUNCTION OF TEMPERATURE FOR UO_{2+x} SINGLE CRYSTALS TESTED AT 10,000 PSI

FIGURE C-21 ACTIVATION ENERGIES FOR CREEP OF UO_{2+x} AS A FUNCTION OF $\text{LOG}_{10} x$

FIGURE C-22 CREEP RATE AS A FUNCTION OF TEMPERATURE FOR UO_{2+x} SINGLE CRYSTALS TESTED AT 3000 PSI

usually associated with grain-boundary sliding or Nabarro-Herring diffusional creep, two processes which are frequently invoked to explain the creep behavior of fine-grained polycrystalline solids. Furthermore, the creep rates in the low-stress region are nearly independent of composition, which, as will be seen below, is in contrast to results obtained with polycrystalline UO_{2+x} in the low-stress region, where creep rates increase linearly with the oxygen excess, x . It is hoped that studies of the dislocation structures of UO_2 specimens tested in the various stress regions will aid in obtaining an understanding of the operative creep mechanisms for the conditions of stress, temperature, and composition imposed on the specimens.

Transmission-electron microscopy has been initiated on a specimen, tested in the high-stress region, having the composition $\text{UO}_{2.01}$ after creep at 1100 C to about 10 percent creep strain. Thin slices were cut from the specimen parallel to a $\{111\}$ plane using a diamond saw. The slices were then shaped into disks by grinding, and thinned chemically using the method of Manley⁽⁸⁾. Figure C-23a shows a representative area including the main characteristics of the substructure. These are the faults marked "A", the voids or spherical precipitates marked "B", and a low dislocation density. The detailed character of the faults and the spherical voids or precipitates must still be determined.

The large density of the faults and "voids" may be characteristic of the large non-stoichiometry of this specimen. Yust and McHargue⁽⁵⁾, in their study of deformation substructure in stoichiometric UO_2 , did not observe either of these features. The low dislocation densities observed here are related to the low stress levels associated with the creep.

Figure C-23b is a transmission micrograph from a recent monograph⁽⁹⁾ showing UO_2 irradiated to 1.6×10^{20} fissions per cm^3 at 100 C and postirradiation annealed at 1500 C for 1 hr. Certain of the features observed in the two figures appear to be similar, such as the voids or spherical precipitates, some of which are pinning dislocations, and the generally low dislocation density.

In order to further our understanding of the effects of stoichiometry on the compression creep of UO_2 , a series of tests was performed on polycrystalline specimens whose compositions were varied in the range of $2.001 < \text{O/U} < 2.05$. The tests were conducted under stresses of 2,000 to 24,000 psi at 1100 C on specimens with densities of 95 percent of theoretical and average grain diameters of 6 to 7 μ , and on specimens with densities of 92 percent of theoretical and a grain size of 4 μ . Results obtained are included in Figure C-24.

Creep rates for the coarser-grained material are seen to increase linearly with stress for low stresses ($\dot{\epsilon} \propto \sigma$), as was found for the finer-grained specimens, but at high stresses the creep rates follow a power-law stress dependence where $\dot{\epsilon} \propto \sigma^4$. These results are similar to those reported previously⁽¹⁰⁻¹²⁾ for creep of stoichiometric polycrystalline UO_2 . The important feature of the present results is that the two different stress dependencies are found to occur for a number of different compositions and that the transition from a linear stress dependence to a power-law dependence occurs at stresses which decrease with increasing oxygen/uranium ratio. As is seen in Figure C-24 the transition stress decreases from 20,000 psi to 10,000 psi to 5,500 psi as the oxygen/uranium ratio increases from 2.001 to 2.01 to 2.05.

This variation in transition stress comes about because of differences in the composition dependence of the creep rates in the two different stress regions. In the region of linear stress dependence the creep rates increase linearly with x ($\dot{\epsilon} \propto x$). This is true both for the 4- μ and the 6 to 7- μ specimens. In the power-law stress-dependence region, on the other hand, creep rates increase with $x^{1.75}$. This result, which is the first reported measurement of the influence of stoichiometry on creep of polycrystalline UO_{2+x} in the power-law region, is consistent with past work which has shown that different diffusion mechanisms control the creep process in the two different stress

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a. $\text{UO}_{2.01}$ After Creep at 1100 C to ~10 Percent Creep Strain

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b. UO_2 Irradiated to 1.6×10^{20} Fissions per cm^3 at 100 C and Postirradiation Annealed at 1500 C for 1 Hr

FIGURE C-23. TRANSMISSION-ELECTRON MICROGRAPHS OF UO_2 SPECIMENS

FIGURE C-24. CREEP RATE AS A FUNCTION OF STRESS AT 1100 C FOR POLYCRYSTALLINE UO_{2+x} AT VARIOUS COMPOSITIONS

regions. In the σ^1 region (fine grain size and low stress) creep is controlled by uranium grain-boundary diffusion with an activation energy of ~ 90 kcal per mole, and $\dot{\epsilon} \propto \sigma$. In the power-law region (coarse grain size or single crystals and high stresses) creep is controlled by uranium bulk diffusion with a variable activation energy in the range of 55 to 135 kcal per mole and $\dot{\epsilon} \propto \sigma^2$ for high oxygen/uranium ratios. In the experiments with 6 to 7- μ material reported here, $\dot{\epsilon} \propto \sigma^{1.75}$ for high stresses, which may suggest some grain-boundary contribution to the creep process.

Plans for Future Work

Studies with UO_{2+x} single crystals have been completed. In the immediate future, testing will be conducted using polycrystalline specimens from the same material as that employed in the in-pile creep capsules. These are high-density, enriched UO_2 specimens with an average grain diameter of 27 μ . Experiments will be performed to determine the influence of stress, temperature, and composition on creep behavior. The results obtained will be directly applicable to interpretation of in-pile creep data.

Later experiments will be conducted with specimens of varying density and grain size to establish the effects of stress, temperature, and composition on specimens in the density range from 84 to 97 percent of theoretical and having grain sizes from 1 to 30 μ .

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