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Quarterly Status Report on the

# Advanced Plutonium Fuels Program

January 1 to March 31, 1971

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

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# FOREWORD

This is the 19th quarterly report on the Advanced Plutonium Fuels Program at the Los Alamos Scientific Laboratory.

Most of the investigations discussed here are of the continuing type. Results and conclusions described may therefore be changed or augmented as the work continues. Published reference to results cited in this report should not be made without obtaining explicit permission to do so from the person in charge of the work.

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## PROJECT 401

## EXAMINATION OF FAST REACTOR FUELS

Person in Charge: R. D. Baker
Principal Investigators: J. W. Schulte
K. A. Johnson
G. R. Waterbury

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## I. INTRODUCTION

This project is directed toward the examination and comparison of the effects of neutron irradiation on LMFBR Program fuel materials. Unirradiated and irradiated materials will be examined as requested by the Fuels and Materials Branch of DRDT. Capabilities are established for providing conventional pre-irradiation and post-irradiation examinations. Additional capabilities include less conventional properties measurements which are needed to provide a sound basis for steady-state operation of fast reactor fuel elements, and for safety analysis under transient conditions.

Analytical chemistry methods that have been modified and mechanized for hot cell manipulators will continue to be applied to the characterization of irradiated fuels. The shielded electron microprobe and emission spectrographic facilities will be used in macro and micro examinations of various fuels and clads. In addition, new capabilities will be developed with emphasis on gamma scanning and analyses to assess spatial distribution of fuel and fission products.

High temperature properties of unirradiated LMFBR fuel materials are now being determined by Contractor in an associated project (ident. No. 07463). Equipment designs and interpretive experience gained in this project are being extended to provide unique capabilities such as differential thermal analysis, melting point determination, high temperature dilatometry, and high temperature heat content and heat of fusion for use on irradiated materials.

## II. EQUIPMENT DEVELOPMENT

### A. Inert Atmosphere Systems

(D. D. Jeffries, P. A. Mason, R. F. Velkinburg, L. A. Waldschmidt)

1. Disassembly Cell. The inert atmosphere in the disassembly cell was maintained continuously during this quarter by a purifier system capable of removing $O_2$ and $H_2O$ from the gas stream. Typical concentrations during the report period were < 10 ppm $O_2$ and < 3 ppm $H_2O$. Minimum concentrations of 2.8 ppm $O_2$ and 0.6 ppm $H_2O$ were achieved numerous times. Both manipulator boots were replaced during March due to increased leak rates.

2. Metallography Cells and "Blister". The metallography cells were maintained on an Ar purge until replacement tanks for the gettering chemicals for $O_2$ could be fabricated. The original stainless steel tanks were severely damaged by corrosion described in LA-4595-MS. New tanks were designed and fabricated of 1/8-in. thick copper with externally mounted heaters. Installation was completed early in March and the purifier system has performed satisfactorily since that time. Typical concentrations of < 5 ppm $O_2$ and < 5 ppm $H_2O$ are being achieved in both cells. Minimum concentrations of 2.6 ppm $O_2$ and 0.6 ppm $H_2O$ have been observed.

The metallograph blister was operated on an Ar purge throughout the report period, with concentrations of < 15 ppm $O_2$ and < 8 ppm $H_2O$ being maintained. Minimum concentrations of 5.5 ppm $O_2$ and 2.5 ppm $H_2O$ were achieved.

3. Miscellaneous Items. Equipment was installed in the two chemistry cells to permit an Ar purge of alpha boxes in these areas when required.

Fabrication of the 7-in.-alpha-can, "inerting" station was completed and installed. Several modifications were made to improve the reliability of the unit.

The SPI-10 analyzer was returned to the factory for repairs. Upon receipt of the unit from the factory, tests were performed using air, Ar supply gas, and sample gas from the disassembly cell. Partial pressure readings in the 10 ppm range were detectable.

A new water jacket was fabricated and installed on a purifier purge vent line to correct leaks caused by corrosion after three months of service.

A vacuum regeneration system was designed and fabricated for the U. S. Dynamics RSD purifier system for removing moisture. Installation is planned in April during a scheduled power outage.

## B. Manipulators

(P. A. Mason, C. D. Montgomery, R. F. Velkinburg)

Leak tests were performed on the two model "L" manipulators received during the previous quarter. A boot assembly was attached to the manipulator arm and the boot purged and pressurized to 5 in. water column. No leakage was observed through either manipulator assembly using a Veeco Helium Leak Detector with a sensitivity of $1.3 \times 10^{-10}$ atm cc/sec. Two previously fabricated manipulator adapter sleeves were modified to include provisions for an Ar gas purge of the boot interior. Experiments were performed on a modified boot seal-collar assembly to permit gas from the recirculating purifier to be vented through the boot and into the alpha box.

Molds for the manipulator through-tube seals were modified to achieve the specified diameters; some difficulty was encountered in predicting the shrinkage of the molded material.

Thirty-five-lb lead weights were installed in the slave end of the AMF manipulators in the metallography cells. This corrected the problem of leaks due to the imbalance described in the preceding quarterly report, LA-4595-MS.

Use of butyl acetate as a solvent in the metallography cells has caused rapid deterioration of the molded PVC gauntlets on the manipulator boots and of the neoprene finger pads. A complete change of boots was required in January and March. An experiment exposing PVC, neoprene, polyurethane, and polyethylene films to butyl acetate vapors caused rapid and severe deterioration of the PVC and some swelling of the neoprene. Consideration is being given to fabricating manipulator boots from polyurethane. Inquiries are being made to locate an economical gauntlet (or bellows) from a commercial supplier.

## C. Thermal Diffusivity

The furnace has been tested to maximum power, and a temperature of 2850°C has been attained. The supplier has guaranteed a temperature of 3000°C and will supply a transformer to boost the power of the present unit to attain the specified temperature.

## D. In-Cell Equipment

(J. W. Dahlby, F. J. Fitzgibbon, M. E. Lazarus, J. L. Lehmann, P. A. Mason, C. D. Montgomery, A. E. Tafoya, J. R. Trujillo)

1. Sodium Distillation Apparatus. The unit has been installed in a hot cell and is undergoing final testing. It will use the vacuum system formerly attached to the carbon evaporator.

2. Microsampling System. A precision X-Y coordinate positioning stage has been ordered for incorporation into the sampling system. Slo-Syn stepping motors and a control unit have also been ordered. A new type of rotary ultrasonic core drill head is presently being investigated for this system.

Fabrication of the metallography mount holder has been completed. Tests were performed on mounts from "Noryl" plastic. Although the material withstood $1.4 \times 10^{8}$ r gamma exposure from a $^{60}$Co source and was resistant to the customary acid etch solutions and some solvents, it was not compatible with the butyl acetate and Hyprez solutions currently being used as vehicles for the grinding-polishing operations. Consequently, other plastics will be tested to find a suitable material.

3. Sealed Tube System for Chemical Dissolution. The equipment for the dissolution of irradiated materials by the sealed tube method has now been installed in one

of the analytical chemistry cells. Preliminary tests were carried out satisfactorily.

4. Remote Cut-Off Saw. Modifications have been accomplished on the new remote cut-off saw to provide a manipulator actuation on the power feed engagement. A rolling closure curtain over the table feed and ball bushing mechanism is being incorporated to protect the sensitive parts from dust and film accumulations. These changes will improve the reliability and extend the service life of the saw.

5. Optical Gauge for Diameter Measurements. A Bausch and Lomb DR 25 B optical gauge is being modified for use in a beta-gamma cell for making diameter measurements on capsules and pins. The device will replace the remotely operated micrometers now being used for these measurements. The instrument which has a reported accuracy of better than ± 0.0001 in. will also be considered as backup equipment for the Optical Profilometer to be installed in the DP West Facility.

6. Improved Method for Sealing Gas Sampling Holes. A new means of sealing the holes in capsule or pin cladding following gas sampling was developed to assure that the pin was tightly sealed with a radiation resistant material. Such materials as Silicone RTV, rubber tubing, Apiezon Q, had been considered but each had some deficiency. The heat shrinkable silicone rubber tubing was therefore investigated.

Hot air from a blower type heat gun was passed over a 2-in. length of heat-shrinkable silicone rubber tubing which had been placed on a capsule or pin cladding in the punctured area. The heat caused the silicone tubing to shrink uniformly onto the cladding and effect a seal. A typical rubber tubing shrank from 3/8 in. i.d. to 3/16 in. i.d.

A silicone tubing-stainless steel tube was exposed to 4 x $10^8$ r with a $^{60}$Co source. Following exposure, the silicone tubing was resilient and adhered to the stainless steel tubing as firmly as in the unirradiated condition.

7. Alternate Method for Removing Sodium from Capsules. The method previously developed for removing sodium from a capsule entailed melting the sodium in hot mineral oil with the capsule maintained in a horizontal position. Although this method was effective, it introduced the possibility of melting and redistributing the bonding-sodium used in some experimental mixed-carbide fuel pins. It is desirable to maintain the post-irradiation configuration of the sodium within the pin to comply with data preservation practices. This requirement is especially important if there is a possibility that the fuel pins will be re-encapsulated for TREAT irradiations.

Consequently, equipment has been fabricated and is being tested to melt sodium in an irradiated fuel capsule held vertically. It is desirable to remove residual sodium from the fuel pin surface in an environment which protects that surface from exposure to moist air in the presence of sodium.

The procedure entails removing the bottom end plug of the capsule using a saw and placing the capsule assembly quickly in the well of the vertical heater containing mineral oil. The temperature of the oil is raised to about 130°C to melt the sodium which is removed through a valve system. After cooling, the capsule cladding is removed and the remaining sodium in the mineral oil and on the fuel pin cladding is reacted with Dowanol EB. The fuel pin is then removed from the bath and washed with water and alcohol (in the same manner used with the "horizontal bath" method) to remove water-soluble deposits and films.

8. Development of Other Equipment. A tool to remove fuel from the inner surface of a section of fuel pin cladding prior to density measurements and other tests is being developed. A small-diameter, motor-operated, wire brush is being considered as a reaming tool for in-cell use.

A suggestion from ANL (Ill.) personnel was made regarding the scribing of a fiducial mark on the cladding at a known distance from the bottom of the fuel pin prior to profilometry measurements. This mark will serve as an accurate reference point and will be reproduced on each profilometer chart. Various tools and fixtures are being considered for applying the fiducial mark in an area which will not disturb other measurements or the integrity of the pin.

## E. New Metallograph Installation

(F. J. Fitzgibbon, K. A. Johnson, T. Romanik, C. D. Montgomery, R. F. Velkinburg)

The new installation for housing the two metallographs (new Leitz unit and the Bausch and Lomb unit currently in service) is in the design and fabrication stage. An ion etcher, which is still under development, and the image analyzer interface are also to be incorporated into this installation. Present status of this work is as follows:

1. Mini-Manipulator. Various tests have been made in the mockup blister to study the coverage and manipulating ability of the Mini-Manipulators. In an effort to improve this coverage, the manufacturer was called regarding the possibility of adjusting the angle of the vertical master-slave members. It was determined that this adjustment was feasible; additional tests will be carried out to establish the final conditions.

2. Alpha Containment Box. The new alpha containment box is presently being fabricated. The design is somewhat complicated by the requirements to accommodate the Leitz and Bausch and Lomb metallographs as well as the Ion Etcher in this sealed box system. Final modifications will have to be made after the box is received in order to custom-fit the penetrations, transfer ports, and other components previously mentioned.

3. Shielding. The design of the shielding for the new blister is approximately 90% complete. There is a considerable departure from previous designs in this shielding because of the need for thinner walls to accommodate the Leitz metallograph entry. It therefore became necessary to stack Pb bricks in a staggered array for one side to provide 8 in. of Pb plus steel encasement. The other walls will be made up of steel encased modules 12 in. thick and filled with Pb shot. The top of the blister shielding is presently planned as a steel box filled with Pb bricks to a 6-in. depth; additional shielding may be added if necessary. The viewing window contains 11.5 in. of 6.2 density Pb glass plus two 1-in.-thick cover plates of cerium stabilized glass. This design provides shielding equivalent to approximately 6 tenths-thicknesses which should be adequate for an activity of 3000 curies of 1.3 MeV (assumed average fission product energy) gamma-emitting materials.

The shielding enclosure is of modular construction which allows removal of separate sections for maintenance of the metallographs.

4. Metallographs. Negotiations are in progress to obtain a new stage of improved design for the Bausch and Lomb metallograph.

The Leitz unit has been checked out and is ready for installation.

## F. Scanning Electron Microscope

Special alpha-active materials have been examined during this quarter. In the next few months it is planned to examine unirradiated LMFBR-type fuel pellets.

A design was initiated to develop the specialized apparatus and shielding which are required for examining irradiated fuel and clad sections with this instrument.

## G. Miscellaneous Improvements

1. Betatron Radiography. Sometime during 1970 it was observed that the negatives obtained from radiography with the Betatron were not as "sharp" as usual. Although the exact source of the trouble was not determined, it was concluded that the capsule was vibrating during the 2 to 3 minute exposure to the beam. The difficulty was eliminated by placing a 3/4-in.-thick felt pad under the lead cask and by strengthening the supports which hold the 5-ft.-long positioning device above the cask.

2. Cooling System for Top of Alpha Boxes. Excessive heat buildup, principally from the mercury vapor lighting within the boxes, has been a cause of concern for some time. This heat has an adverse effect on the equipment within the boxes, the manipulator boots, and the purifier systems. Preliminary tests were conducted with chilled water flowing through copper tubing attached to the top of a stainless steel containment box. The tubing was mechanically fastened to the box, and an overspray of aluminum from a metal spray gun provided the contact and thermal path for dissipating the heat. Temperature reductions of approximately 20° were observed near the top of the box with the system in operation.

The results of planned tests may have some influence on the design of future alpha containment boxes.

3. Shipping Casks. Fabrication was started on a second cask (DOT SP-5885) for shipping irradiated EBR-II fuel capsules.

DOT Special Permit 6421 for the small cask for shipping fuel element sections has now been received and fabrication has been started. It is expected that both of these casks will be ready for use early in FY 1972.

An insert and tubes have been provided for shipping 61-in.-long unencapsulated, EBR-II fuel pins in a 21-ton Rover cask.

## III. HOT CELL FACILITY AT DP WEST

(F. J. Fitzgibbon, J. M. Ledbetter, J. R. Phillips, C. D. Montgomery, J. R. Trujillo, J. W. Schulte, M. E. Lazarus)

Considerable delay has been experienced in completing the structural modifications at the DP West facility because of the unavailability of personnel from the various crafts. The target readiness date for most of the examination capabilities in the facility is July 1.

### A. Structures and Building Equipment

1. The building modifications are now complete except for electrical service to the 25-ton crane.

2. An obsolete vacuum system, contaminated with $^{238}$Pu from another operation, is scheduled to be removed by May 1.

3. Twelve liner adapters have been installed in the corridor storage holes.

4. Work surface tables have been installed in two of the hot cells.

### B. Hot Cell Equipment

1. Gamma Scanning System. Modifications have been made to incorporate positive limits of travel, to add electrical cutout safety switches, and to reduce chatter in the fuel pin handling system. An order will be issued to install the base and tracks in front of the cell for accommodating the shielded detector.

2. Macrophotography. This system is complete and ready for installation.

3. Profilometer. The new lighting system has been shipped by the vendor and should arrive within a few days. The profilometer will then be ready for installation. Data will be recorded on a strip chart until the high speed data acquisition system is completed.

## IV. METHODS OF ANALYSIS

### A. Measurement of U and Pu

(J. W. Dahlby)

Controlled-potential coulometric measurements of U and Pu in (U,Pu)$O_2$ fuel having undergone 6 at.% burnup showed variations in uranium contents between 64.3 and 66.4% and in plutonium contents between 16.8 and 17.6% among five samples from one failed fuel pin containing some coolant sodium. For the Pu titrations, the average of the integrated currents for the coulometric oxidation of Pu(III) to Pu(IV) and for the reduction of Pu(IV) to Pu(III) at a platinum electrode was used as a measure of the Pu content. The integrated current for the coulometric reduction of U(VI) to U(IV) at a mercury electrode, following a preliminary reduction of easily reduced impurities, was used in calculating the U content. As the samples were quantitatively dissolved and the precisions ($1\sigma$) of the methods were 0.3% for the U titration and 0.1% for the Pu titration, the large ranges in contents for the two metals indicated either variable amounts of Na in the fuel or nonuniformity of the fuel itself.

Spectrographic measurement of Na in eight samples from this fuel pin showed that the Na content was significant and variable, ranging between 1.1 and 2.3%. The observed variations in U and Pu contents probably were the result of the large variation in Na content.

One problem that has plagued coulometric titrations is the difficulty in detecting malfunction of the reference calomel electrode. Two simple tests were developed for determining satisfactory operation of the electrode. In one test, a solution containing exactly equal amounts of Pu(III) and PU(IV) was prepared by coulometric oxidation of half of the Pu in a solution originally containing only Pu(III), and the potential was measured between the calomel electrode and a Pt electrode dipping into this solution. Under the particular conditions used, the measured potentials for satisfactory electrode systems were 500 ± 3 mv. In the second test, the resistance was measured of the calomel electrode alone and also when it was connected in series with a precision resistor. The internal resistance of the calomel electrode, which should be less than 5000 ohms, was obtained from these measurements.

Electrodes which tested within the stated electrical limits operated satisfactorily on coulometric titrations.

As a further check on the reliability of the coulometric titration method, known quantities of U and Pu will be added to analyzed aliquots of solutions of the irradiated fuels, and the resulting solutions will be analyzed again for total U and total Pu. The results will show if the added U and Pu are being measured quantitatively under the conditions existing in the irradiated fuel solutions. In addition, samples having undergone 8.5 at.% burnup are being dissolved quantitatively for analysis by this method.

### B. Sealed-Tube Dissolution of Irradiated Oxide Fuels
(J. W. Dahlby and G. R. Waterbury)

Refractory materials, including platinum metals and sintered oxide fuels, are quantitatively dissolved in HCl at a temperature of 300°C and a pressure of 3000 to 4000 lb/in.$^2$. This is accomplished by sealing the refractory sample and a measured volume of 12 $\underline{M}$ HCl in a thick-walled silica tube, and heating the tube at 300°C in a sealed steel shell containing a compensating pressure of $CO_2$ gas. Equipment was remotized and mechanized for sealing the silica tubes and heating the samples in-cell. A high-pressure Ar system supplied the compensating pressure around the tube. Initial tests showed that various alloys composed of Ru, Tc, Rh, Pd, and Mo, and irradiated sintered $(U,Pu)O_2$ were quantitatively dissolved in 2 to 12 hr by this method. Samples of $(U,Pu)O_2$ having undergone 8.5 at.% burnup are now being dissolved using this equipment.

### C. Detection of Internal Cladding Failure in Doubly Encapsulated Fuel Elements
(J. R. Phillips, J. W. Schulte, and G. R. Waterbury)

A nondestructive method utilizing precision gamma-ray scanning was developed for detecting fuel cladding failure in doubly encapsulated fuel elements. Detection of fission products, in particular $^{137}Cs$, outside the fuel pin envelope was used to indicate the failure. The method was tested by examining eleven fuel elements fueled with (U,Pu)C and two fueled with $(U,Pu)O_2$. Gamma-ray scanning indicated that six of the thirteen fuel envelopes had failed. These results were confirmed by mass spectrometric analyses of the gases in the outer encapsulation which were found to contain 1.76 to 9.31% of fusion product Kr and 11.7 to 65.0% Xe. The cover gas from the seventh element contained only 0.016% Xe and < 0.003% Kr, and the presence of $^{137}Cs$ outside of the fuel cladding was not conclusively detected by gamma-ray scanning. Gamma-ray scanning did not detect $^{137}Cs$ in the outer encapsulation of the six other fuel elements, and mass spectrometric analyses confirmed that the cladding had not failed.

### D. Determination of $O_2$ in Irradiated Materials
(C. S. MacDougall, M. E. Smith, and G. R. Waterbury)

Following preliminary tests of an analysis system for measuring $O_2$ in various irradiated materials by satisfactorily analyzing several $U_3O_8$ samples, testing of the system was continued using irradiated stainless steel and $(U,Pu)O_2$ fuel samples. In this system, the sample was reacted with C at 2000°C, and the CO and $CO_2$ produced were swept from the furnace by Ar and measured either gravimetrically or manometrically. Consistent results were obtained for the stainless steel samples, and no difficulties were experienced.

In the analysis of oxide fuels, the samples are ground, blended with C, and pressed into a pellet prior to heating to 2000°C. Initial results obtained for $O_2$ in a $(U,Pu)O_2$ fuel that had undergone 6 at.% burnup were low and erratic. It was found that this difficulty was surmounted by grinding the oxide more finely in a mixer mill before pressing the analysis pellet. Under these conditions, the precision ($1\sigma$) of the method ranged between 0.2 and 0.4 relative percent as compared to the 0.1 to 0.2 relative percent for similar analyses out-of-cell. The averages of repeated analyses on four samples ranged between 11.86 and 11.95% oxygen.

Testing of the method by analyzing $(U,Pu)O_2$ and (U,Pu)C fuels having burnups higher than 6 at.% is planned as the fuel becomes available. No difficulty because of the higher burnup is anticipated.

### E. Spectrochemical Measurement of Na in Irradiated $(U,Pu)O_2$
(O. R. Simi)

A method was developed for the spectrographic measurement of Na in irradiated $(U,Pu)O_2$ following dissolution of the fuel in $HNO_3$-$H_2SO_4$. A $PbSO_4$ matrix was chosen because it was amenable to $H_2SO_4$. Tests showed that 1% of total U and Pu in $PbSO_4$ would not interfere with the spectrographic determination of Na. Because the limit of detection of Na in $PbSO_4$ is 1 ppm, a detection limit of 100 ppm Na in $(U, Pu)O_2$ was thus attained using purified reagents. This limit is well below the expected 0.1 to 1% Na content of the samples. In this analysis, a small aliquot of the $(U, Pu)O_2$ solution was added to enough $Pb(NO_3)_2$ solution to produce a sample with 1% $(U, Pu)O_2$ in $PbSO_4$ when the solution was acidified with $H_2SO_4$ and dried. Dilutions of the samples with pure $PbSO_4$ were made to reduce the Na content of the mixtures to range between 1 and 100 ppm, which was suitable for spectrographic measurement.

The $PbSO_4$ was then mixed with graphite powder and excited with an 8 amp d.c. arc using a 30-sec exposure time. The Na content of the samples was determined from the intensity of the Na line at 5890 Å which was measured photometrically. Average deviations of duplicate measurements ranged between 4 and 11% in applications of the method to measurements of 1.1 to 2.3% Na in six $(U, Pu)O_2$ fuels.

Random occurrence of sample contamination, principally with Al, Ca, Fe, Mg, and Si, in the hot cell was traced to dust coatings on manipulator boots. When new boots that have been cleaned by washes with alcohol and water are installed, further tests of sample contamination will be made.

## V. REQUESTS FROM DRDT

### A. Examination of Irradiated Material

(K. A. Johnson, E. D. Loughran (GMX-2),
R. A. Morris (GMX-1), J. R. Phillips,
J. W. Schulte, G. R. Waterbury)

Argonne National Laboratory (Illinois). Eighteen samples of stainless steel cladding from irradiated fuel elements, following cleaning at ANL to remove surface contamination, were analyzed in-cell for oxygen by an inert-gas-fusion method.

Atomics International. The remaining sections of irradiated UC-W fuel pellets from NRX-101 were released by AI personnel for disposition in the contaminated waste pits at LASL.

Los Alamos Scientific Laboratory: OWREX-16

OWREX-16, irradiated in the Omega West Reactor (thermal) at LASL, was received during this period. The examinations and tests conducted on this assembly are shown in Table 401-I.

TABLE 401-I

Post-Irradiation Examination of OWREX-16

| | Examinations and Operations |
|---|---|
| 1. | Visual Inspection and Photography |
| 2. | Measurements of Contamination and Radiation |
| 3. | Radiography |
| 4. | Gamma Scanning (3 gross and 2 multispectral scans) |
| 5. | Na and Clad Removal |
| 6. | Na Distillation from the Fuel-Clad Sections |
| 7. | Sectioning |

Operations 5 through 7 were conducted in an Ar atmosphere.

Microstructural examinations consisting of macrophotography, alpha and beta-gamma autoradiography, and optical microscopy were completed on two samples each of fuel-clad, clad, and stainless steel end pellets from the OWREX-16 assembly.

LASL 36-B. Nondestructive tests were completed on this mixed-carbide capsule in the preceding quarter. The capsule is currently being stored for possible re-insertion in the EBR-II.

LASL 42-B. A two-dimensional measurement of distributions of fission products was made by gamma scanning a 0.050-in.-thick cross section from this irradiated mixed-carbide fuel element. Three metallographic specimens from this same element were examined in the shielded electron microprobe.

Nuclear Materials and Equipment Corporation:

A-Series Pins. The examinations and tests performed on NUMEC pins are listed in Table 401-II.

The following program of examination was agreed upon by representatives of ANL, LASL and ORNL and approved by DRDT.

1. Nondestructive and destructive tests will be conducted at LASL on pins A-5, A-8, A-9, A-10, and A-11; the residual fuel will be shipped to ORNL.

TABLE 401-II

Post-Irradiation Examination of NUMEC Materials

| Tests | NUMEC A-Series Pin No. | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| 1. Betatron Radiography | | | | X | X | X | X | X | X | X | X |
| 2. Gamma Scanning[a] | X | X | X | X | X | X | X | X | X | | |
| 3. Measurements of Temperature | X | | X | X | X | | X | | | | |
| 4. Center Point Balance | X | | X | X | X | | X | | | | |
| 5. Profilometry | X | | X | X | X | | X | | | | |

[a] Three diametral and one axial gross gamma scans were made on each of nine irradiated mixed-oxide fuel elements. In addition, multispectral gamma scans were made on six of these fuel elements that are scheduled for sectioning and more complete examinations.

2. Pins A-4 and A-7 will be shipped intact to ANL for processing studies. (Pins A-4 and A-7 were shipped on March 16.)

3. Routine nondestructive tests will be conducted on pins A-1, A-2, A-3, A-4, A-6, and A-7.

United Nuclear Corporation. Examination of 24 capsules and pins from UNC were made by performing tests shown in Table 401-III.

TABLE 401-III

Post-Irradiation Examination of UNC Material

| Tests | UNC Pin Number |
|---|---|
| 1. Measurement of Temperature (Capsule) | 138, 146 |
| 2. Micrometer Measurement (Capsule) | 138, 146 |
| 3. Center Point Balance (Capsule) | 138, 146 |
| 4. Radiography | 138, 146 |
| 5. Gamma Scanning[a] | 107, 109, 111 |
| 6. Photography | 92, 104, 138, 146 |
| 7. Gas Sampling of Cover Gas | 107, 108, 109, 111, 112 |
| 8. Na Removal | 92 |
| 9. Clad Removal | 92 |
| 10. Measurement of Temperature (Pin) | 92, 96, 99, 104, 210 through 221 |
| 11. Center Point Balance (Pin) | 92, 96, 99, 104, 210 through 221 |
| 12. Profilometry | 92, 96, 99, 104 |
| 13. Sectioning | 210 through 221 |
| 14. Na Distillation | 214, 215, 216, 217, 218 |

[a] Gross and multispectral gamma scans were completed on each of the three fuel elements. In addition, measurements were made to locate $^{137}$Cs near the capsule end plugs as a means of detecting failure of the fuel cladding.

Tests 10 through 14 were conducted in an Ar atmosphere.

Microstructural examinations consisting of macrophotography, alpha and beta-gamma autoradiography, and optical microscopy were carried out in an argon atmosphere on fuel-clad samples shown in Table 401-IV.

TABLE 401-IV

Metallography of UNC Material

| UNC Pin Number | No. of Samples | UNC Pin Number | No. of Samples |
|---|---|---|---|
| 210 | 1 | 216 | 2 |
| 211 | 1 | 217 | 2 |
| 212 | 2 | 218 | 2 |
| 213 | 2 | 219 | 2 |
| 214 | 2 | 220 | 2 |
| 215 | 2 | 221 | 2 |

Specimens UNC-125-F, -126-F, -127-F and -128-F were repolished and etched for 525X photography. Microprobe examinations were completed on UNC-126-L and UNC-128-H

## VI. PUBLICATIONS

1. M. E. Lazarus, "Electro-Optical Profilometer," submitted for publication in the Proceedings of the 19th Conference on Remote Systems Technology, ANS Meeting, October 1971.
2. C. E. Frantz, "Apparatus for Determining Heat Content on Irradiated Fuels," submitted for publication in the Proceedings of the 19th Conference on Remote Systems Technology, ANS Meeting, October 1971.
3. D. D. Jeffries and L. A. Waldschmidt, "A Technique for Hot Cell Autoradiography," Proceedings of the Third Annual Technical Meeting of the International Metallographic Society, November 1970.
4. C. D. Montgomery, T. Romanik, and J. R. Trujillo, "Equipment for Preparing Sealed Metal Tubes for Long-Term Storage of Irradiated Uranium-Plutonium Fuel Element Sections," submitted for publication in the Proceedings of the 19th Conference on Remote Systems Technology, ANS Meeting, October 1971.
5. C. Baker and K. A. Johnson, "An Etching Technique for Some Plutonium-Based Oxides," Proceedings of the Third Annual Technical Meeting, International Metallographic Society, Inc. (1970).

6. J. H. Bender and K. A. Johnson, "An Automated Camera for Hot Cell Metallography," Proceedings of the Third Annual Technical Meeting, International Metallographic Society, Inc. (1970).

7. K. A. Johnson, "A Minimum Error Analysis for Automatic Image Analyzing," Proceedings of the Third Annual Technical Meeting, International Metallographic Society, Inc. (1970).

8. P. A. Mason, C. E. Frantz, and C. D. Montgomery, "Inert Atmosphere Hot Cells for Examination of Irradiated U-Pu Fuel Elements," submitted for publication in the Proceedings of the 19th Conference on Remote Systems Technology, ANS Meeting, October 1971.

9. J. R. Phillips, J. W. Schulte, and G. R. Waterbury, "The Use of High-Resolution Gamma-Ray Spectrometry for Detecting Failure of Cladding in Encapsulated Fast Reactor Fuel Pins," submitted for publication in the Proceedings of the 19th Conference on Remote Systems Technology, American Nuclear Society, October 1971.

# PROJECT 463

# CERAMIC PLUTONIUM FUEL MATERIALS

Person in Charge: R. D. Baker
Principal Investigator: J. L. Green

## I. INTRODUCTION

The primary objective of this program is the overall evaluation of the most promising of the candidate fuel systems for advanced LMFBR application. Emphasis currently is placed on the study of the relative merits of stainless steel clad nitride and carbide fuels under conditions that appropriately exploit the potential of these materials to operate to high burnup at high power densities. The major portion of the program is the evaluation of the irradiation performance of these fuel element systems. A continuing series of irradiation experiments is being carried out under steady state conditions in fast reactor environments to assess the effects of damage and burnup on stainless steel clad, sodium bonded, monocarbide fuel elements. These experiments are designed to investigate fuel swelling, interactions between the fuel and clad and thermal bonding medium, fission gas release, and the migration of fuel material and fission products as a function of burnup and irradiation conditions. In addition, experiments are being designed to allow the study of the effects of rapid, overpower, reactor transients on sodium bonded monocarbide fuel assemblies. Contiguous efforts are necessary in the development of fuel material preparation and fabrication procedures as well as the techniques required for the characterization of fuel materials both before and after irradiation.

A second objective in the program is the determination of thermophysical, mechanical and chemical properties and characteristics of plutonium containing ceramics that are required for their evaluation and use as fuel materials. A broad range of capabilities in this area has been developed, including the study of (1) phase relationships using differential thermal analysis, (2) thermal transport, (3) thermal stability and compatibility, (4) hot hardness and its temperature dependence, (5) structure and phase relationships using high temperature x-ray and neutron diffraction, (6) thermal expansion, and (7) compressive creep rates as a function of temperature and stress. These techniques are available for use with unirradiated material and several are used with irradiated fuels.

## II. IRRADIATION TESTING

The objective of the irradiation testing program is the overall evaluation of the most promising of the candidate fuel systems for advanced LMFBR application.

The irradiation experiments are carried out under conditions that appropriately exploit the potential of these materials to operate to high burnup at high power densities.

### 1. Fuel Synthesis and Fabrication

(R. Honnell, C. Baker, W. Hayes,
G. Moore, and R. Walker)

The preparation and characterization of fuel materials for use in irradiation testing is a continuing effort. Solid solution carbides are being prepared to meet current requirements for irradiation assembly fabrication. Process development is being carried out to define the conditions necessary for the production of the carbide fuel required for the singly encapsulated 19-pin subassembly.

Current technology for the production of solid solution nitride fuel forms is being reviewed and evaluated.

Two high temperature, W mesh, inert gas-vacuum furnaces are being obtained for use in fuel production. One of these is currently being installed and the second is on order. This equipment will improve our present capability for carbide production and will provide for the fabrication of nitride fuel forms on the scale which will be required for future irradiations.

### 2. EBR-II Irradiation Testing

(J.O. Barner)

Steady state irradiations under prototypical conditions are currently being carried out in EBR-II on high purity, solid solution carbides which are sodium bonded to stainless steel cladding. The results of these studies in conjunction with data from irradiation tests of other carbide and nitride systems are continuously correlated to identify the most advantageous variable combinations for continued study.

Three series of doubly encapsulated experiments are currently in progress. These capsules are being irradiated under the conditions shown in Table 463-I.

Multipin EBR-II subassemblies will be used to simultaneously test nitride and carbide systems under identical conditions, to allow directly correlatable parametric studies and, eventually, the accumulation of statistical performance and reliability data. A 19-pin subassembly is currently being designed which will contain both carbides and nitrides. The major variables will be fuel type, smear density and cladding strength.

TABLE 463-I

DESCRIPTION OF EXPERIMENTS

| | Condition | Series 1 | Series 2 | Series 3 |
|---|---|---|---|---|
| 1. | Lineal Power, kw/ft | ~ 30 | ~ 45 | ~ 30 |
| 2. | Fuel Composition | $(U_{0.8}Pu_{0.2})C$, Single-phase, Sintered | | |
| 3. | Fuel Uranium | $^{235}U$ | $^{233}U$ | $^{235}U$ |
| 4. | Fuel Density | 90% | 95% | 95% |
| 5. | Smear Density | 80% | 80% | 80% |
| 6. | Clad Size | 0.300-in.-i.d. x 0.010-in. wall | | |
| 7. | Clad Type | 316 SS | 316 SS | 316 SS |
| 8. | Max Clad Temp. °F (°C) | 1250 (677) | 1275 (690) | 1250 (677) |
| 9. | Max Fuel Centerline Temp. °F (°C)* | 2130 (1165) | 2550 (1399) | 2100 (1149) |
| 10. | Burnup | 3 at.% to 8 at.% | | |

*Calculated for solid fuel pellet.

### Results

During this quarter, destructive examination of capsule 42B from Series 1 was completed. This capsule operated without failure at 29-30 kW/ft in EBR-II to a calculated peak burnup of 5.0 at.%. The peak burnup determined by Idaho Nuclear Corporation was 4.4 at.%.

Four metallographic sections were taken from the regions of the element which represented extremes in both temperature and burnup. A section from the high fuel temperature, high burnup region is shown in Fig. 463-1. Axial splitting and general fragmentation of the fuel was observed in all sections, but was more severe in the high fuel temperature, high burnup region. Due to fragmentation, irradiated fuel density measurements could not be made. "Necklaces" of small diameter pores around fuel grains were observed to have formed in regions near the reactor core midplane and the fuel centerline. This porosity did not appear to a significant degree in the low fuel temperature, low fuel burnup regions. No new phases were observed in the etched fuel sections.

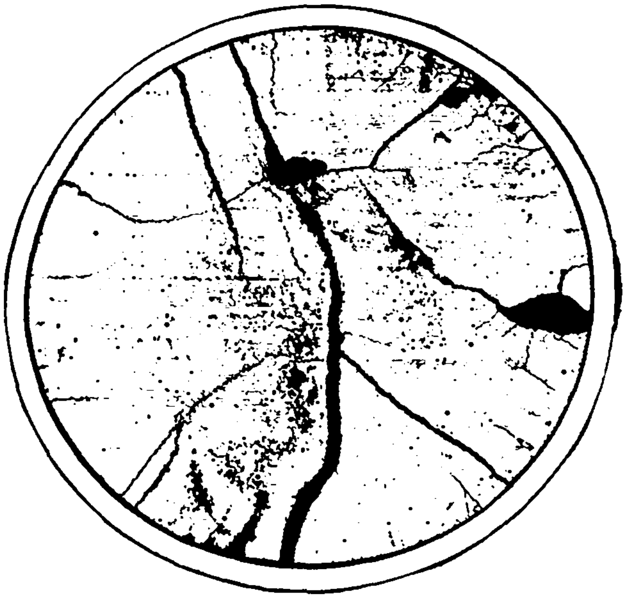

Fig. 463-1. As-polished mosaic of high fuel temperature, high burnup region of capsule 42B. Mean clad temperature was 604°C.

Alpha-autoradiographs of the fuel sections indicated that there was no detectable plutonium redistribution. Beta-gamma autoradiographs of the fuel indicated that in the low fuel temperature regions very little fission product migration had occurred. In the high fuel temperature regions, a significant depletion of beta-gamma activity was observed near the fuel centerline. This depletion occurred in the same region that contained the bubble "necklaces." These observations indicate that the high burnup, high temperature regions operated at temperatures significantly higher than calculated for uncracked fuel pellets.

Microprobe analyses for U, Pu, and fission product distributions were prevented by a surface stain on the metallographic specimens which occurred on the outer one-half of the fuel section. Presumably this stain was due to sodium reaction products which seeped out of porosity in the sodium logged portion of the fuel. Sodium was present in the stained areas but was not detected on unstained surfaces.

Microprobe examination of the cladding from the high burnup, intermediate clad temperature region section indicated a general nickel depletion of up to 4.3 μm from the inner surface. In the same section, a thin nickel deposit was observed on the inside cladding surface in isolated areas.

In general, the low burnup sections showed no depletion of Fe, Ni, or Cr, although in some isolated areas Fe and Ni depletion was observed to depths of up to 5μm. No evidence of reactions between the cladding and uranium, plutonium or fission products was observed.

A slight surface reaction, presumably due to carburization, was observed on the inner surface of the etched cladding sections. The degree of the reaction increased with increasing cladding operating temperature. The surface reaction had penetrated to a depth of approximately 6% of the wall thickness in the high temperature cladding section. Grain boundary precipitation of carbides was also observed in the clad sections.

Three capsules from Series 1, designated K-37B, K-38B, and K-39B, and two capsules from Series 3, designated K-43 and K-44 are currently being irradiated in the EBR-II subassembly X086 at approximately 30 kW/ft. The current maximum burnup in these capsules is 1.5 at.%.

Three capsules from Series 2, designated K-49, K-50 and K-51, and two additional capsules from Series 3, designated K-45 and K-46, are at EBR-II for assembly into subassembly X119. The assembly of X119 is pending the evaluation of unusual eddy current test results on several nitride-fueled BMI capsules.

New sodium-bonding and hot eddy current testing equipment has been designed and currently is being fabricated.

### 3. TREAT Irradiation Testing

(J. F. Kerrisk, R. E. Alcouffe, D. G. Clifton, K. L. Walters, and J. O. Barner)

In order to assess the behavior of carbide and nitride fueled elements under fast reactor accident conditions, transient irradiations will be conducted in the TREAT facility. Investigations will be conducted on both irradiated and unirradiated fuel pins to determine (1) the threshold power levels at which damage or failure occurs, (2) the effect of bond and cladding defects, and (3) the failure propagation mechanism in multipin assemblies.

A cooperative effort has been initiated with the United Nuclear Corporation in the area of TREAT testing. Four unfiltered experiments are planned. Two sodium bonded pins prepared by UNC will be tested, one irradiated and one unirradiated. Also, two UNC helium bonded pins will be examined; again, one irradiated and one unirradiated. Neutronic and heat transfer analysis of these experiments is being carried out.

The first experiments utilizing LASL fabricated fuel pins will be directed toward defining the threshold conditions at which boiling occurs in the sodium bond, and also determining the behavior of the thermal bond after the onset of boiling. These tests will be run in a pressure vessel assembly incorporating a thermal neutron shield to provide for power generation and temperature distributions in the fuel that are more typical of fast reactor systems.

### Neutronic Analysis
(R. E. Alcouffe and K. L. Walters)

Neutronic analysis of experiments in the TREAT reactor environment are being conducted in order to determine the fission profile in the experimental fuel pins. The experiments are to be shielded from the thermal neutron flux by an appropriate filter. The ratio of power produced in the pin to that produced in the reactor is being computed.

For this work, a 29-group library of microscopic cross sections was generated from ENDF/B data. The broad group library emphasizes the epithermal region (up to the sodium resonance) in order to accurately account for the effects of the neutron filter. Also, for the preliminary one-dimensional transport computations, five thermal groups are included. The details of the group structure are presented in Table 463-II.

TABLE 463-II

TREAT EXPERIMENT BROAD GROUP STRUCTURE

| Group | Upper Energy (ev) | Lower Lethargy | Group | Upper Energy (ev) | Lower Lethargy |
|---|---|---|---|---|---|
| 1 | $1.0 \times 10^7$ | 0.0 | 16 | 61.0 | 12.0 |
| 2 | $3.0 \times 10^6$ | 1.20 | 17 | 37.3 | 12.5 |
| 3 | $1.4 \times 10^6$ | 1.97 | 18 | 22.6 | 13.0 |
| 4 | $9.0 \times 10^5$ | 2.41 | 19 | 13.7 | 13.5 |
| 5 | $4.0 \times 10^5$ | 3.22 | 20 | 8.3 | 14.0 |
| 6 | $1.0 \times 10^5$ | 4.61 | 21 | 5.0 | 14.5 |
| 7 | $1.7 \times 10^4$ | 6.38 | 22 | 3.1 | 15.0 |
| 8 | $3.4 \times 10^3$ | 8.0 | 23 | 1.9 | 15.5 |
| 9 | $2.0 \times 10^3$ | 8.5 | 24 | 1.1 | 16.0 |
| 10 | $1.2 \times 10^3$ | 9.0 | 25 | 0.77 | 16.37 |
| 11 | $7.5 \times 10^2$ | 9.5 | 26 | 0.28 | 17.39 |
| 12 | $4.5 \times 10^2$ | 10.0 | 27 | 0.12 | 18.22 |
| 13 | $2.8 \times 10^2$ | 10.5 | 28 | 0.048 | 19.19 |
| 14 | $1.7 \times 10^2$ | 11.0 | 29 | 0.018 | 20.12 |
| 15 | $1.0 \times 10^2$ | 11.5 | | | |

Preliminary computations on the TREAT reactor including the experimental pin (0.666 cm diam) and capsule have been performed using the 29-group library. The purpose of these calculations is to investigate the influence of filters on the spatial power distribution in the pin. Also, the effect of the filter on the reactor system is estimated as a function of position in the capsule. The effect of the filter on the so-called figure of merit (ratio of power density in the experimental pin to the total power produced in the reactor) is estimated, although absolute values will have to wait on two-dimensional calculations of the system. The results obtained to date are summarized in Table 463-III.

From these results and those of previous experiments, it appears that a filtered experiment can be designed which will not degrade the performance of TREAT and also will significantly flatten the power distribution in the pin. At the same time, sufficient power can be generated in the pin by a TREAT transient to accomplish the objectives of the experiment.

### Heat Transfer Analysis
(J. F. Kerrisk)

Heat transfer calculations on the (U, Pu)C fuel pin-heat sink capsule for TREAT tests were continued. An estimate of the total energy required to completely melt the fuel was made both with and without sodium bond vaporization. With bond vaporization at 980°C,

TABLE 463-III

TREAT EXPERIMENT CALCULATIONAL RESULTS

| Type of Filter | Thickness (cm) | Position from Center (cm) | Reactor $\% \Delta k/k$ | Power Dist.[a] Edge/Center | Figure of Merit |
|---|---|---|---|---|---|
| none | --- | --- | --- | 6.23 | 1.0[b] |
| BN | 0.266 | 2.97 | -0.040 | 1.21 | 0.16 |
| Dy[c] | 0.136 | 1.24 | -0.014 | 1.28 | 0.28 |
| Dy | 0.136 | 1.65 | -0.018 | 1.28 | 0.27 |
| Dy | 0.136 | 2.97 | -0.031 | 1.28 | 0.26 |

(a) Mesh spacing is a uniform 0.0333 cm through the pin.

(b) A one-dimensional estimate of the figure of merit for the base case is $1.363 \times 10^{-4}$ (watt/cm$^3$ in the pin)/watt reactor power; or 10.3 (Joules/gm carbide)/Mw-sec reactor energy.

(c) The isotope used is Dy-164. A filter of natural dysprosium would be thicker by a factor of approximately three, based on the thermal absorption cross section values.

approximately 200 cal/gm of fuel is required. If the sodium bond remains liquid, on the order of 300 cal/gm of fuel is required, but in this case clad failure would probably occur at approximately 200 cal/gm of fuel. The calculations assumed a pulse width at half maximum of 250 msec and an edge-to-centerline power generation ratio of 1.4.

The time constant for heat transfer in the fuel is of interest in selecting possible transients. A series of calculations was made using an energy pulse of the same shape but with varying width at half maximum. The results, presented as the fraction of the deposited energy remaining in the fuel at the pulse maximum as a function of the pulse width at half maximum are shown in Table 463-IV. The calculations were made for a total energy deposition of 200 cal/gm of fuel, an edge-to-centerline power generation ratio of 1.4, and the assumption that the sodium bond remains liquid at all temperatures. These calculations indicate that pulse half-widths of less than a few milliseconds would be required to deposit essentially all of the energy in the fuel before significant heat losses occur.

Programming for heat transfer calculations in the pressure vessel assembly and for stress calculations in the fuel pin capsule assembly is in progress.

### 4. Thermal Irradiations of Sodium Bonded Mixed Carbides
(J. C. Clifford)

Sodium bonded mixed carbides have been irradiated in the LASL Omega West Reactor, a 6 mW MTR-type facility, to determine whether fuel, clad, and sodium remain mutually compatible as burnups of interest to the LMFBR program are approached. Experimental conditions included fuel surface operating temperatures of 600-700°C, a fuel radial temperature gradient of 180°C, and fuel power densities varying from approximately 670 w/g at the surface to 50 w/g at the centerline. Experiments that reached approximately 4 and 8 at.% surface burnup have been examined destructively without revealing any significant deleterious effects on compatibility.

TABLE 463-IV

ENERGY TRANSFER FROM FUEL
DURING TREAT TRANSIENT

| Pulse Width at Half Maximum (m sec) | Fraction of Deposited Energy Remaining in the Fuel at the Pulse Maximum |
|---|---|
| 1 | .98 |
| 10 | .94 |
| 100 | .83 |
| 1000 | .51 |

A third and final experiment was operated successfully to an estimated 13 at.% surface burnup, and presently is being examined destructively. Autoradiography and metallography have been completed on fuel and cladding specimens from the last experiment, and electron beam microprobe examinations of a fuel-clad specimen and of a stainless steel insulation pellet are in progress. A topical report is being prepared describing the experiments and their results.

## III. FUEL PROPERTIES

### 1. $B_4C$ Structural Study
(K. L. Walters and J L. Green)

Neutron and x-ray diffraction structural studies on carbon saturated boron carbide have been completed. Coherent scattering amplitudes and position parameters have been reported previously.[1] Refinements of lattice parameters for powders obtained from high purity single crystals have been completed. Table 463-V indicates the final lattice parameters. Table 463-VI contains the powder diffraction data on which these lattice parameters are based. It should be noted that this pattern contained no detectable x-ray impurities and no unindexable lines. Extraneous diffraction lines can no longer be ascribed to errors in the structure description. Unindexable lines and intensity anomalies must be accounted for in terms of phases other than pure, carbon-rich $B_4C$. Table 463-VII shows the chemical analysis for the powder derived from the single crystals. Optical and scanning electron microscopy showed that no detectable impurity inclusions were present.

Interpretation of the structural data has been completed. Chemical analyses and metallographic data showed that the B/C ratio in the single crystals was

## TABLE 463-V

## LATTICE PARAMETERS OF CARBON SATURATED $B_4C$

| Hexagonal Setting | Rhombohedral Setting |
|---|---|
| $a_0$ = 5.602 ± 0.001 Å | $a_0$ = 5.1635 Å |
| $c_0$ = 12.075 ± 0.003 Å | α = 65.70 deg. |

essentially 4 to 1. This requires that the average content of the unit cell be $B_{12}C_3$. The neutron diffraction scattering amplitude data clearly showed that the central chain in the rhombohedral unit cell is a (CBC) group. In order to maintain the required average composition, the icosahedral groups must then be, on the average, $(B_{11}C)$ groupings. Thus, the formulation $(B_{11}C)$CBC is consistent with all the experimental observations.

A literature search on bonding theory for boron carbide has been completed. The work of Longuet-Higgins and Roberts[2] and Scott[3] is of primary interest.

### TABLE 463-VI

### POWDER DIFFRACTION PATTERN OF CARBON SATURATED $B_4C$

| HKL | Intensity | | d (Å)[c] | | HKL | Intensity | | d (Å) | |
|---|---|---|---|---|---|---|---|---|---|
| (Rhomb.) | Obs. | Calc. | Obs.[e] | Calc. | (Rhomb.) | Obs. | Calc. | Obs.[e] | Calc. |
| 100 | 6 | 8 | 4.5063 | 4.5017 | $42\bar{2}\alpha_1$ | 2 | 2.6 | 0.8773 | 0.8773 |
| 111 | 8 | 26 | 4.0293 | 4.0261 | $42\bar{2}\alpha_2$ | 1 | 1.2 | 0.8773 | 0.8773 |
| 110 | 7 | 58 | 3.7681 | 3.7818 | $4\bar{1}\bar{2}\alpha_1$ | 2 | 3.1 | 0.8692 | 0.8691 |
| $10\bar{1}$ | 4 | 11 | 2.7978 | 2.8010 | $553\alpha_1$ | 3 | 6.6 | 0.8678 | 0.8674 |
| 211 | 8 | 87 | 2.5629 | 2.5631 | $553\alpha_2$ | 1 | 2.9 | 0.8679 | 0.8674 |
| $11\bar{1}$ | 10 | 100 | 2.3805 | 2.3782 | $32\bar{3}\alpha_1$ | 3 | 6.2 | 0.8627 | 0.8624 |
| 210 | 2 | 6 | 2.2998 | 2.2991 | $32\bar{3}\alpha_2$ | 2 | 3.2 | 0.8626 | 0.8624 |
| 222 | 1 | 0.4 | 2.0132 | 2.0126 | $61\bar{1}\alpha_1$ | 5 | 12.1 | 0.8572 | 0.8572 |
| $20\bar{1}$ | 3 | 8 | 1.8112 | 1.8120 | $622\alpha_1$ | 6 | 8.7 | 0.8560 | 0.8557 |
| 311 | 8 | 12 | 1.7100 | 1.7116 | $61\bar{1}\alpha_2$ | | 6.2 | | 0.8572 |
| 322 | 2 | 9 | 1.6246 | 1.6253 | $622, 533\alpha_1$ | | 5.1 | | 0.8544 |
| 310 | 1 | 2 | 1.5635 | 1.5672 | $632\alpha_1$ | 3 | 4.8 | 0.8508 | 0.8508 |
| $22\bar{1}$, 300 | 6 | 12 | 1.5000 | 1.5006 | $63\bar{2}\alpha_1$ | (d) | 2.4 | (d) | 0.8506 |
| 320 | 8 | 19 | 1.4604 | 1.4604 | $62\bar{1}\alpha_1$ | | 2.0 | | 0.8470 |
| 332 | 8 | 17 | 1.4407 | 1.4413 | $44\bar{1}\alpha_1$ | | 1.8 | | 0.8457 |
| $20\bar{2}$ | 8 | 16 | 1.3998 | 1.4006 | $62\bar{1}\alpha_2$ | | 1.0 | | 0.8470 |
| $21\bar{2}$ | 4 | 12 | 1.3370 | 1.3373 | $44\bar{1}\alpha_2$ | | 0.9 | | 0.8457 |
| $31\bar{1}$ | 4 | 12 | 1.3227 | 1.3227 | $821, 504\alpha_1$ | 2 | 5.9 | 0.8311 | 0.8311 |
| $30\bar{1}$ | 4 | 11 | 1.3126 | 1.3132 | $821, 640\alpha_2$ | 2 | 2.8 | 0.8311 | 0.8311 |
| 422 | 3 | 4 | 1.2808 | 1.2818 | $43\bar{2}\alpha_1$ | (d) | 1.4 | (d) | 0.8196 |
| 421 | 4 | 10 | 1.2570 | 1.2564 | $631\alpha_1$ | | 1.1 | | 0.8184 |
| $43\bar{2}$ | 3 | 2 | 1.2090 | 1.2100 | $43\bar{2}\alpha_2$ | | 0.9 | | 0.8198 |
| $22\bar{2}$ | 3 | 5 | 1.1891 | 1.1891 | $642\alpha_1$ | | 1.8 | | 0.8172 |
| 410 | 2 | 2 | 1.1748 | 1.1734 | $631\alpha_2$ | | 0.6 | | 0.8184 |
| 431 | 2 | 6 | 1.1658 | 1.1654 | $411\alpha_1$ | | 1.8 | | 0.8162 |
| 420 | 3 | 3 | 1.1495 | 1.1496 | $661\alpha_1$ | 4 | 8.6 | 0.8139 | 0.8139 |
| 400 | 1 | 0.8 | 1.1258 | 1.1254 | $351\alpha_2$ | 2 | 4.6 | 0.8139 | 0.8139 |
| $31\bar{2}$ | 1 | 0.5 | 1.0960 | 1.0946 | $22\bar{4}, 4\bar{2}\bar{2}\alpha_1$ | 3 | 6.1 | 0.8086 | 0.8086 |
| 442 | 1 | 2 | 1.0818 | 1.0810 | $22\bar{4}, 4\bar{2}\bar{2}\alpha_2$ | 2 | 2.6 | 0.8086 | 0.8084 |
| $41\bar{1}$ | 3 | 4 | 1.0443 | 1.0443 | $655\alpha_1$ | 1 | 2.8 | 0.8049 | 0.8050 |
| 441, 622 | 3 | 7 | 1.0323 | 1.0328 | $666\alpha_1$ | 1 | 1.4 | 0.8031 | 0.8030 |
| 444 | 1 | 1.4 | 1.0060 | 1.0063 | $40\bar{3}\alpha_1$ | 2 | 2.7 | 0.7959 | 0.7958 |
| $531\alpha_2$ | 1 | 1.4 | 0.9696 | 0.9688 | $6\bar{1}\bar{1}, 33\bar{3}\alpha_1$ | 9 | 24.3 | 0.7928 | 0.7927 |
| $30\bar{3}\alpha_1$ | 2 | 4.4 | 0.9333 | 0.9337 | $6\bar{1}\bar{1}, 33\bar{3}\alpha_2$ | 6 | 12.9 | 0.7909 | 0.7927 |
| $644\alpha_2$ | 1 | 1.6 | 0.9126 | 0.9123 | $41\bar{3}\alpha_1$ | | 5.9 | | 0.7907 |
| $41\bar{2}\alpha_1$ | 2 | 2.4 | 0.9097 | 0.9096 | $41\bar{3}\alpha_2$ | 2 | 2.1 | 0.7907 | 0.7907 |
| $412\alpha_1$ | 1 | 1.7 | 0.9069 | 0.9096 | $853\alpha_1$ | 3 | 4.0 | 0.7806 | 0.7806 |
| $40\bar{2}\alpha_1$ | | 1.7 | | 0.9086 | $853\alpha_2$ | 2 | 2.0 | 0.7806 | 0.7805 |
| $40\bar{2}\alpha_2$ | 1 | 0.8 | 0.9068 | 0.9066 | $4\bar{1}\bar{3}, 31\bar{4}\alpha_1$ | 2 | 2.2 | 0.7769 | 0.7769 |
| $600\alpha_1$ | 2 | 2.8 | 0.8996 | 0.9003 | $4\bar{1}\bar{3}, 31\bar{4}\alpha_2$ | 1 | 1.2 | 0.7769 | 0.7769 |
| $641\alpha_1$ | | 2.2 | | 0.8987 | | | | | |
| $630\alpha_1$ | 6 | 11.2 | 0.8959 | 0.8958 | | | | | |
| $630\alpha_2$ | 4 | 5.8 | 0.8959 | 0.8959 | | | | | |

[a] Relative intensities based on visual estimates as assigned on a 10 step scale.

[b] Calculated intensities based on Table II.

[c] Calculated interplanar spacings for $a_0$ = 5.6020 Å and α = 65.70 deg.
For 2θ < 90°, λ (α) = 1.54178 Å
For 2θ > 90°, λ ($\alpha_1$) = 1.54051 Å and λ ($\alpha_2$) = 1.54433 Å.

[d] Broad unresolved band - not measurable.

[e] Interplanar spacings for conglomerate lines calculated using λ ($\alpha_1$).

## TABLE 463-VII

## ANALYTICAL DATA $B_4C$ SINGLE CRYSTAL

| Element | Conc.[(a)] | Element | Conc. |
|---|---|---|---|
| B | 79.0% | | |
| C | 20.53% | | |
| Li | < 30 | | |
| Be | < 3 | Fe | < 30 |
| Na | < 100 | Co | < 100 |
| Mg | < 3 | Ni | < 30 |
| Al | < 30 | Cu | < 10 |
| Si | < 10 | Zn | < 100 |
| K | < 300 | Sr | < 100 |
| Ca | < 100 | Zr | < 100 |
| Ti | < 100 | Ag | < 10 |
| Cr | < 10 | Cd | < 10 |
| Mn | < 30 | Ba | < 30 |
| Sn | < 30 | Bi | < 10 |
| Pb | < 30 | | |

(a) Chemical analysis reported as ppm by weight unless otherwise indicated.

These papers provide theoretical support for our findings and suggest that the structure should be written as $(CBC)^+ (B_{11}C)^-$. Neither of these articles provides experimental supporting evidence.

### 2. Differential Thermal Analysis

(J.G. Reavis and L.W. Reese)

A method has been developed for the encapsulation of (U, Pu)C for temperatures up to 2500°C. It is expected that this method can be used for containment of irradiated (U, Pu)C for DTA. Requests have been made for additional irradiated oxide specimens for DTA investigations. Observations of $(U_{0.8}Pu_{0.2})C$ specimens of selected C concentrations have been carried out to partially delineate the phase boundaries of the single phase monocarbide.

DTA of Irradiated Fuel Materials: A sealed capsule has been developed and used to contain $(U_{0.8}Pu_{0.2})C$ for DTA observations. A tantalum capsule was carburized in methane, filled with unirradiated $(U_{0.8}Pu_{0.2})C$ and a lid was welded in place. The capsule remained intact for two DTA cycles to ~ 2500°C, but failed during cooling from the second cycle. It is anticipated that this type of capsule can be used for the study of irradiated carbides.

Arrangements have been made with GE-Sunnyvale for a cooperative program whereby LASL will be furnished specimens of irradiated (U, Pu)$O_2$ for DTA. Some of these specimens will have been irradiated to burnups of approximately 100, 000 MWD/MTM. Observations of these specimens will provide additional melting behavior data and should resolve some of the uncertainties regarding thermal arrests noted in previous specimens irradiated to lower burnups.

Phase Boundaries of Single Phase $U_{0.8}Pu_{0.2}C$: The DTA furnace has been used for thermal cycling and annealing a series of $(U_{0.8}Pu_{0.2})C$ specimens having various carbon concentrations. These specimens were quenched and the microstructures were examined by use of metallographic techniques to determine whether or not they were single phase at the temperatures of quenching. DTA traces were examined to determine if significant fractions of the specimens had undergone transformation during cooling.

The temperature range 1400-2100°C has been most extensively investigated. The phase boundary between single phase $(U_{0.8}Pu_{0.2})C$ and the two phase region containing liquid metal and the monocarbide appears to be at a C/M atomic ratio of 0.96 ± 0.01 at 1400°C and 0.95 ± 0.01 at 2100°C. The boundary between the single phase monocarbide phase field and the region containing the monocarbide and the sesquicarbide appears to be at a C/M atomic ratio of 0.99 ± 0.01 at 1400°C and at a slightly higher value at 1900°C. There are strong indications that specimens containing the sesquicarbide undergo a phase transformation at 2050°C. The nature of this transformation has not been defined.

These observations of slightly sloping phase boundaries for the monocarbide region show that sintering processes for the preparation of single phase monocarbide should have a slow cooling cycle as the final step, and the sintering temperature should be lower than 2050°C. It is possible to prepare single phase material by quenching from high temperatures, e.g., 1800°C, which will contain metal or sesquicarbide after annealing at intermediate temperatures. Slow cooling and/or annealing at intermediate temperature will allow the precipitation and consolidation of metal or sesquicarbide to make the second phase visible in the microstructure if C/M ratios are outside the correct limits.

### 3. High Temperature Calorimetry
(D.G. Clifton)

Enthalpy measurements have been made in the LASL hot cells on irradiated and unirradiated samples of $(U_{0.8}Pu_{0.2})O_2$ over the temperature ranges 1195 to 1970 and 1245 to 2096°C, respectively.

The irradiated sample was taken from the NUMEC-B-9 fuel capsule which had been exposed in EBR-II to a burnup of 57,000 MWD/Te (6.2 at.%). The unirradiated specimen was prepared from equal amounts of archival $(U_{0.8}Pu_{0.2})O_2$ taken from two batches of material obtained from NUMEC designated Batch Run No. 12 and Batch Run No. 25. NUMEC advised that the irradiated fuel for NUMEC-B-9 had been made from equal quantities of these two batches.

The enthalpy values obtained to date are shown in Fig. 463-2. Also shown are enthalpy data reported by

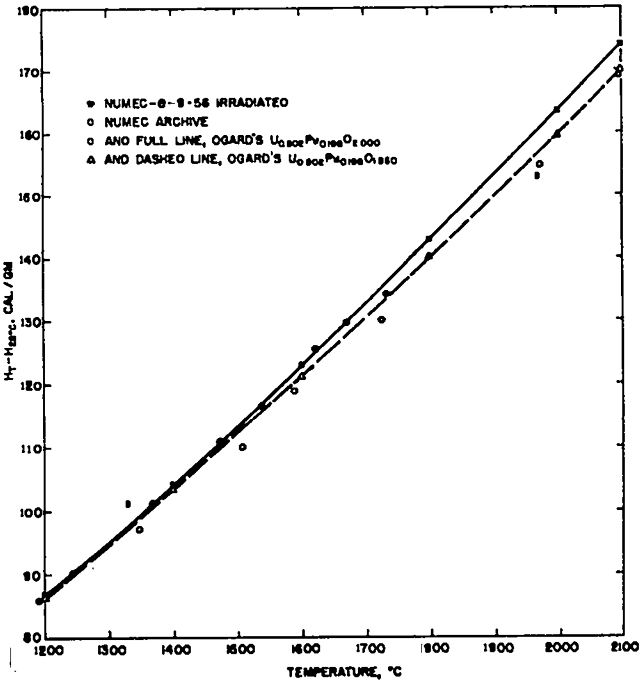

Fig. 463-2. Heat content of irradiated and archival oxides from the NUMEC-B series.

Ogard[4] for samples of unirradiated $U_{0.802}Pu_{0.198}O_{2.00}$ and $U_{0.802}Pu_{0.198}O_{1.98}$ which were provided by the General Electric Company.

On the basis of these data, several tentative conclusions have been drawn: (1) In general, the data for the irradiated NUMEC sample agree closely with those for the unirradiated stoichiometric $U_{0.802}PuO._{198}O_{2.00}$ except for the highest temperature point at 1970°C and the point at 1330°C. More experimental data are being obtained, particularly in the high temperature range. (2) The data for the unirradiated NUMEC $(U_{0.8}Pu_{0.2})O_2$ are definitely lower than those for the irradiated material from NUMEC-B-9, and also are lower than Ogard's data for the unirradiated $U_{0.802}Pu_{0.198}O_{1.98}$. (3) Ogard's data show a definite decrease in enthalpy in going from the stoichiometric to the hypostoichiometric mixed oxide.

The 2 to 4% difference between the measured enthalpies for the irradiated and unirradiated NUMEC samples is attributed to burnup effects. The agreement between the enthalpy data for irradiated NUMEC material and unirradiated GE $U_{0.802}Pu_{0.198}O_{2.00}$ is probably coincidental. The analytical determination of the O/M ratio for the NUMEC archival material has not been completed. It was reported that the fuel fabrication variables for the NUMEC Series-B fuel were the same as for the Series-A fuel.[5] The oxygen-to-metal ratio for the Series-A fuel was reported to vary from 1.940 to 2.004. It would appear possible that material used in this study was hypostoichiometric as fabricated.

On fission, each fissioning atom is replaced with two fission fragment atoms, thus increasing the number of atoms in the sample. Using the Dulong-Petit approximation, one can assign a heat content value per atom and thereby postulate an increase in the total heat content corresponding to the increase in the number of atoms. For a burnup of 6.2 at.%, the total number of atoms increases by 2.1%, so approximately a 2.1% increase in heat content is expected. This assumes no loss of gaseous or volatile fission products. Such losses would reduce the "increased number of atoms effect."

Other effects which can be expected to increase the observed enthalpy of an irradiated sample are heats of fusion, sublimation, or chemical interaction of the fission products. O'Boyle et al.[6] have studied the metallic ingots in irradiated $(U_{0.8}Pu_{0.2})O_2$ that are an alloy of the noble metal fission products whose oxides are not stable under operating conditions. The alloy consists of Ru, Mo, Tc, Pd, and Rh, and is expected to melt between 1800 and 1900°C. Some oxides that are not necessarily expected to remain in solution in the $(U, Pu)O_2$ matrix, such as BaO, $Cs_2O_2$, and $Rb_2O_2$, have low melting, decomposition and sublimation temperatures. Interaction of Mo and excess O in irradiated $(U, Pu)O_2$ would contribute heat effects. Molybdenum metal, molybdenum oxides, and $(U, Pu)O_2$ are involved in chemical equilibria which shift as functions of temperature, with any associated heats of reaction entering into the measurements. Also, any molybdenum oxides present melt, decompose, or sublime at rather low temperatures. Although the amounts of the individual fission products and associated thermal effects are rather small for a burnup of 6.2 at.%, the accumulated effects, which can occur over a broad temperature range, could reasonably account for changes in high temperature enthalpy of several percent.

The number of enthalpy measurements made on either the irradiated or unirradiated samples are so limited that further analysis at this time is not yet warranted. The present program of measurements should not only be extended in temperature range but some reproducibility checks are needed.

### 4. Mechanical Properties

(M. Tokar)

In an effort to determine the effect of the U/Pu ratio on hardness of (U, Pu)C at elevated temperatures, hot hardness measurements have been continued on monocarbide specimens as a function of the U/Pu ratio. Plots of log hardness versus temperature for some of these compositions are shown in Fig. 463-3. Each point represents the mean of 5 to 15 readings taken over 1 to 4 runs. The shapes of these curves have a similar pattern. The hardness decreases gradually as the temperature rises to approximately 400 to 500°C. There is then an increase in softening rate with increasing temperature after which the materials again soften less rapidly.

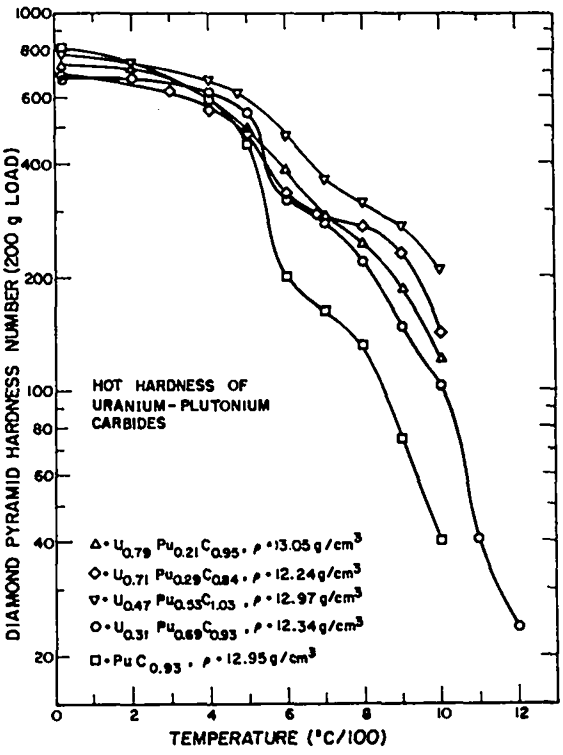

Fig. 463-3. Hot hardness of uranium-plutonium carbides.

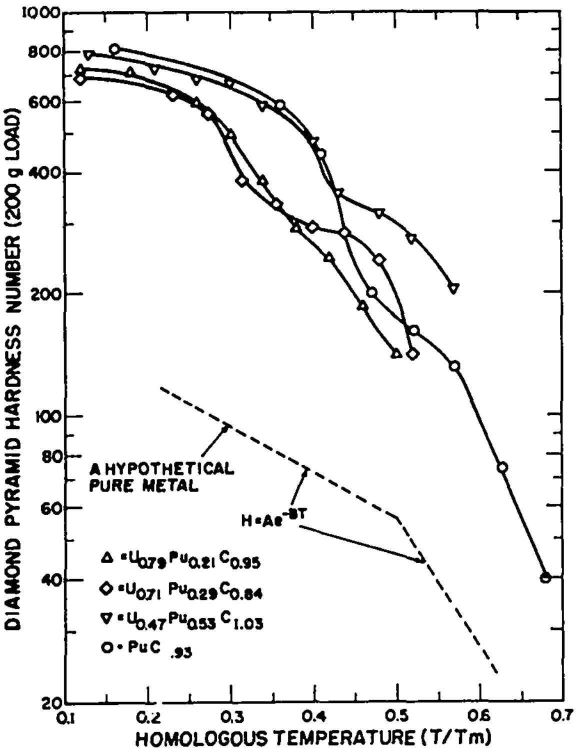

Fig. 463-4. Hot hardness of uranium-plutonium carbides as a function of homologous temperature.

For pure metals, plots of log hardness versus temperature often have a unique shape; i.e., two straight line segments which intersect at approximately half the melting point, 0.5 $T_m$.[7] Hardness plots for certain intermetallic compounds have been found to have the same shape, but the point of intersection varies between 0.4 and 0.75 Tm.[8] This form of the log hardness versus temperature plots may be represented by the so-called Ito-Shishshokin equation[9, 10]

$$H = Ae^{-BT}$$

where H is the hardness, A is a constant, B is the "softening coefficient," and T is the temperature. The constants A and B have different sets of values at low and high temperatures. It is theorized that different mechanisms of deformation are operative above and below the intersection temperature; below this temperature, slip processes predominate, while above this temperature, diffusion-controlled processes prevail.

A plot of some of the hardness data as a function of homologous temperature, $T/T_m$, is shown in Fig. 463-4. For the solid solution carbides, which melt over a temperature range, solidus temperatures were arbitrarily chosen as a basis for calculating the homologous temperature. It is apparent that except for the PuC specimen, none of the measurements were made at temperatures where high temperature deformation processes are certain to be operative, i.e., temperatures significantly greater than 0.5 $T_m$.

At temperatures below 0.5 $T_m$, the Ito-Shishshokin relationship is clearly not followed in these materials. Sufficient data are not yet available at temperatures above 0.5 $T_m$ to establish the applicability of this relationship at high temperatures. An effort is being made to obtain more high temperature (> 1000°C) data, since it is at these temperatures that the mechanisms for both creep and indentation hardness deformation should be the same (assuming that differences in type of loading and strain

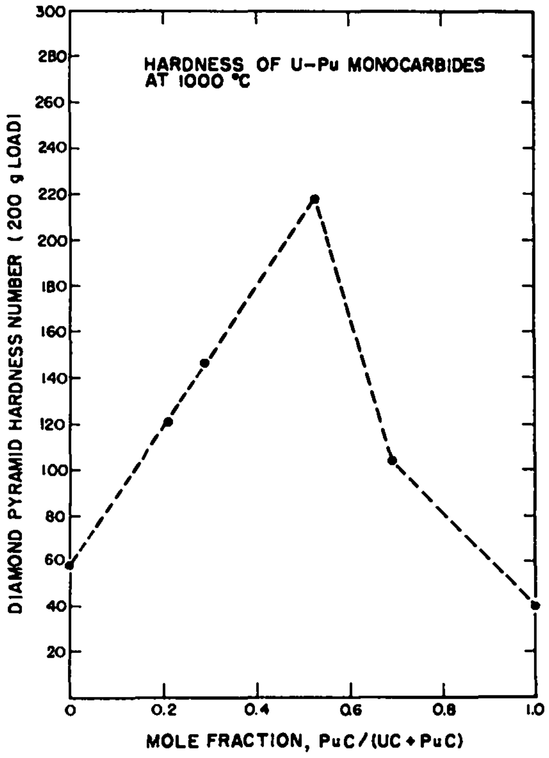

Fig. 463-5. Hot hardness of uranium-plutonium carbides at 1000°C showing the effect of solid solution hardening.

rate have a negligible effect). At temperatures below 0.5 $T_m$ the non-linearity of the log H versus T plots is possibly the result of dislocation-impurity interactions such as have been reported for UN[11] and UC.[12]

The effect of solid solution hardening at 1000°C in alloys of UC and PuC is shown in Fig. 463-5. Although the composition survey is incomplete, it appears that most of the solid solution carbides are significantly harder than UC at 1000°C. If this pattern held at higher temperatures, the solid solution carbides would be expected to be more creep resistant than UC; but comparison of the creep rates of $(U_{0.79}Pu_{0.21})C_{1.02}$ with literature values for $UC_{1.08}$ have shown that the $UC_{1.08}$ was more creep resistant in the temperature range 1300 to 1500°C. A possible explanation for the apparent contradiction lies in the theory of solid solution strengthening. At very high temperatures the deformation mechanism is almost certainly diffusion-controlled, but if in (U, Pu) C the diffusivity of the solute Pu ions is sufficiently high, there may be no "impurity" retardation of dislocation motion. At intermediate temperatures, however, the drift velocity of the solute Pu atoms might be expected to decrease to the point that dislocation motion is hindered, yielding a higher hardness than that obtained for pure UC. Since self-diffusion data for Pu in the solid solution carbides are not available, this hypothesis remains unsupported, but similar dislocation-solute atom interactions have been held responsible for anomalous mechanical property measurements in other materials in the temperature range from 0.25 to 0.45 $T_m$.[12-15]

## 5. Thermal Transport Properties

(J.F. Kerrisk)

Modifications of the inert atmosphere glovebox which will contain the thermal diffusivity furnace, have been completed and installation is in progress. Until the inert atmosphere glovebox is complete and plutonium-containing fuel materials can be studied, measurements on various standard materials are being made. This work is being done to improve the technique, in general, and also to develop highly precise and accurate data for reference materials for use in testing and standardizing the procedures and apparatus used by different laboratories to measure fuel transport properties.

The thermal diffusivities of two samples of molybdenum have been measured from 8 to 2037°C. These measurements investigated the following variables:

(1) Sample thickness - 0.1024 and 0.1505 in.

(2) Sample temperature transient detector - chromel alumel thermocouples and photomultiplier tube.

(3) Furnace atmosphere - vacuum, He and Ar.

No significant differences were observed between the two sample thicknesses over the entire temperature range. The thermocouple detector was used from 8 to 1158°C and the photomultiplier from 792 to 2037°C. In the temperature range where they overlapped, the results from the two detectors were not significantly different. Measurements in vacuum, He or Ar were not significantly different, but heat losses from the sample, as evidenced by the temperature decay of the sample with time, were greater in the He and Ar atmospheres, especially for the thicker sample. Corrections for heat losses from the sample were calculated using Cowan's method.[16] The maximum heat loss correction to the thermal diffusivity was 4.5% (at 2037°C in He). No heat loss corrections were required below 800°C. At temperatures above 1000°C in an Ar furnace atmosphere with the photomultiplier detector, a significant increase in signal noise was observed. This was attributed to convection currents above the sample causing distortion in the photomultiplier view of the sample back face. An increase in noise was not observed in a He atmosphere. These results and the probable source of the noise are consistent with problems found in optical thermal expansion measurements in various atmospheres in a similar geometry.[17]

Table 463-VIII lists the thermal diffusivities for the Mo standards as calculated from the equation

$$\alpha = \frac{w\ell^2}{t_{1/2}}$$

where $\ell$ is the sample thickness corrected for thermal expansion, $t_{1/2}$ is the half time for the temperature rise on the back face of the sample, and w is a factor depending on the heat losses (w = 0.139 for no heat losses).[16] A comparison of the results with other diffusivity and conductivity data is in progress.

## 6. Mass Spectrometric Studies of the Vaporization of Pu Fuels

(R.A. Kent)

Modifications of the RM6-K and Quadrupole Mass Spectrometers: It has been reported in previous reports that several modifications of the RM6-K magnetic mass spectrometer are required before the unit can be installed in the glovebox assembly. Of the components necessary for these modifications, all are available except the sliding door for the hood assembly and the Fox-type ion source which are being fabricated. When this unit is in operation, it will be used primarily to study the vaporization behavior of fuel components and fission products when high resolution in the higher mass ranges is required.

The existing quadrupole unit will be used primarily for the study of post-irradiated materials. The types of data to be obtained were discussed in detail in the previous quarterly report.[1] A number of changes must

TABLE 463-VIII

THERMAL DIFFUSIVITY OF MOLYBDENUM

| Temp, °C | α cm²/sec | Ref. | Temp. °C | α cm²/sec | Ref. |
|---|---|---|---|---|---|
| 8 | 0.603 | b | 1186 | 0.347 | c |
| 9 | 0.588 | a | 1186 | 0.349 | c |
| 11 | 0.603 | b | 1200 | 0.338 | d |
| 92 | 0.554 | a | 1248 | 0.328 | e |
| 118 | 0.542 | b | 1275 | 0.328 | f |
| 225 | 0.509 | b | 1291 | 0.323 | d |
| 390 | 0.453 | b | 1308 | 0.335 | c |
| 424 | 0.461 | a | 1341 | 0.322 | e |
| 552 | 0.435 | b | 1402 | 0.312 | d |
| 604 | 0.430 | a | 1402 | 0.311 | f |
| 677 | 0.420 | b | 1417 | 0.321 | c |
| 745 | 0.403 | a | 1419 | 0.322 | c |
| 787 | 0.396 | b | 1452 | 0.298 | d |
| 792 | 0.389 | f | 1453 | 0.299 | e |
| 792 | 0.401 | f | 1453 | 0.301 | e |
| 827 | 0.386 | a | 1501 | 0.292 | d |
| 838 | 0.377 | e | 1526 | 0.311 | f |
| 852 | 0.382 | d | 1526 | 0.296 | c |
| 870 | 0.382 | a | 1582 | 0.288 | e |
| 880 | 0.368 | b | 1596 | 0.279 | d |
| 886 | 0.378 | f | 1615 | 0.294 | c |
| 903 | 0.362 | c | 1620 | 0.289 | c |
| 903 | 0.368 | c | 1664 | 0.278 | f |
| 925 | 0.361 | e | 1694 | 0.271 | d |
| 973 | 0.371 | a | 1699 | 0.272 | e |
| 978 | 0.354 | b | 1699 | 0.268 | e |
| 979 | 0.369 | d | 1714 | 0.294 | c |
| 999 | 0.343 | b | 1781 | 0.264 | f |
| 999 | 0.344 | b | 1794 | 0.264 | d |
| 1037 | 0.338 | f | 1795 | 0.264 | e |
| 1050 | 0.352 | c | 1796 | 0.262 | c |
| 1059 | 0.346 | e | 1881 | 0.258 | c |
| 1068 | 0.334 | b | 1911 | 0.250 | f |
| 1071 | 0.364 | a | 1920 | 0.242 | d |
| 1079 | 0.343 | d | 1920 | 0.256 | e |
| 1095 | 0.351 | d | 1920 | 0.250 | e |
| 1150 | 0.326 | b | 1988 | 0.242 | c |
| 1150 | 0.320 | b | 2037 | 0.238 | c |
| 1150 | 0.331 | b | 2037 | 0.232 | d |
| 1155 | 0.332 | e | 2037 | 0.238 | e |
| 1158 | 0.340 | a | 2037 | 0.235 | f |
| 1172 | 0.340 | f | | | |

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| Ref. | Thickness in. | Furnace Atmosphere | Detector |
|---|---|---|---|
| a | 0.1024 | Argon | Thermocouple |
| b | 0.1505 | Argon | Thermocouple |
| c | 0.1505 | Vacuum | Photomultiplier |
| d | 0.1505 | Helium | Photomultiplier |
| e | 0.1024 | Vacuum | Photomultiplier |
| f | 0.1024 | Helium | Photomultiplier |

be made in this unit before irradiated materials may be studied. The major change is the installation of a radiation shield, consisting of a one-inch thick cylinder of $^{238}U$ metal, mounted within the oven assembly.

The existing quadrupole unit has been in operation with radioactive materials for approximately five years, and there has been a substantial deterioration in performance. In order to upgrade the performance, several new components have been purchased and installed. Among these are a new ion source, new quadrupole rods and a 14-stage electron multiplier that has ten times the gain of the original 10-stage multiplier.

Tritium: The first area to be investigated will be the location and mobility of tritium in both fuel and clad. Tritium is produced in small quantities by ternary fission from both $^{235}U$ and $^{239}Pu$. A series of calculations was performed in order to estimate the production of tritium as a function of burnup when $^{235}U_{0.8}$-$^{239}Pu_{0.2}O_2$ is exposed to fast neutrons (700 KeV). The results are listed in Table 463-IX.

Additional tritium may be produced by the (n, T) reaction in $^6Li$ present as an impurity in either the fuel or clad.

The calculations indicate that approximately 10 to 200 x $10^{-9}$ g of tritium will be produced per g of fuel, depending on the burnup. These amounts of tritium, while small, are sufficient for detection with the mass spectrometer provided that the tritium produced remains in either the fuel or the clad.

Ionization Cross Section Studies: A series of experiments is being performed in order to determine the reliability of published ionization cross section values. In practice the study of the vaporization behavior of the fission products in irradiated samples will involve complex systems containing many components. In order to allow the measurement of absolute vapor pressures, standard reference materials will be used and corrections will be made for relative ionization cross sections.

The ion current is measured at a given temperature for some standard material for which the vapor pressure is known as a function of temperature. The ion current for the unknown species is then measured and the vapor pressure of the unknown is calculated from the equation

$$P_{UNK} = (K_{UNK} I_{UNK} T_{UNK} / K_{STD} I_{STD} T_{STD}) P_{STD} \qquad (1)$$

where $P$ is the vapor pressure, $I$ the ion current, $T$ the temperature, and $K$ is a constant that is a function both of the gain of the electron multiplier for a given ion and of the ionization cross section for that ion. At a given temperature, the $T$ terms in Eq.(1) cancel and the vapor pressure of the unknown can be calculated if the relative values of $K_{UNK}$ and $K_{STD}$ are known. The gain of the electron multiplier for a given ion can be measured directly. Thus the accuracy of vapor pressures calculated from Eq.(1) depends on the reliability of the relative ionization cross section values. Ionization cross sections are usually calculated by means of quantum mechanics. Mann[18, 19] has calculated values for the various elements at ionizing voltages ranging from 0 to 200 eV.

National Bureau of Standards vapor pressure reference samples of Au and Ag have been obtained. Ion

TABLE 463-IX

TRITIUM PRODUCED BY FISSION OF $^{235}U_{0.8}{}^{239}Pu_{0.2}O_2$

| Burnup (percent) | Tritium Produced (ppb per weight of fissionable fuel) |
|---|---|
| 10 | 185 |
| 8 | 148 |
| 6 | 111 |
| 4 | 74 |
| 2 | 37 |

TABLE 463-X

ION CURRENT DATA FOR SILVER

| Ionizing Energy (eV) | Relative Ion Current* | Relative Ionization Cross Section (Mann) |
|---|---|---|
| 39 | 9.91 | 9.99 |
| 37.6 | 10.02 | 10.00 |
| 37.3 | 10.00 | 10.00 |
| 30 | 9.38 | 9.83 |
| 27.6 | 9.02 | 9.65 |
| 25 | 8.69 | 9.36 |
| 20 | 7.66 | 8.23 |
| 17.6 | 7.26 | 7.22 |

* Ion current data taken for $^{107}Ag^+$ and corrected to account for $^{109}Ag$.

current data for these materials are being obtained as a function of ionizing electron voltages over a wide temperature range in order to test the validity of the ionization cross sections calculated by Mann.

The ion current for Ag has been measured as a function of the ionizing voltage. The results are compared with Mann's calculated values in Table 463-X. The experimentally observed peak in the ion current for Ag occurred at 37.6 ± 0.5 eV as compared to the value 37.3 eV calculated by Mann.

The data in Table 463-X indicate good agreement between the measured and calculated values over most of the range, the values being identical at the maximum in the ionization curve and at about 10 eV above the ionization potential of Ag.

Similar measurements on Au showed that the maximum ion current signal for $^{197}Au^+$ occurred at an ionizing voltage of 39.2 ± 0.5 eV, in agreement with the value 37.4 eV calculated by Mann.

Comparison of Silver and Gold Ionization Cross Sections: At 1400°K, the ratio of the vapor pressures of Ag and Au is 772.3 as given by the NBS. At this same temperature, the experimentally determined ratio of IT for $Ag^+$ at 37.3 eV (corrected for the isotopic ratio) and IT for $Au^+$ at 39.2 eV was 836.8. These values, together with the experimentally determined gains of the electron multiplier for these ions, when inserted into Eq.(1), require an ionization cross section ratio at these voltages of $\sigma_{Ag}/\sigma_{Au} = 1.25$. The ratio calculated at these voltages from Mann's values is 1.16, in good agreement when the experimental error in the ion current data is considered. Thus, at least for these two species, at the peaks in the ionization curves, the cross sections calculated by Mann seem to be reliable. Further studies are in progress and should be completed by the time the quadrupole unit is ready for use with irradiated fuel materials.

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2. "Compressive Creep and Hot Hardness of Uranium-Plutonium Monocarbide, (U, Pu)C," M. Tokar and J.A. Leary, presented at the 73rd Annual Meeting of the American Ceramic Society, Chicago, Ill., April 24-29, 1971.

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## PROJECT 472

## ANALYTICAL STANDARDS FOR FAST BREEDER REACTOR OXIDE FUEL

Person in Charge: R. D. Baker
Principal Investigator: C. F. Metz

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### I. INTRODUCTION

Necessary to the development of the high quality fuel and cladding required by the LMFBR/FFTF program are reliable analytical methods for the chemical characterization of the raw materials and the manufactured fuel and for the examination of irradiated fuel.

The more immediate objectives of this project are (1) the evaluation of existing analytical methods used by potential producers of FFTF fuel, (2) upgrading those methods found to be inadequate and the development of new methods as required by additional specifications, (3) the preparation of standardized calibration materials required by various analytical methods used for specification analyses and the distribution of these materials to producers of FFTF fuel, (4) the preparation of a manual of analytical methods for FFTF fuel, (5) development of a statistically designed quality assurance program for the chemical characterization of FFTF fuel as required by commensurate specifications, and (6) provide aid, as requested, for the prequalification programs of potential FFTF fuel producers.

These more immediate objectives will be continued, as required by the development of new fuel compositions for LMFBR demonstration plants and the new or additional chemical specifications that will be necessary for their characterization.

Additional objectives of this program involve studies of irradiated fuel including (1) the development of fuel burnup measurement methods based on conventional and spark source mass spectrometric determinations of actinide and fission product isotopes, (2) the development of faster fuel burnup measurement methods based on chemical analysis techniques for use for larger routine sample loads, (3) the applications of burnup methods correlated with other measurement techniques including microprobe and metallographic examination to assess the irradiation behavior of LMFBR/FFTF fuels, (4) the measurement of fission yields, and cross sections, as necessary, to ensure highly reliable burnup methods, (5) the development of analytical methods for gases including hot cell techniques for the evaluation of their effects on cladding stability, (6) the development of mass spectrometer methods, including hot cell techniques, for studies of the gas retention properties of fuels as a function of temperature-time cycling, and (7) the application of ion emission microanalysis to elucidate migration mechanisms in irradiated fuels.

At the request of RDT, a program has been initiated to evaluate the status of analytical methods for the chemical characterization of boron carbide, the proposed neutron absorber material for the LMFBR/FFTF control rods.

### II. FFTF ANALYTICAL CHEMISTRY PROGRAM

The preparation of the calibration materials and quality control samples to be used by all participating laboratories during periods of LMFBR/FFTF fuel production has been essentially completed. For the chemical analyses, five calibration materials and three quality control samples having $U_3O_8$ matrices, and an equal number having (U, Pu)$O_2$ matrices, were prepared. Previously developed or modified chemical methods are being used in analyzing four samples from each of these sixteen materials for C, Cl, F, N, P, S, and W. In addition, one calibration material containing Fe added to a (U, Pu)$O_2$ matrix and one containing U added to a $PuO_2$ matrix were prepared and analyzed for the added impurity. Five calibration materials and three quality control samples for each of the matrices $U_3O_8$, $PuO_2$, and (U, Pu)$O_2$ were prepared and analyzed spectrographically. Each material contained 29 specification impurities at concentrations ranging from one-tenth to twice the specification maximum value. Verification of the impurity contents and the homogeneity of each material by these careful chemical analyses is expected to be completed by June 1971, which meets the present schedule for the LMFBR/FFTF fuel pin qualification program. In collaboration with WADCO personnel, a detailed program has been established for the distribution of these materials to participating laboratories and for the statistical program associated with the quality control samples.

The LASL compilation of methods of chemical analysis for FBR uranium-plutonium oxide fuel and source materials has been published (see section V). This compilation consists of 24 methods which include dissolution procedures and measurements of uranium, plutonium, uranium and plutonium isotopic abundances, metal and nonmetal impurities, and other specifications relating to total gas, water, and the oxygen-to-metal atom ratio. These methods apply to (U, Pu)$O_2$ fuel pellets, $UO_2$ insulator pellets, and the source materials of ceramic grade $UO_2$ and $PuO_2$ used for their manufacture.

The mass spectrometer to be used for nuclear fuel burnup measurements has satisfactorily passed acceptance tests at LASL. The instrument is being calibrated for burnup measurements and standard solutions are being prepared for the burnup analysis of fuel samples from experimental pins processed as part of Project 401. The mass spectrometer to be used for gas analysis has been shipped to LASL and final acceptance tests will be started early next quarter.

## III. ANALYTICAL CHEMISTRY PROGRAM FOR BORON CARBIDE

The proposed neutron absorber material for LMFBR/FFTF control rods is boron carbide pellets. At the request of RDT, a program has been initiated to determine the status of analytical methods for the chemical characterization of $B_4C$. In view of the fact that bid requests have to be let in about four months for the $B_4C$, this project is of highest priority at this time.

The status of the analytical chemistry of $B_4C$ was reviewed at a meeting held at Richland, Washington, with attendees from HEDL, ORNL, and LASL. Samples of $B_4C$, both in pellet form and pulverized form, will be distributed to the above three laboratories for complete chemical analysis in accordance with present specifications for the material. LASL is responsible for the statistical evaluation of the data similar to the evaluation done for the mixed oxide fuel.[1] Analytical measurement precision and pellet-to-pellet variability will be calculated for each specification analysis.

Certain of the analyses appear capable of improvement which will be studied at all three laboratories. Experience at HEDL indicates that a major contributor to the variability of the analyses is the dissolution procedure now used for pellet and pulverized samples. This method is based on fusions with sodium carbonate which require close operator control to obtain complete solubilization without loss of sample. A program will be undertaken to improve dissolution procedure in addition to the studies for the purpose of improving methods of analysis for certain specifications.

## IV. INVESTIGATION OF METHODS

An important objective of this project is the development of new analytical methods and improvement of existing methods for the analysis of various raw materials and fuels in the FFTF program. Work on most of the methods necessary to this project was completed and descriptions of these methods were published (see Section V). Some additional testing was done on two of the methods.

### 1. Determination of Dysprosium, Europium, Gadolinium, and Samarium (H. M. Burnett)

Final testing of the spectrographic measurement of Dy, Eu, Gd, and Sm in $U_3O_8$, $PuO_2$, and $(U,Pu)O_2$ consisted of the analysis of the prepared calibration materials, quality control samples, and of other test samples. In this method, U and Pu were extracted from a 6.7M HCl solution into 20% tri-n-octylamine (TNOA) in xylene in three passes. The aqueous phase containing the rare earths, added Y internal standard, and other non-extracted impurities was ignited to remove B and organic material, and a portion of the residue was analyzed by a copper-spark technique in an Ar atmosphere.

The calibration materials were not completely dissolved by successive treatments with 15M $HNO_3$-0.05M HF, 12M $HClO_4$, and 6M HCl. The small amount of insolubles, however, did not interfere with the separation and subsequent measurement of rare earths. The calibration materials were then used as standards in triplicate analyses of three test samples prepared similarly to the quality control samples. The results showed that the precision (1 σ) of the method was no greater than 10 relative percent and that the method was unbiased for samples of this type.

### 2. Determination of Sulfur (G. C. Swanson)

Spectrophotometric measurement of sulfur as Lauth's Violet, following separation from $UO_2$, $PuO_2$, or $(U,Pu)O_2$ by distillation as $H_2S$, was shown previously to be satisfactory, but the precision of the initial results was not as good as anticipated. For this reason, each operation in the method was considered in order to improve the precision. In this method, samples containing 5 to 60 μg of sulfur are dissolved in $HNO_3$-HF, formic acid is added to reduce nitrate, and the sulfur is reduced in boiling HI-$H_2PO_3$ to $H_2S$ which is distilled into zinc acetate solution. The resulting ZnS is reacted with $FeCl_3$, HCl, and p-phenylenediamine to form Lauth's Violet which is measured spectrophotometrically at a wavelength of 595 nm.

Each of the operations following dissolution were checked by repeated analyses of solutions containing known amounts of sulfur, and were found to contribute very little to the variability of the results. A study of the dissolution and formic acid reduction steps showed that minute quantities of solids were deposited on the beaker walls during the energetic reaction of nitrate with formic acid. These traces of solids were not quantitatively washed from the container walls into the solution with water or formic acid, but rinsing with 3M HCl was effective for this purpose. Higher and more consistent recoveries of sulfur were obtained. Relative standard deviations were 6 to 3% in measuring 50 to 600 μg/g of sulfur in 0.1-g samples and 12 to 5% in measuring 10 to 120 μg/g of sulfur in 0.5-g samples. No further work on this method is planned.

## V. PUBLICATIONS

1. J. E. Rein, G. M. Matlack, G. R. Waterbury, R. T. Phelps, and C. F. Metz, "Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials," LA-4622 (1971).

## VI. REFERENCES

1. J. E. Rein, R. K. Zeigler, and C. F. Metz, LA-4407 (1970).

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