# OUT-OF-PILE PROPERTIES OF
# MIXED URANIUM-PLUTONIUM CARBIDES

Final Report

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December 6, 1963

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## FOREWORD

The United States and the European Atomic Energy Community (Euratom), on May 29 and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint U.S.-Euratom Research and Development Program which is aimed at reactors to be constructed under the Joint Program.

The work described in this report represents the Joint U.S.-Euratom effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in Western Europe and the United States.

The measurement of the out-of-pile properties of solid solution uranium-plutonium carbides was sponsored jointly by the USAEC and Euratom. The prime contractor was the United Nuclear Corporation, Development Division, and the subcontractor was The Carborundum Company. The United Nuclear Corporation performed the property determinations and The Carborundum Company prepared the fuel samples.

The report covers the entire program from Feb. 6, 1962 to Dec. 6, 1963, but particularly the period from November 1, 1962 to December 6, 1963. Details of

the previous period, February 6, 1962 to October 31, 1962, are reported in UNC-5065.

The program is closely coordinated with the USAEC-sponsored Carbide Fuel Development program, whose major objectives have been to develop fabrication methods for (U,Pu)C and to evaluate its in-pile behavior.

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# 1. INTRODUCTION

Fuels made of solid solutions of (U,Pu)C can reduce fuel cycle costs of plutonium-fueled power reactors. The fuel cycle cost reduction is anticipated because of the high burnup and power generation capability of (U,Pu)C.

(U,Pu)C irradiation tests show that carbide fuels have considerably greater dimensional stability and fission gas retention ability than metallic and oxide fuels. The irradiation tests of (U,Pu)C are being sponsored at United Nuclear Corporation by the USAEC, in a program closely allied to the out-of-pile property program. The goal of the out-of-pile property program is to determine the properties of (U,Pu)C which have the most significant effect on the operational characteristics of the fuel. They are:

## 1. Melting Point

A high melting point is desirable to minimize fission gas release and maximize dimensional stability.

## 2. Thermal Conductivity

A high thermal conductivity is desirable to permit high power operation without excessive temperatures causing high fission gas release and dimensional instability.

## 3. Thermal Stability and Vapor Pressure

A high thermal stability is desirable to prevent fuel decomposition and chemical reaction of the fuel at high temperatures.

4. Fuel-Cladding Compatibility

   Minimum fuel-cladding reactions are desirable to prevent fuel diffusion through the cladding and to prevent deterioration of the cladding properties.

5. Coefficient of Expansion

   Knowledge of the thermal expansion behavior is necessary to evaluate the fuel-cladding gap at operating conditions.

The out-of-pile property measurements made on this program indicate that the performance of carbides will reduce fuel cycle costs.

## 2. SUMMARY

### 2.1 GENERAL CONCLUSIONS

The out-of-pile properties measured by this program indicate that solid solution uranium-plutonium carbides are high performance fuels capable of reducing fuel cycle costs.

Specifically, the higher than expected melting point of $(U_{0.8}Pu_{0.2})C_{0.95}$ will be a strong factor in permitting high temperature operation of the fuel. The good compatibility with ferritic steel, austenitic steel, vanadium, and niobium will permit a clad selection based on a wide range of materials. The vapor pressure of Pu over $(U_{0.8}Pu_{0.2})C_{0.95}$ does not appear to be higher than that of U, as thought from preliminary experiments of other investigators. The thermal conductivity of $(U_{0.8}Pu_{0.2})C_{0.95}$ is still to be measured; however, the in-pile value obtained on the AEC-sponsored United Nuclear program is about 80% that of UC.

### 2.2 FUEL SAMPLE FABRICATION

Fabrication studies to produce high density solid solutions of 80% UC-20% PuC, with reproducible structure, composition, and density, were completed. Solid solution (U,Pu)C powder was produced by the oxide-carbon reaction, and the powders were consolidated by cold pressing and sintering. The studies were a continuation of work performed on Contract AT(30-1)-2899 with the USAEC. Two types of material were produced:

1. $(U_{0.8}Pu_{0.2})C_{0.95}$, single-phase monocarbide pellets with average densities of 12.8 $g/cm^3$ (94% of theoretical), sintered at 1925°C;

2. $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 w/o Ni sintering aid, major monocarbide phase and minor amount of sesquicarbide phase pellets, with average densities of 13.1 $g/cm^3$ (96.5% of theoretical), sintered at 1550°C.

Test samples of both materials were produced using the basic fabrication procedure developed. Some modifications to the procedure were required by the different shapes of the test samples. These shapes are as follows:

| | |
|---|---|
| Melting Point Specimens | 0.20 in. diam cylinders with black body hole |
| Compatibility Test Specimens | 0.20 in. diam cylinders |
| Coefficient of Expansion Bars | 2 in. long, 0.2 in. $\times$ 0.3 in. cross section |
| Thermal Conductivity Specimens | 0.625 in. diam cylinders with and without central holes. |

## 2.3 PROPERTY DETERMINATIONS

The coefficient of thermal expansion was measured as $11.9 \times 10^{-6}$/°C for $(U_{0.8}Pu_{0.2})C_{0.95}$ at 25 to 1400°C and $12.3 \times 10^{-6}$/°C for $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 w/o Ni at 25 to 1400°C. The presence of the nickel sintering aid did not make a significant difference. The values are similar to those of UC, compared at 950°C, the maximum temperature to which UC has been measured.

The melting point of $(U_{0.8}Pu_{0.2})C_{0.95}$ was found to be 2480 ± 20°C. The solidus is estimated to be about 2430°C.

The vapor pressure data in the temperature range of 2100 to 2600°K show that the pressure of plutonium is about the same as uranium over $(U_{0.8}Pu_{0.2})C_{0.95}$. While the uranium data are about an order of magnitude higher than anticipated, based on data for U over UC (probably due to carbon diffusion across the cell), the thermal stability of the fuel in the temperature range of power reactors is still quite good.

Thermal conductivity capsules containing $(U_{0.8}Pu_{0.2})C_{0.95}$, $(U_{0.8}Pu_{0.2})C_{0.95}$ plus 0.12 w/o Ni, and UC plus 0.12 w/o Ni (standard) were fabricated. Repairs required by the Mound Laboratory equipment have delayed the measurements.

$(U_{0.8}Pu_{0.2})C_{0.95}$, with and without nickel sintering aid, was compatible with type 316 stainless steel, niobium, niobium-1% zirconium, $2\frac{1}{4}$ Cr-1 Mo steel, and vanadium at 593°C and 816°C for 1000 and 4000 hr. There was no reaction with Inconel-X after 1000 hr at 593°C, but there was a slight reaction after 1000 hr at 816°C. A reaction was noted with Zircaloy-2 after 1000 hr at both 593° and 816°C. The results were similar to those obtained with UC under AEC Contract AT(30-1)-2899.

# 3. FUEL SAMPLE FABRICATION

## 3.1 INTRODUCTION

The goal of the fabrication effort was to produce pellets and bars of 80% UC-20% PuC solid solutions with reproducible structure, composition, and density, suitable for property determinations. The development of the fabrication process was detailed in the first report (UNC-5065) and in the USAEC reports issued under Contract AT(30-1)-2899.

The desired microstructure is single-phase monocarbide. Any variation from this was controlled to be toward structures containing higher carbides, since free metal is not desirable in a high temperature fuel.

A substoichiometric amount of carbon was used with the mixed $UO_2$ and $PuO_2$ to produce single-phase or two-phase material. The equilibrium (U,Pu)(OC) relationships are such that a stoichiometric amount of carbon with 2000 to 4000 ppm oxygen promotes the formation of sesquicarbide.

All the fabrication work was done in a high purity recirculating helium atmosphere and the materials were heated in a graphite resistance furnace in carburized tantalum-lined graphite crucibles. Synthesis reaction end-points were determined by analyzing the exhaust gas for CO.

## 3.2 MELTING POINT AND COMPATIBILITY SPECIMENS

### 3.2.1 Synthesis

Four 100-g synthesis batches were prepared from mixtures of $UO_2$, $PuO_2$ and carbon to obtain (U,Pu)C for melting point and compatibility specimens and for thermal expansion bars. Each of the batches was intimately blended, and cold pressed at 5000 psi into 0.6 in. diameter by 0.6 in. high compacts. The compacts were then broken into slices about 1/4 in. in height and heated to 1625°C with a hold-time of 6 hr.

The reaction products resulting from the four synthesis runs were crushed in small lots in the Spex mixer. Small samples from each experiment were analyzed for total carbon. The results are shown in Table 1. The material from all the runs was intimately mixed by milling for 24 hr in a rubber-lined mill using stainless steel balls. Chemical analysis of the milled powder gave a total carbon content of 4.66%, which is very close to the desired (U,Pu)$C_{0.95}$ content of 4.56%. A sample was analyzed by the x-ray diffractometer technique. The major phase was (U,Pu)C having a unit cell size $a_0 = 4.9652 \pm 0.0005$ Å. A minor (U,Pu)$_2$C$_3$

Table 1 — Results of Synthesis of $(U_{0.8}Pu_{0.2})C_{0.95}$

| Run No. | Reaction Temperature and Hold-Time | Total Carbon, % | X-Ray Diffractometer Analysis |
|---------|------------------------------------|-----------------|-------------------------------|
| 1 | 1625°C – 6 hr | 4.64 | – |
| 2 | 1625°C – 6 hr | 4.55 | – |
| 3 | 1625°C – 6 hr | 4.67 | – |
| 4 | 1625°C – 6 hr | 4.69 | – |
| Composite | | 4.66 | Major (U,Pu)C $a_0 = 4.9652 \pm 0.0005$ Å Weak (U,Pu)$_2$C$_3$ Faint (U,Pu)O$_2$ |

phase and a very faint $(U,Pu)O_2$ phase were also evident. To prepare powder with sintering aid, a 140-g portion of the milled powder was placed in another mill with 0.12 w/o nickel powder and milled for another 24 hr.

## 3.2.2 Fabrication

Pellets with 1/4 w/o Carbowax binder were pressed at 30,000 psi from the milled powders. The size of the cold formed pellets for the melting point and compatibility specimens was 0.225 in. in diameter by about 0.22 in. high. The pellets for melting point studies were fabricated in a special ram and die to produce specimens with a centrally located cone-shaped cavity 0.025 in. in diameter by 0.177 in. deep. Twenty-nine pellets with and without nickel were cold pressed. Of these, seven had the conical cavity.

The $(U_{0.8}Pu_{0.2})C_{0.95}$ pellets without sintering aid were sintered at 1925°C; those with 0.12 w/o nickel were sintered at 1550°C. The hold-time in each case was one hour. The results are shown in Table 2.

The carbon and oxygen contents for the $(U_{0.8}Pu_{0.2})C_{0.95}$ without sintering aid were somewhat lower than those for material with sintering aid. This may be due to reaction of the carbon and oxygen at the higher sintering temperature, but data on other samples are contradictory.

The pellets from the two large batches were acceptable and were subsequently surface ground to 0.197 ± 0.002 in. in diameter. Twenty-five pellets from each batch were then selected and put aside for property measurement.

## 3.3 COEFFICIENT OF EXPANSION BARS

The $(U_{0.8}Pu_{0.2})C_{0.95}$ powder described in Section 3.2 was used to fabricate the coefficient of expansion bars.

Table 2 — Results of Sintering of $(U_{0.8}Pu_{0.2})C_{0.95}$ Pellets

| Material | Reaction Temp and Hold-Time | Sintering Temp and Hold-Time | Sintered Density (and Range), g/cm$^3$ | Total Carbon, % | Oxygen Analysis,* ppm |
|---|---|---|---|---|---|
| $(U_{0.8}Pu_{0.2})C_{0.95}$ plus 0.12 w/o Ni (29 pellets) | 1625°C − 6 hr | 1550°C − 1 hr | 12.90 (12.86-12.98) | 4.70 | 2000-4000 |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ (29 pellets) | 1625°C − 6 hr | 1925°C − 1 hr | 12.47 (12.32-12.56) | 4.53 | 1000-2000 |

*Dow Chemical Co.  The method is described in UNC-5065.

Eight bars of $(U_{0.8}Pu_{0.2})C_{0.95}$ were fabricated from the powder, five with the addition of 0.12 w/o nickel and the remainder without. The size of the cold pressed bars was 2.30-in. long by 0.233-in. wide and 0.340-in. high. The bars were cold pressed at 13,000 psi and contained the usual 1/4 w/o Carbowax binder. The data for five sintering runs are given in Table 3.

The first run was performed with three $(U_{0.8}Pu_{0.2})C_{0.95}$ plus 0.12 w/o nickel bars. The sintering temperature was 1550°C with a hold-time of one hour. The sintered bars contained many surface fractures which probably were the result of removing the temporary binder too rapidly. The heating schedule for this run was 10°C/min to 600°C, then 7°C/min to 1550°C. These bars were considered unacceptable and another run was performed.

An additional 100 g of $(U_{0.8}Pu_{0.2})C_{0.95}$ plus 0.12 w/o nickel powder were prepared by blending $(U_{0.8}Pu_{0.2})C_{0.95}$ powder with nickel powder by the process described in Section 3.2. Two bars were pressed from this material and they were run at a lower rate of temperature rise: 4°C/min to 600°C, followed by 8°C/min to 1300°C and 4°C/min to 1550°C. The bars from this run had an acceptable surface finish and were within specifications for warpage. The resulting density of 12.80 g/cm$^3$ was slightly lower than anticipated. A subsequent heat treatment run at 1550°C for an additional hour did not increase the density or change the physical appearance of the bars. The somewhat lower density was still within the acceptable range for thermal expansion measurements. A minimum of 85% of theoretical (11.6 g/cm$^3$) is required for reliable measurements.

The $(U_{0.8}Pu_{0.2})C_{0.95}$ bars were sintered at 1925°C in runs 4 and 5 with varying hold-times, i.e., 1 hr for run 4 and $1\frac{1}{2}$ hr for run 5. The heating schedule was 4°C/min to 600°C, 11°C/min to 1600°C, and 4°C/min to 1925°C. The sintered density for the bar from run 4 was 11.8 g/cm$^3$ while that for the two bars from run 5 was 12.00 and 12.07 g/cm$^3$. These latter two bars were used for thermal expansion measurements.

Table 3 — Results of Sintering of $(U_{0.8}Pu_{0.2})C_{0.95}$ Bars

| Run No. | Material | Sintering Temp and Hold-Time | Average As-Sintered Bar Density, $g/cm^3$ | Total Carbon, % | X-Ray Diffractometer Analysis |
|---------|----------|------------------------------|-------------------------------------------|-----------------|-------------------------------|
| 1 | $(U_{0.8}Pu_{0.2})C_{0.95}$ plus 0.12 w/o Ni | 1550°C – 1 hr | Not determined | 4.73 | Major (U,Pu)C $a_0 = 4.9662 \pm 0.0001$ Å Weak/mod $(U,Pu)_2C_3$ $a_0 = 8.0947 \pm 0.0008$ Å Very faint $(U,Pu)O_2$ Indication $(U,Pu)C_2$ |
| 2 | $(U_{0.8}Pu_{0.2})C_{0.95}$ plus 0.12 w/o Ni | 1550°C – 1 hr | 12.79 | – | – |
| 3* | As above | 1550°C – 1 hr | 12.80 | – | – |
| 4 | $(U_{0.8}Pu_{0.2})C_{0.95}$ | 1925°C – 1 hr | 11.80 | 4.53 | Single-phase (U,Pu)C $a_0 = 4.961 \pm 0.002$ Å |
| 5* | $(U_{0.8}Pu_{0.2})C_{0.95}$ | 1925°C – 1½ hr | 12.03 | – | – |

*Bars from these runs were chosen for measurement.

The bars to be tested were then surface ground to the final dimensions: 2.005 ± 0.005 in. long by 0.205 ± 0.005 in. wide and 0.290 ± 0.005 in. high.

## 3.4 THERMAL CONDUCTIVITY SPECIMENS

### 3.4.1 Synthesis

A total of 550 g of $UO_2$, $PuO_2$ and carbon powder was synthesized in 70 to 100-g batches. The reaction temperature was 1625°C with a hold-time of about 5 hr. The results for the seven runs are given in Table 4. Run 5 represents a recrushing, pressing, and reheating of material from runs 3 and 4 which gave high carbon contents. The powder from all the runs was combined and blended for 24 hr. The composite had a carbon content of 4.75% and was mostly single-phase as indicated by x-ray diffractometer analysis.

Several sintering experiments were then performed with pellets cold pressed from this large composite batch of powder to determine the best sintering conditions for maximum density of the larger (0.625 in. diameter) thermal conductivity pellets.

### 3.4.2 Sintering Experiments

To obtain 0.625-in. diameter pellets for the thermal conductivity specimens, the diameter of the cold pressed pellets was set at 0.725 in.

### Effect of Temperature

Three 0.225-in. diameter pellets and one 0.725-in. diameter pellet were cold pressed from part of the 500-g composite blend. The binder was 1/4 w/o Carbowax and the cold forming pressures were 30,000 and 20,000 psi, respectively. Pressures higher than 20,000 psi could not be reached for the large pellets with the available press.

Table 4 — Results of Synthesis of $(U_{0.8}Pu_{0.2})C_{0.95}$ Powder
for Thermal Conductivity Specimens

| Run No. | Batch Size, g | Reaction Temp and Hold-Time | Total Carbon, % | X-Ray Diffractometer Analysis |
|---|---|---|---|---|
| 1 | 100 | 1625°C − 5¼ hr | 4.68 | — |
| 2 | 100 | 1625°C − 5¾ hr | 4.70 | — |
| 3 | 80 | 1625°C − 5 hr | 5.02 | — |
| 4 | 70 | 1625°C − 4½ hr | 4.80 | — |
| 5* | ~130 | 1625°C − 2 hr | 4.80 | Major (U,Pu)C $a_0 = 4.9650 \pm 0.0007$ Å Weak (U,Pu)C$_2$ Faint (U,Pu)$_2$C$_3$ |
| 6 | 100 | 1625°C − 5 hr | 4.63 | Major (U,Pu)C $a_0 = 4.9662 \pm 0.0002$ Å Weak (U,Pu)C$_2$ |
| 7 | 100 | 1625°C − 5 hr | 4.69 | — |
| Composite | − | — | 4.75 | Major (U,Pu)C $a_0 = 4.9657 \pm 0.0006$ Å Weak (U,Pu)C$_2$ Faint/weak (U,Pu)$_2$C$_3$ |

*Product from runs 3 and 4 crushed, pressed, and reheated.

The large pellet and two small ones were then sintered at 1925°C with a hold-time of one hour. The rate of temperature rise was 2°C/min to 300°C, and 20°C/min to 1925°C. The resulting density of 11.95 g/cm$^3$ was the same for the large and small pellets. One of the small pellets was then reheated to 1940°C and subsequently to 1960°C, with hold-times of 1/2 hr. Pellet density was determined after each heat treatment. The third small pellet was heated directly to 1960°C at the same time for comparison. Results are shown in Table 5. It is evident from the table that a small increase in density was obtained by the higher sintering temperature. The carbon content was also considerably lower after experiment 3, probably due to the reaction of carbon with the oxygen either in solution or present in the atmosphere, or both.

### Effect of Carbon Content

It was thought that the lower carbon content material might yield sintered pellets of higher density. The large pellet from experiment 1 was then crushed and ball-milled for 24 hr to obtain $(U_{0.8}Pu_{0.2})C$ with 4.62% carbon instead of the initial content of 4.75%. Several 0.225-in. diameter pellets were cold pressed from this powder in the usual manner and sintered at 1925°C with an initial hold-time of one hour. Some of these were subsequently heated to 1925°C for an additional hold-time of one hour. The results, also shown in Table 5, indicate that no appreciable gain in density is obtained over that of experiments 3 or 4. However, there is a small increase in density when pellets from experiment 5 are compared to those of experiment 1.

### Effect of Ball-Milling and Hold-Time

Two additional techniques were tried to increase the sintered pellet density. The variables investigated were ball-milling time and hold-time at sintering temperature. For this purpose, the remaining $(U_{0.8}Pu_{0.2})C$ powder (about 450 g of 4.75% carbon) was ball-milled for an additional 24 hr. Pellets of 0.225-in. diameter were cold compacted in the usual manner and sintered at 1925°C with hold-times

Table 5 — Results of Sintering Experiments for Thermal Conductivity Specimens

| Experiment No. | Batch Size | Sintering Temp and Hold-Time | Sintered Density, g/cm$^3$ | Total Carbon, % |
|---|---|---|---|---|
| 1 | One large pellet<br>Two small pellets | 1925°C − 1 hr | 11.95 | 4.62 |
| 2 | One small pellet from experiment No. 1 | 1925°C − 1 hr plus<br>1940°C − 1/2 hr | 12.02 | — |
| 3 | Same pellet as No. 2 | 1925°C − 1 hr plus<br>1940°C − 1/2 hr plus<br>1960°C − 1/2 hr | 12.17 | 4.46 |
| 4 | One small pellet | 1960°C − 1/2 hr | 12.15 | 4.62 |
| 5* | Three small pellets | 1925°C − 1 hr | 12.10 | 4.62 |
| 6 | One pellet from No.5 | 1925°C − 1 hr plus<br>1925°C − 1 hr | 12.15 | 4.42 |

*The large pellet from experiment 1 was crushed and re-pressed into small pellets.

of 1, $2\frac{1}{2}$, and 4 hr. The results are shown in Table 6. The 4-hr hold-time gave a consistently higher density, and this time was chosen for subsequent fabrication of specimens without sintering aid.

Table 6 — Effect of Hold-Time on Sintering of $(U_{0.8}Pu_{0.2})C$ Powder Milled 48 hr

| Experiment No. | Sintering Temp and Hold-Time | As-Sintered Density, g/cm$^3$ | As-Ground Density, g/cm$^3$ |
|---|---|---|---|
| 7 | 1925°C – 1 hr | 12.27 | — |
| 8 | 1925°C – $2\frac{1}{2}$ hr | — | 12.31 to 12.63 |
| 9 | 1925°C – 4 hr | 12.48 to 12.64 | 12.66 to 12.81 |
| 1* | 1925°C – 1 hr | 11.95 | — |

*Twenty-four hour milling time.

Effect of Heating Rate

Pellets of 0.725-in. diameter by about 0.550-in. high were cold pressed with 1/4 w/o Carbowax binder at 20,000 psi. The pellets were sintered at 1925°C with a hold-time of 4 hr. The rate of temperature rise was 2°C/min to 300°C, and 20°C/min to 1925°C. Some of the pellets so treated developed fractures, while others had surface imperfections.

Several experiments were performed to determine the cause of pellet deterioration during sintering and to evaluate ultrasene as a binder material. For this purpose, several UC pellets, 0.725 in. in diameter, were cold pressed at 20,000 psi. Some contained the ultrasene binder, while others contained the usual 1/4 w/o Carbowax. The results of this study are shown in Table 7. The data indicate that 10°C/min is the better heatup rate for binder removal. The lower rate of 2°C/min, while theoretically better, led to disintegration, probably due to oxidation.

Table 7 — Effect of Heating Rate on Binder Removal

| Experiment No. | Binder | Rate of Temp Rise | Results |
|---|---|---|---|
| 10 | Ultrasene * | 2°C/min | Disintegrated at about 200°C |
| 11 | 1/4 w/o Carbowax-6000 | 2°C/min | Circumferential cracks developed at end of pellet at about 230°C |
| 12 | 1/4 w/o Carbowax-6000 | 20°C/min | Slight deterioration over surface of pellet occurred at about 230°C |
| 13 | 1/4 w/o Carbowax-6000 | 10°C/min | No visible evidence of deterioration |

*Purified kerosene.

### 3.4.3 Fabrication of $(U_{0.8}Pu_{0.2})C_{0.95}$ and UC Thermal Conductivity Specimens

The powder described in Section 3.4.1 which was $(U_{0.8}Pu_{0.2})C_{0.95}$, milled for 48 hr, was pressed at 20,000 psi with 1/4 w/o Carbowax binder. The pellets were successfully sintered at 1925°C with a hold-time of 4 hr. The temperature rise for binder removal was 10°C/min. The pellet surfaces were good. These pellets were then surface ground to the specified diameter of 0.625 ± 0.001 in. and height of 0.470 ± 0.005 in. Three of the six pellets were solid and three contained a central hole for a thermocouple well of 0.121 ± 0.001 in. in diameter. The density and analysis data are shown in Table 8.

The pellets of $(U_{0.8}Pu_{0.2})C_{0.95}$ containing 0.12 w/o nickel sintering aid were fabricated from powder which was milled for 24 hr with the nickel addition; carbon content of the blend was 4.80%. Six pellets were cold compacted in the usual manner and sintered at 1550°C with a hold-time of 1 hr. The density and analysis data are also given in Table 8.

Six UC plus 0.12 w/o Ni pellets were fabricated from powder containing 4.65% carbon and 650 ppm oxygen. The UC was intended as a standard. The pellets were cold pressed and sintered in the same manner as the $(U_{0.8}Pu_{0.2})C_{0.95}$ plus 0.12 w/o Ni pellets. The pellets were subsequently surface ground to size. The data for these pellets are also given in Table 8.

## Table 8 — Fabrication Data on Thermal Conductivity Specimens

| Material | Oxygen Analysis, ppm | Average As-Sintered Density, $g/cm^3$ | Total Carbon, % | X-Ray Analysis |
|---|---|---|---|---|
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | ~3000* | 12.40 | 4.46 | Major $(U,Pu)C$<br>$a_0 = 4.9664 \pm 0.0004$ Å<br>Faint/weak $(U,Pu)C_2$ |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.12 w/o Ni | ~3000* | 13.02 | 4.82 | Major $(U,Pu)C$<br>$a_0 = 4.9677 \pm 0.0001$ Å<br>Faint $(U,Pu)_2C_3$<br>Faint $(U,Pu)C_2$ |
| UC + 0.12 w/o Ni | ~650† | 13.08 | 4.78 | Major UC<br>$a_0 = 4.9648 \pm 0.0006$ Å<br>Faint $U_2C_3$<br>Indication of $UO_2$ and $UC_2$ |

*Dow Chemical Company.
†Carborundum Company.

# 4. PROPERTY DETERMINATIONS

The experimental equipment for the measurement of thermal expansion, thermal stability and vapor pressure, melting point, thermal conductivity, and fuel-clad compatibility were completed and standardized during the first phase of the program. The equipment is described in detail in the progress report (UNC-5065) and will be only briefly mentioned in this report.

## 4.1 COEFFICIENT OF THERMAL EXPANSION

The coefficient of thermal expansion was determined from room temperature to 1400°C in vacuum for sintered $(U_{0.8}Pu_{0.2})C_{0.95}$ with and without nickel sintering aid. The presence of the sintering aid did not affect the coefficient of expansion significantly. The values obtained for the mixed uranium-plutonium carbides were similar to those for UC. The results of this investigation are in general agreement with those of other investigators. The comparison is made in Table 9.

The detailed data for $(U_{0.8}Pu_{0.2})C_{0.95}$ are given in Tables 10 and 11 and include the results of two heating and cooling runs for each specimen. The accuracy of the values is about ±5%. The expansion curves were smooth, and did not show any transformations.

The coefficients were determined with a differential dilatometer consisting of high purity, high density tubular alumina elements. The difference in expansion between the alumina and the specimen was sensed by both a dial gage and a linear transformer. These differences were plotted against temperature, as shown in

### Table 9 — Summary of Carbide Thermal Expansion Coefficients

| Material | Source | Temperature Range, °C | Coefficient, $10^{-6}$/°C |
|---|---|---|---|
| Sintered UC | Taylor (Carborundum Co.)[1] | 25-950 | 11.2 |
| Sintered UC | Crane (United Nuclear)[2] | 25-950 | 11.4 |
| Cast UC | Crane (United Nuclear)[2] | 25-950 | 11.6 |
| Cast UC | Secrest (BMI)[3] | 25-950 | 11.4 |
| Cast $(U_{0.87}Pu_{0.13})C$ | Ogard (LA)[4] | 25-900 | 11.1 |
| Cast $(U_{0.85}Pu_{0.15})C$ | (Harwell)[5] | 25-1000 | 11.1-11.8 |
| Sintered $(U_{0.85}Pu_{0.15})C$ | (Harwell)[5] | 25-1000 | 11.1 |
| Hot pressed $(U_{0.85}Pu_{0.15})C$ | (Harwell)[5] | 25-1000 | 10.8 |
| Sintered $(U_{0.8}Pu_{0.2})C_{0.95}$ | Stahl (United Nuclear) | 25-950 | 11.3 |
|  |  | 25-1400 | 11.9 |
| Sintered $(U_{0.8}Pu_{0.2})C_{0.95}+0.1\%$ Ni | Stahl (United Nuclear) | 25-950 | 11.4 |
|  |  | 25-1400 | 12.3 |

Table 10 — Coefficient of Expansion of $(U_{0.8}Pu_{0.2})C_{0.95}$

Thermal Expansion Coefficients, $10^{-6}/°C$

| Temperature Range, °C | Transformer | | | | Dial Gage | | | | Overall (All Runs)* |
|---|---|---|---|---|---|---|---|---|---|
| | 1st Heating | 1st Cooling | 2nd Heating | 2nd Cooling | 1st Heating | 1st Cooling | 2nd Heating | 2nd Cooling | |
| 30-200 | 8.55 | 9.30 | 8.55 | 8.13 | 9.30 | 10.0 | 9.30 | 10.0 | 8.8 |
| 30-400 | 9.67 | 10.0 | 9.55 | 8.92 | 10.8 | 10.9 | 10.0 | 10.9 | 9.6 |
| 30-600 | 10.5 | 10.5 | 10.3 | 9.85 | 11.6 | 11.6 | 10.7 | 11.5 | 10.4 |
| 30-800 | 11.1 | 10.9 | 10.8 | 10.7 | 12.1 | 12.2 | 11.3 | 12.1 | 11.0 |
| 30-1000 | 11.6 | 11.3 | 11.2 | 11.3 | 12.5 | 12.6 | 11.7 | 12.5 | 11.4 |
| 30-1200 | 11.9 | 11.7 | 11.4 | 11.5 | 12.6 | 12.9 | 12.0 | 12.7 | 11.7 |
| 30-1400 | 12.2 | 11.9 | 11.6 | 11.8 | 12.8 | 13.1 | 12.1 | 12.9 | 11.9 |

*Transformer only.

Table 11 — Coefficient of Expansion of $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 w/o Ni

Thermal Expansion Coefficients, $10^{-6}/°C$

| Temperature Range, °C | Transformer | | | | Dial Gage | | | | Overall (All Runs)* |
|---|---|---|---|---|---|---|---|---|---|
| | 1st Heating | 1st Cooling | 2nd Heating | 2nd Cooling | 1st Heating | 1st Cooling | 2nd Heating | 2nd Cooling | |
| 30-200 | 8.83 | 9.12 | 9.40 | 8.82† | 10.0 | 9.70 | 9.12 | 10.6† | 9.0 |
| 30-400 | 9.60 | 9.85 | 10.0 | 9.73 | 10.9 | 10.7 | 10.3 | 11.1 | 9.8 |
| 30-600 | 10.4 | 10.4 | 10.7 | 10.5 | 11.6 | 11.4 | 11.0 | 11.7 | 10.5 |
| 30-800 | 11.0 | 10.1 | 11.3 | 11.0 | 12.0 | 11.9 | 11.5 | 12.0 | 11.0 |
| 30-1000 | 11.5 | 11.5 | 11.7 | 11.5 | 12.4 | 12.4 | 12.0 | 12.4 | 11.5 |
| 30-1200 | 11.9 | 11.9 | 11.9 | 12.0 | 12.6 | 12.8 | 12.3 | 12.7 | 11.9 |
| 30-1400 | 12.4 | 12.3 | 12.1 | 12.3 | 12.8 | 13.3 | 12.5 | 13.1 | 12.3 |

*Transformer only.
†Interpolated.

Fig. 1. Since the $(U_{0.8}Pu_{0.2})C_{0.95}$ specimens expanded more than the alumina dilatometer tube, these data points are added to the expansion curve for alumina to obtain the true expansion of the specimen. A smooth curve was then drawn through the points and the coefficients of thermal expansion were calculated.

Prior to the testing of carbides, a tantalum standard was tested in vacuum, to 1485°C, to obtain a calibration curve for the alumina dilatometer. The curve obtained for alumina checked those of previous investigators within ±7%. The spread of values for alumina among previous investigators is ±3%. The conversion factor from transformer and dial gage readings to extension in inches was verified with a micrometer in place of the dilatometer tube and specimen. The deviation from a constant factor was ±5.7% for the dial gage but only ±1.7% for the transformer. Hence, the coefficients were computed from transformer data only.

The nominal specimen size was 0.2 in. by 0.3 in. by 2.0 in. long. No appreciable changes in dimensions were found after testing of the specimens. In addition, no appreciable changes in structure or composition of the test specimens were noted. The slight changes in carbon and plutonium contents were within experimental error. The data are given in Table 12.

## 4.2 THERMAL STABILITY AND VAPOR PRESSURE

### 4.2.1 Introduction

Thermal stability and vapor pressure of $(U_{0.8}Pu_{0.2})C_{0.95}$ were determined by the Knudsen effusion technique. The major conclusion drawn from the data was that plutonium does not vaporize preferentially to uranium, and that the vapor pressure of the uranium is within an order of magnitude of that measured by other investigators. This indicates that the stability of $(U_{0.8}Pu_{0.2})C_{0.95}$ is as good as that of UC for high power operation.

Table 12 — Analyses of Thermal Expansion Bars

| Analysis | Sintered $(U_{0.8}Pu_{0.2})C_{0.95}$ | Sintered $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1% Ni |
|---|---|---|
| **Untested** | | |
| Density, g/cm$^3$ | 12.0 | 12.8 |
| Carbon, % | 4.76 | 4.69 |
| Plutonium, % | — | 18.4 |
| Metallography | Major (U,Pu)C<br>Minor second phase | Major (U,Pu)C<br>Minor (U,Pu)$_2$C$_3$ |
| X-ray | Single phase (U,Pu)C<br>$a_0$ = 4.962 ± 0.001 Å | Major (U,Pu)C<br>$a_0$ = 4.9662 ± 0.0001 Å<br>Weak/mod. (U,Pu)$_2$C$_3$<br>$a_0$ = 8.0947 ± 0.0008 Å |
| **Tested** | | |
| Carbon, % | 4.61 | 4.68 |
| Plutonium, % | 17.8 | — |
| Metallography | Same as untested<br>specimen | Same as untested<br>specimen |
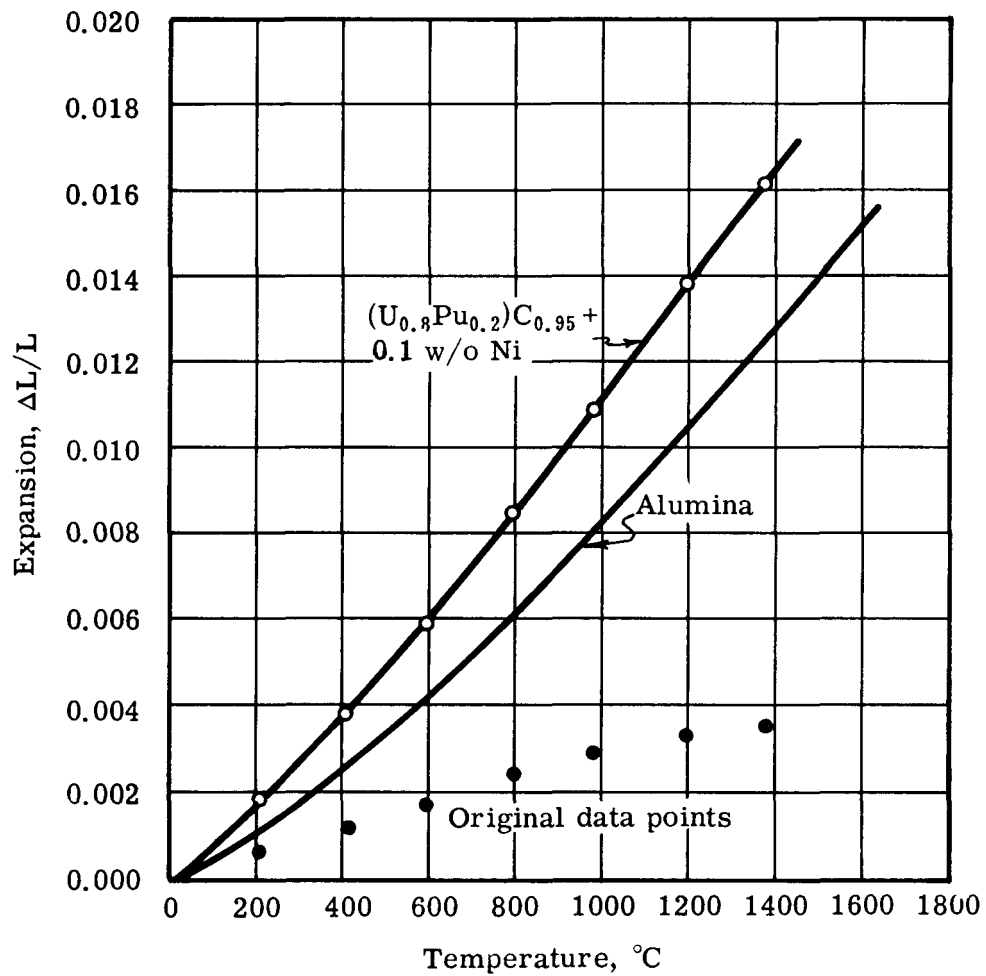
Fig. 1 — Typical heating cycle data for thermal expansion of $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 w/o Ni (run No. 2). Final curve is obtained by adding original transformer data points to expansion curve for alumina.

The problems of measuring the vapor pressure of carbides at very high temperatures were also emphasized by these experiments. The generally increasing vapor pressure, with increasing number of runs on the same sample, indicated a change in sample composition with time. The most likely cause for this is a reaction with the internally carburized tantalum cell; other causes, discussed later, could also be the reason for the change in sample composition.

### 4.2.2 Experimental Equipment

The Knudsen effusion experiment was described in report UNC-5065 and is shown schematically in Fig. 2.

In summary, the Knudsen effusion cell was centered in a tubular tantalum heating element and standing on a tantalum pedestal. The 3/8-in diameter by 5/8-in. high cell was formed from a spun tantalum cup and cover, welded as shown in Fig. 3. The cover of the cell contains the 0.030 in. diameter orifice in a thinned-out (0.0015 in.) portion to reduce channeling effects. The small ratio of hole-to-cell areas assures a vapor pressure near equilibrium in the cell. Prior to welding the cups were internally carburized to avoid the reaction of (U,Pu)C with tantalum which would produce free uranium and plutonium metal. Heating the tantalum cups at ~2000°C for 1 hr in contact with graphite flour produced a continuous 0.003-in. tantalum carbide coating. A carburization cycle of ~1700°C for 1/2 hr was used for the tantalum covers to produce a 0.0005 to 0.0008-in. coating on the 0.0015-in. orificed section. Zones, 1/8-in. max., next to the top edges were left uncarburized for welding.

During the experiment, perforations in the tantalum heat shield collimate a known fraction of the vapor beam which then condenses on a water-cooled counting planchet. Eight planchets, located on a wheel, can be lined up with the vapor beam successively without breaking the vacuum. In practice, a maximum of seven planchets was used so that direct optical pyrometer sighting on the orifice was
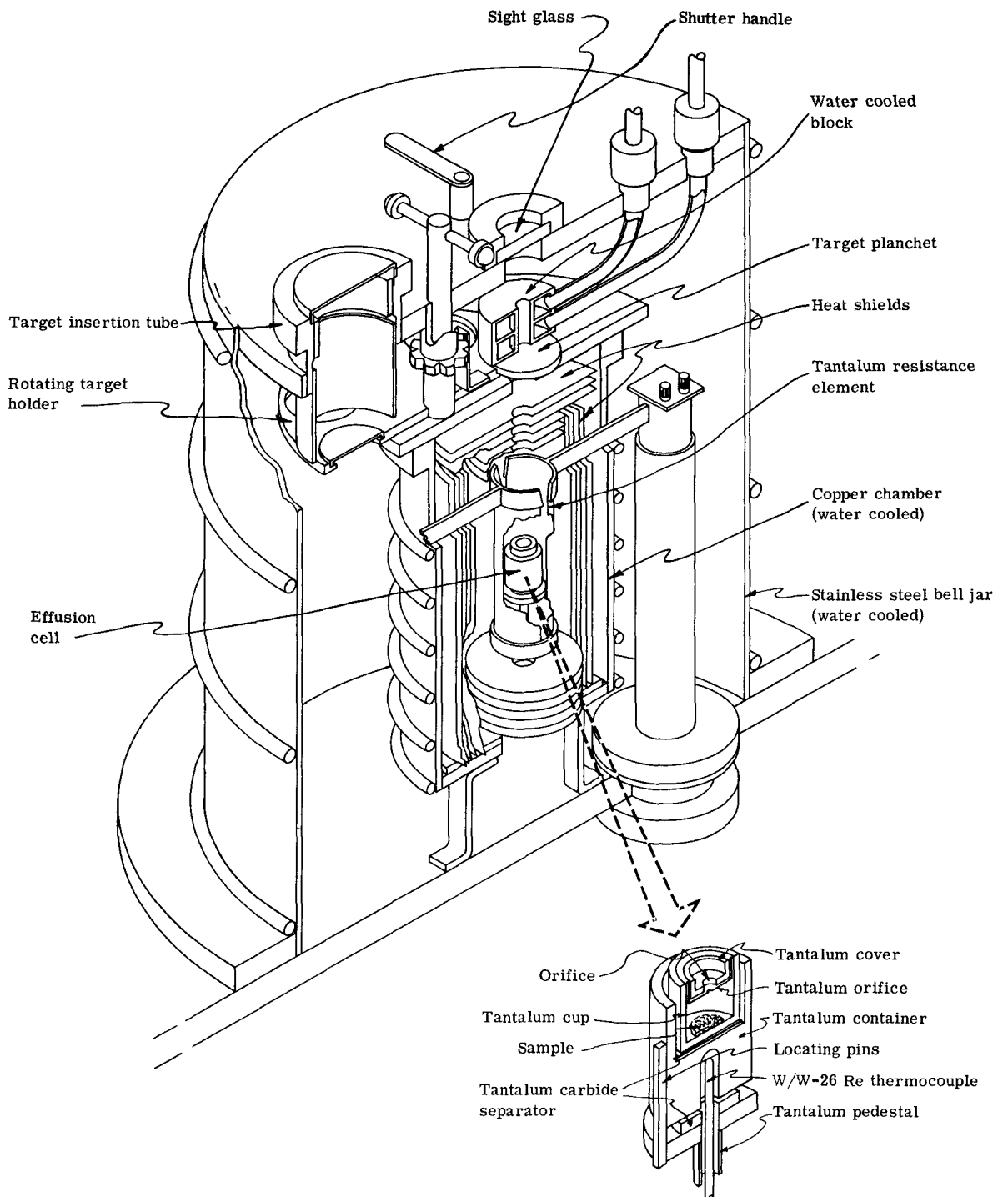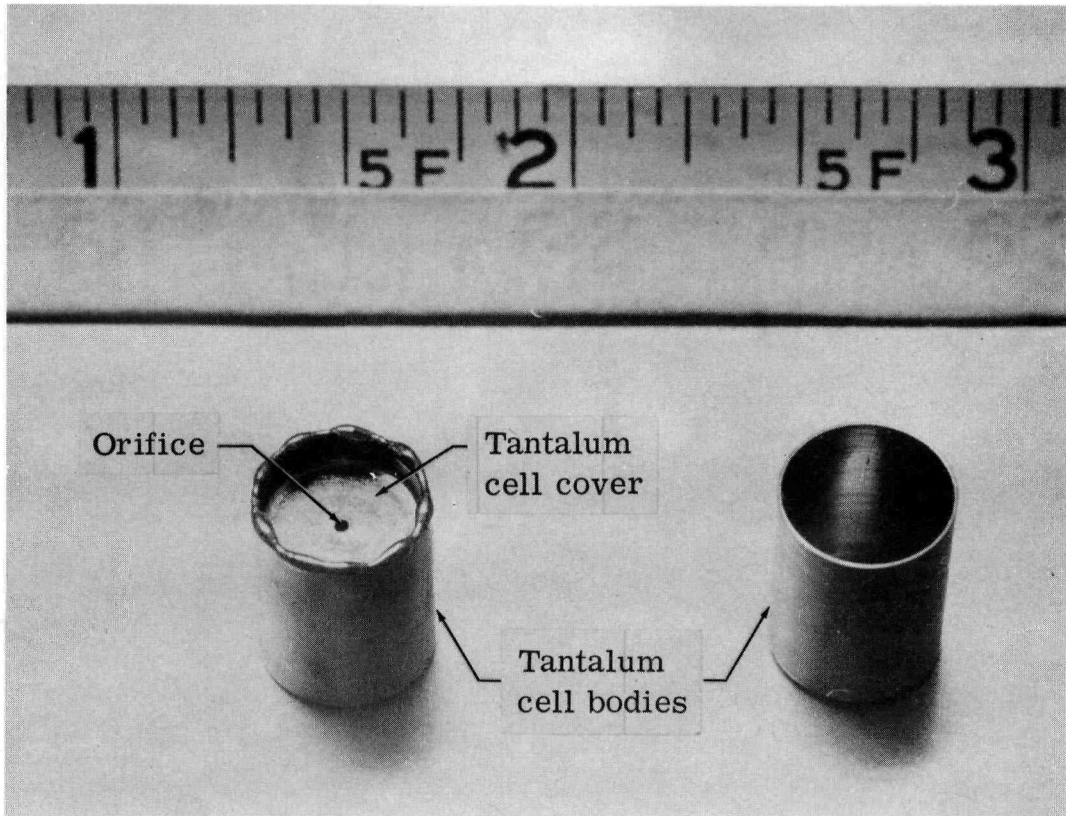
Fig. 2 — Schematic of thermal stability experiment

Fig. 3 — Knudsen vapor pressure cell

possible. Swaged, commercial, W-W/26% Re thermocouples located in the tantalum pedestal under the cell were intended to be used. However, their poor reliability and short lifetime at these temperatures prevented their use. An improved, un-swaged thermocouple design with insulating beads was completed and is being procured for future work on Contract AT(30-1)-2899.

## 4.2.3 Experimental Data

The geometry of the collimator and collection system was calibrated with a cell containing high purity (99.999%) silver. The fraction of vapor collected was cal-culated from a preliminary run at 1160 to 1400°K to be 0.022.

Another run was made with this cell as part of the USAEC program.[6] The fraction of vapor collected in this second run was calculated and found to be fairly constant at 0.0224 over the temperature range of 1400 to 1600°K. This value was used in the calculations of the vapor pressure of (U,Pu)C. Because of the good agreement between the first and second runs, which were run at low and intermediate temper-ature ranges, respectively, no correction for the fraction collected was made at the higher temperatures (2100°K and above). Calculations show that, at most, a 5% error would be introduced.

Two cells with $(U_{0.8}Pu_{0.2})C_{0.95}$ were tested at 2100 to 2600°K with background pres-sures of $6 \times 10^{-5}$ to $2 \times 10^{-4}$ mm Hg. The deposits on the planchets were analyzed for uranium fluorometrically and for plutonium by alpha counting. (See Section 5 for chemical analysis techniques.) The exposure times, temperatures, and the weights of uranium and plutonium found on the planchets are given in Table 13. The mass effusion rate was calculated from these data assuming a constant factor for collection efficiency and a condensation coefficient of unity. The change in orifice diameter as a function of temperature was used in the calculation. The vapor pressure was then calculated using the Knudsen equation:

## Table 13 — Data From Vapor Pressure Runs

| Cell No. | Run No. | Time of Test, min | Temperature, °K | Deposited U, μg | Deposited Pu, μg |
|---|---|---|---|---|---|
| 1 | 1 | 60 | 2400 | 16.1 | 29.7 |
|   | 1 | 45 | 2400 | 21.1 | 9.90 |
|   | 1 | 45 | 2510 | 71.7 | 55.5 |
|   | 1 | 30 | 2500 | 98.5 | 8.23 |
|   | 1 | 20 | 2600 | 593 | 5.71 |
|   | 1 | 10 | 2600 | 418 | 3.11 |
|   | 2 | 60 | 2285 | 270 | 0.095 |
|   | 2 | 60 | 2270 | 220 | 0.266 |
|   | 2 | 45 | 2390 | 380 | 0.235 |
|   | 2 | 30 | 2400 | 123 | 0.155 |
|   | 2 | 25 | 2500 | 142 | 0.945 |
|   | 2 | 25 | 2490 | 82.5 | 0.950 |
|   | 2 | 10 | 2620 | 79.0 | 2.25 |
|   | 2 | 10 | 2615 | 57.5 | 1.95 |
| 2 | 1 | 120 | 2070 | 30.0 | 167 |
|   | 1 | 120 | 2055 | 17.1 | 16.6 |
|   | 1 | 90 | 2170 | 6.05 | 66.0 |
|   | 1 | 90 | 2185 | 17.3 | 34.0 |
|   | 1 | 60 | 2295 | 32.0 | 31.5 |
|   | 1 | 60 | 2285 | 32.1 | 13.6 |

$$P_{atm} = C \frac{m}{a} \sqrt{\frac{2\pi RT}{M}}$$

where C = constant = $9.8697 \times 10^{-7}$ atm/dyne/cm$^2$

     m = mass effusion rate, g/cm$^2$-sec

     a = condensation coefficient

     R = gas law constant, ergs/g-mole-°K

     T = absolute temperature, °K

     M = molecular weight of vapor species, g/g-mole

It was assumed here that the molecular weight of the metal vapor was that of atomic uranium and plutonium. Since the atomic weights of U and Pu are close to those of UC and PuC, any error introduced by this assumption is small. The mass effusion rates and vapor pressure for the three runs are given in Table 14. The vapor pressure data for uranium are plotted in Fig. 4. The dashed line shows the trend in the present data.

The samples were inspected after the runs were completed. No sample was left in cell No. 1 after two runs. Calculations show that more than half of the 500-mg sample was evaporated during Run No. 1 of cell No. 1. There was, however, a residue from the sample in cell No. 2 in the form of a thin sintered disc. The (U,Pu)C disc had apparently not reacted with the carburized layer of the tantalum cell. This disc was analyzed for carbon and found to contain 4.28% as opposed to the original content of 4.62%. This difference may be due to a difference in oxygen content.

Several additional planchets were analyzed by x-ray diffraction in an attempt to determine the structure of the condensed vapor. However, the sample size was insufficient on all but one planchet. The analysis of the one planchet showed a definite but small amount of a $(U,Pu)O_2$ phase. The carbide probably oxidized on the planchet before the examination. It was not possible to determine a lattice parameter.

Table 14 — Calculated Vapor Pressure Data for $(U_{0.8}Pu_{0.2})C_{0.95}$

| Cell No. | Run No. | Temperature, °K | Mass Effusion Rate $m_U, 10^5$ g/cm²-sec | $m_{Pu}, 10^5$ g/cm²-sec | Vapor Pressure $P_U$, atm × 10⁵ | $P_{Pu}$, atm × 10⁵ |
|---|---|---|---|---|---|---|
| 1 | 1 | 2400 | 3.98 | 7.37 | 0.285 | 0.525 |
|   | 1 | 2400 | 6.94 | 3.26 | 0.496 | 0.232 |
|   | 1 | 2510 | 23.5 | 18.2 | 1.71 | 1.33 |
|   | 1 | 2500 | 48.4 | 4.04 | 3.54 | 0.294 |
|   | 1 | 2600 | 438 | 4.21 | 32.6 | 0.312 |
|   | 1 | 2600 | 617 | 4.59 | 46.0 | 0.342 |
|   | 2 | 2285 | 59.4 | 0.0235 | 4.68 | 0.00164 |
|   | 2 | 2270 | 48.3 | 0.0661 | 3.80 | 0.00459 |
|   | 2 | 2390 | 125 | 0.0773 | 8.95 | 0.00550 |
|   | 2 | 2400 | 60.7 | 0.0764 | 4.34 | 0.00546 |
|   | 2 | 2500 | 83.5 | 0.558 | 6.10 | 0.0407 |
|   | 2 | 2490 | 48.6 | 0.561 | 3.54 | 0.0408 |
|   | 2 | 2620 | 116 | 3.29 | 8.70 | 0.246 |
|   | 2 | 2615 | 84.8 | 2.88 | 6.34 | 0.214 |
| 2 | 1 | 2070 | 3.28 | 18.2 | 21.8 | 120 |
|   | 1 | 2055 | 1.88 | 1.8 | 12.5 | 12 |
|   | 1 | 2170 | 0.846 | 9.61 | 5.76 | 65.2 |
|   | 1 | 2185 | 2.52 | 4.96 | 17.2 | 33.9 |
|   | 1 | 2295 | 6.97 | 6.83 | 48.8 | 34.1 |
|   | 1 | 2285 | 6.97 | 2.94 | 47.7 | 20.5 |
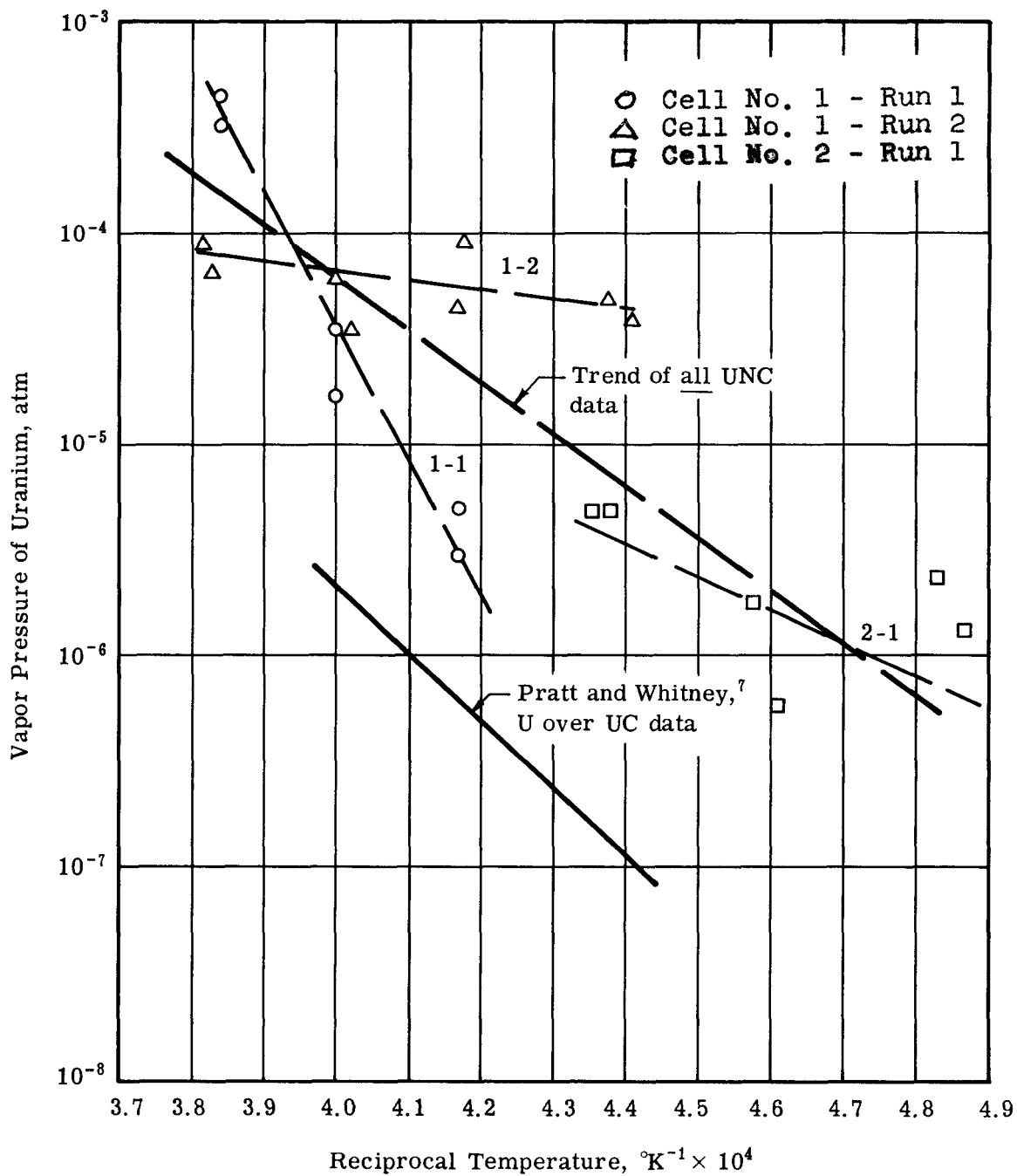
Fig. 4 — Vapor pressure of uranium over $(U_{0.8}Pu_{0.2})C_{0.95}$

## 4.2.4 Discussion of Results

The vapor pressure of uranium over $(U_{0.8}Pu_{0.2})C_{0.95}$ is plotted in Fig. 4 and ranges from about $1 \times 10^{-6}$ atm at 2100°K to $1 \times 10^{-4}$ atm at 2600°K. In comparison, the solid line shows the Pratt and Whitney data of Vozzella, Miller, and De Crescente[7] on the vapor pressure of uranium over sintered UC measured by the Langmuir method. The United Nuclear data are higher than the Pratt and Whitney data by about one order of magnitude.

The increased vapor pressures measured in the second run of cell No. 1, and in the longer test durations of the run with cell No. 2, indicate a change in the sample composition. The sample composition could change for the following reasons:

1. reaction of the sample with the cell, to deplete the sample of carbon and form metal vapor;

2. reaction of the residual oxygen in the (U,Pu)C to form CO and metal vapor; and

3. noncongruent vaporization of the sample constituents.

It is postulated that diffusion of carbon across the TaC layer to the Ta of the cell lowered the partial pressure of carbon in the cell and increased the partial pressure of uranium. This phenomenon was also found recently by Bowman and Krupka at Los Alamos[8] in their Knudsen vapor pressure measurements of UC in carburized tantalum cups. A carburized tungsten cup yielded similar results. Since it has been substantiated that (U,Pu)C does not react with TaC, but may react with Ta behind the TaC layer, it would be advantageous to employ a cell of solid TaC.

Vacuum annealing experiments made for Contract AT(30-1)-2899 (see UNC-5056) show that residual oxygen in (U,Pu)C can be reacted and pumped off as CO, along with the U and Pu metal vapor. In the annealing experiments oxygen was reduced from 2000 to 1000 ppm in 1/2 hr at 2200°C. The reduction in carbon content of the sample in cell No. 2 was a total of 0.34 w/o. If all the carbon were reacted with

oxygen to form CO this would require ~4600 ppm of oxygen. This amount of oxygen could be present in the sample. Unfortunately, the sample left in cell No. 2 was too small for an oxygen analysis.

Noncongruent vaporization can also change the sample composition in a direction to increase the vapor pressure of U and Pu values with time. Work by Pratt and Whitney[7] and Los Alamos[8] have shown that $UC_{1.0}$ loses U at ~2100°C to form congruently vaporizing $UC_{1.1}$. Several hours were required at this temperature for equilibrium to be reached.

Thus, any one, or all three reasons could cause a sample composition change with time.

The vapor pressure of plutonium over $(U_{0.8}Pu_{0.2})C_{0.95}$ was not consistent enough to plot but is given in Table 14.

It is important to note that the pressure of plutonium is the same or lower than that of uranium over the temperature range. This is contrary to the preliminary data of Anselin and Pascard[9] at ~2000°K, who found large quantities of plutonium and essentially no uranium lost from (U,Pu)C containing 30% Pu. The lack of reproducibility of results reported by Anselin and Pascard is also evident in the results presented in Table 13. It is believed to be due to the change in composition of the sample with time as discussed before.

Because of the nonequilibrium conditions, no thermodynamic data were computed from the results of these vapor pressure measurements.

It should be noted also that, although the mass effusion rates are about an order of magnitude higher than the rate for uranium over UC, they are low enough for the $(U_{0.8}Pu_{0.2})C_{0.95}$ fuel to be useful for a high temperature, high power reactor.

## 4.3 MELTING POINT

The melting point (liquidus temperature) of $(U_{0.8}Pu_{0.2})C_{0.95}$ was determined as 2480 ± 20°C. The solidus is estimated to be about 2430°C, based on one experiment. The detailed melting point data are given in Table 15. All specimens contained about 2000 ppm oxygen as-fabricated.

Table 15 — $(U_{0.8}Pu_{0.2})C_{0.95}$ Melting Point Data

| Material | Run No. | Corrected Melting Point, °C |
|---|---|---|
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | 1 | 2480 |
| 2000 ppm O ⎱ impurities<br>200 ppm N ⎰ | 2 | 2430* |
| | 3 | 2480 |
| | 4 | 2490 |

*Melting had just started. This is probably the solidus temperature.

The samples were heated in the tantalum resistance vacuum furnace used for the vapor pressure measurements. Temperature was measured optically with a Pyro Micro-Optical pyrometer, by sighting on the black body hole in the specimen. The measurements were made through a plastic glove box window, prism, and furnace sight glass and were corrected for the resulting absorption errors. The correction was estimated by interposition of additional samples of the above materials. Standards of copper, titanium, alumina, and niobium were then melted to establish the true correction curve (Fig. 5).

The melting point specimens were cylinders about 0.200 in. in diameter by 0.200 in. high. The specimens were fabricated with a central black body hole.
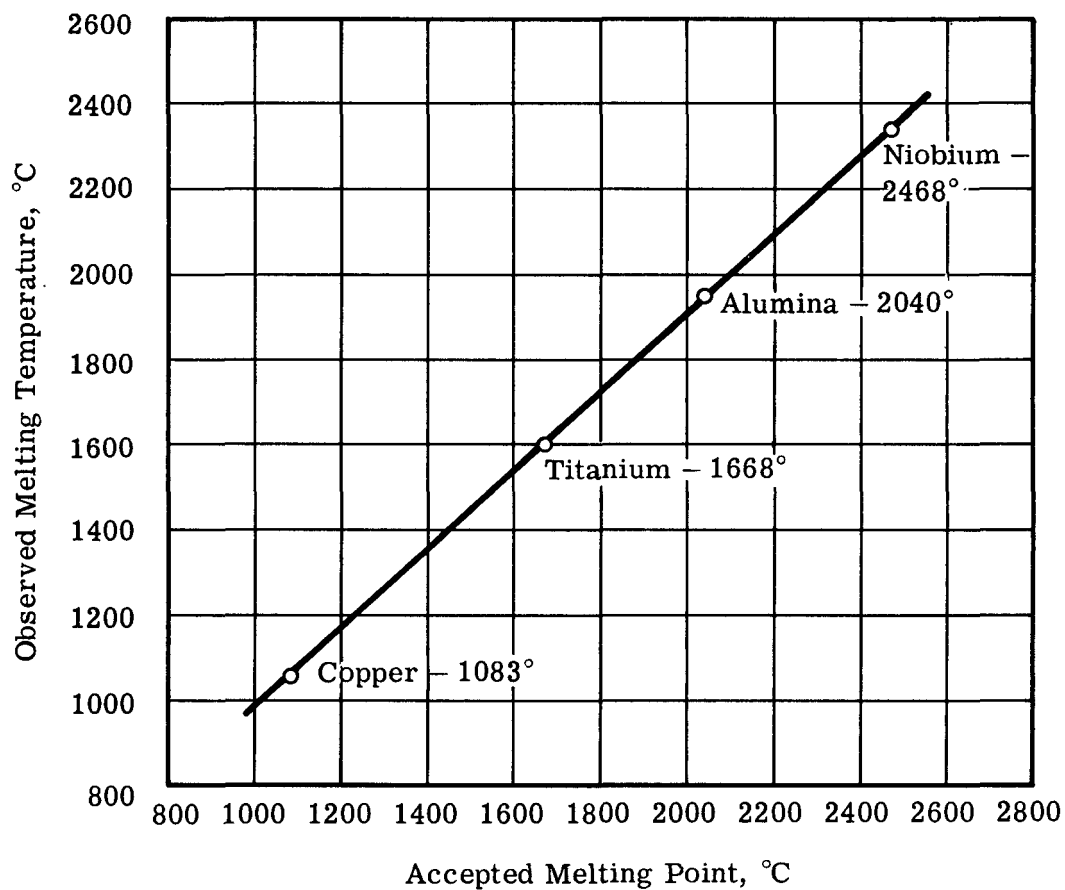
Fig. 5 — Correction curve based on melting of standards

The hole was conical, about 0.150 in. deep with a 0.025-in. diameter top. Melting was observed on the edges of the specimen and in the black body hole itself. Specimens were contained in internally carburized tantalum cups. Metallographic examination of the melted specimens in the cups showed that the tantalum carbide coating was successful in preventing any reactions between the fuel and the tantalum cup. Chemical analysis of one specimen after melting showed a loss of carbon — from 4.62 to 4.43 w/o.

## 4.4 THERMAL CONDUCTIVITY

The USAEC and the Monsanto Research Corporation's Mound Laboratories agreed to measure the thermal conductivity of (U,Pu)C specimens and a UC standard prepared by United Nuclear and Carborundum. Samples of UC + 0.1 w/o Ni, $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 w/o Ni, and $(U_{0.8}Pu_{0.2})C_{0.95}$ will be tested. The thermal conductivity will be calculated from the thermal diffusivity, specific heat, and density. The thermal diffusivity will be determined to 700°C in a thermal gradient apparatus, and the specific heat will be determined in a calorimeter.[10] Repairs required by the Mound equipment have delayed the measurements. Results will be reported as soon as they are available. The following sections describe the specimen design and the specimen assembly method.

### 4.4.1 Specimen Design

The Monsanto apparatus was designed to measure the thermal conductivity of molten plutonium alloys and the specimen had to be modified to accept solid plutonium containing materials. The modification chosen employs a liquid-metal bond between the fuel and tantalum container and fixes the thermal conductivity of the fuel-to-container wall gap at a known value. Preliminary 100-hr tests of UC at 700°C with high purity (99.99% or better) gallium, tin, bismuth, and lead were reported in UNC-5065. Tin and gallium appeared promising and were chosen for further tests with (U,Pu)C.

The compatibility of tin and gallium was tested with $(U_{0.8}Pu_{0.2})C_{0.95}$ pellets with and without the nickel sintering aid in four individual tantalum capsules for 166 hr at 710°C. The results are summarized in Table 16. Gallium wet both the fuel and the tantalum very well; however, one of the fuel pellets was grossly distorted after the test. Gallium was eliminated because of this. Tin wet both the fuel and the tantalum and the pellets appeared unaffected. Metallographic examination of the fuel showed a slight amount of attack or penetration by the tin (Fig. 6), not sufficient to affect the proposed measurements, since the test time at this temperature will be considerably less. The tantalum container was not attacked (Fig. 7). Tin was chosen as the liquid-metal bond, based on the encouraging test results.

A test was made to determine the minimum wetting temperature of tin in a 0.004-in. annulus between fuel and tantalum. A mockup specimen with UC was heated in a vacuum induction furnace and wetting was observed visually. The temperature range for wetting was 700 to 800°C.

The specimens were then designed so that a 0.004-in. radial fuel-container gap existed at room temperature. Three 0.003-in. diameter tantalum wire spacers were placed longitudinally between the fuel and the container, to fix the size of the gap by preventing radial movement of fuel pellets. An isometric drawing of the assembled specimen is shown in Fig. 8.

### 4.4.2 Specimen Assembly

The introduction of tin to the narrow fuel OD-container, and fuel ID-thermocouple well annuli was the most critical portion of the assembly procedure. Tin foil, 0.001 in. thick, 99.99% pure, was placed on the capsule ID, capsule bottom, thermocouple well OD, and thermocouple well bottom prior to assembly of the fuel pellets into the tube. After assembly of the fuel and top plug, the complete assembly was heated in vacuum to 800°C (the wetting temperature of the tin) and was sealed off under vacuum.

Table 16 — Results of (U,Pu)C-Liquid-Metal Screening Tests (710°C, 166 hr)

| Fuel | Liquid Metal | Wetting | | Metallography | |
|---|---|---|---|---|---|
| | | Fuel | Tantalum | Fuel | Tantalum |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | Ga | Excellent | Excellent | None | None |
| $(U_{0.8}Pu_{0.2})C_{0.95} + 0.1$ w/o Ni | Ga | Good | Good | None (fuel pellet swelled and distorted grossly) | None |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | Sn | Good | Good | Slight but not significant (Fig. 6) | No attack (Fig. 7) |
| $(U_{0.8}Pu_{0.2})C_{0.95} + 0.1$ w/o Ni | Sn | Good | Good | | |
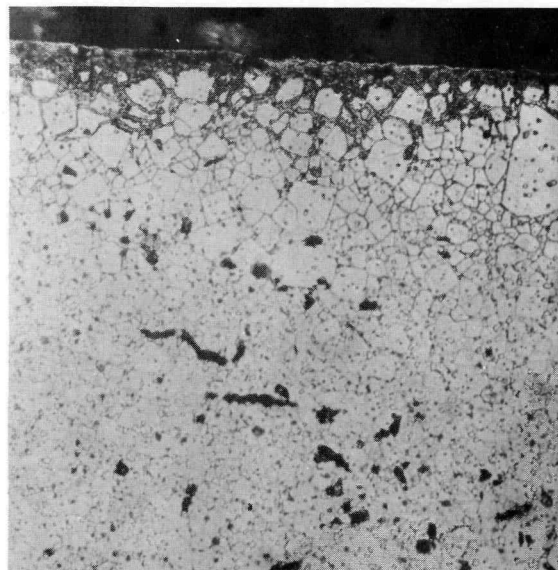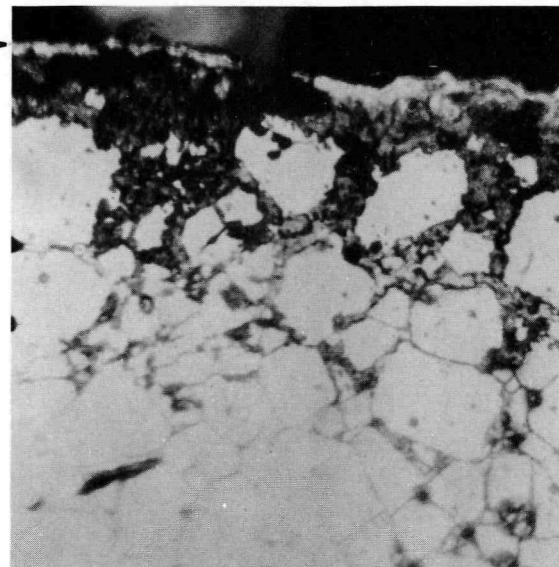
Fig. 6 — $(U_{0.8}Pu_{0.2})C_{0.95}$ from the compatibility test with tin (710°C, 166 hr)
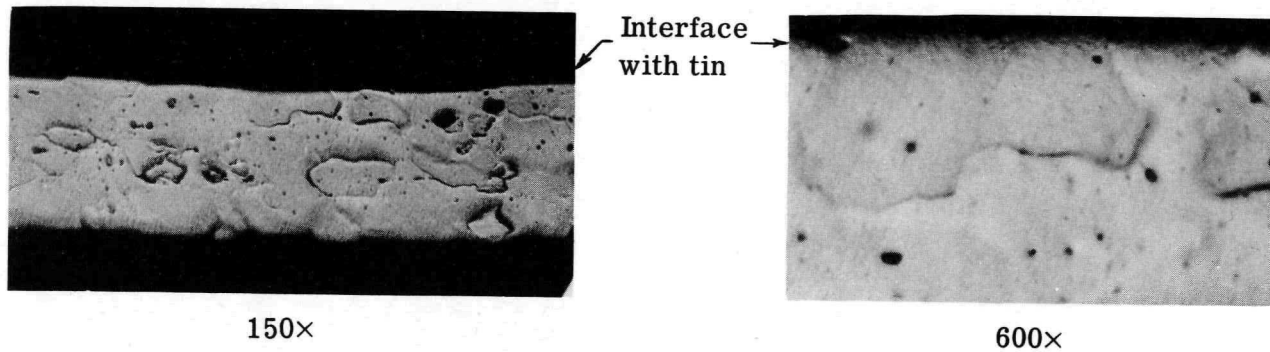
Interface
with tin →

150×

600×

Fig. 7 — Tantalum container from the tantalum-tin-$(U_{0.8}Pu_{0.2})C_{0.95}$
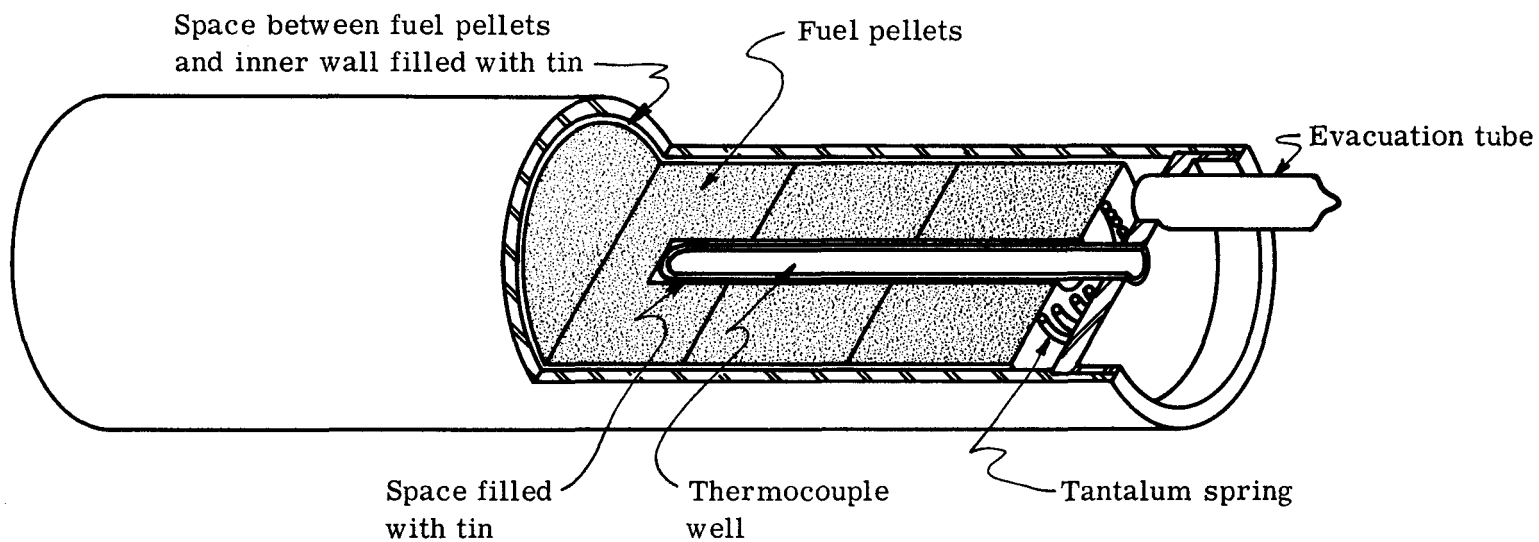compatibility test (710°C, 166 hr)

Fig. 8 — Isometric drawing of the thermal conductivity capsule assembly (material: tantalum unannealed)

The frost test[11] was adapted to the specimens to inspect for the liquid bond integrity after assembly. All the samples had satisfactory bonds by this method of inspection. An acenaphthene solution was used to produce the frost coating. The specimen was introduced into a resistance-heated furnace at 800°C for 15 sec. Melting of the coating was not observed on any of the specimens. Prior to testing of the fueled specimens, standards with known gaps were tested. Gaps of 0.0015 in. could be detected on the standards.

## 4.5 FUEL-CLAD COMPATIBILITY

The compatibility of $(U_{0.8}Pu_{0.2})C_{0.95}$ with potential cladding materials was studied under conditions similar to those that would prevail in a fuel element. Fuel and cladding materials were held in contact with each other in capsules similar to the one shown in Fig. 9. Continued contact between fuel and cladding samples at elevated temperatures was assured by the greater thermal expansion of the stainless steel insert compared to the Inconel container. Most of the capsules contained duplicates of the same cladding materials. The capsules were seal-welded in a glove box containing a helium atmosphere, decontaminated, leak-checked, taken out of the glove box line, and placed in the sealed inner shell of the furnaces. The furnaces stood in a hood in the Plutonium Facility.

Metallographic examination, subsequent to the tests, determined the degree of interaction between fuel and cladding samples.

Fuel. The fuel samples used are described in Section 3.2. All the samples were hypostoichiometric in carbon content, but had sufficient oxygen in solid solution to produce microstructures with higher carbides and no free metal. Typical structures are shown in Figs. 10, 11, and 12.

Seal weld

Inconel

347 stainless steel

Cladding material
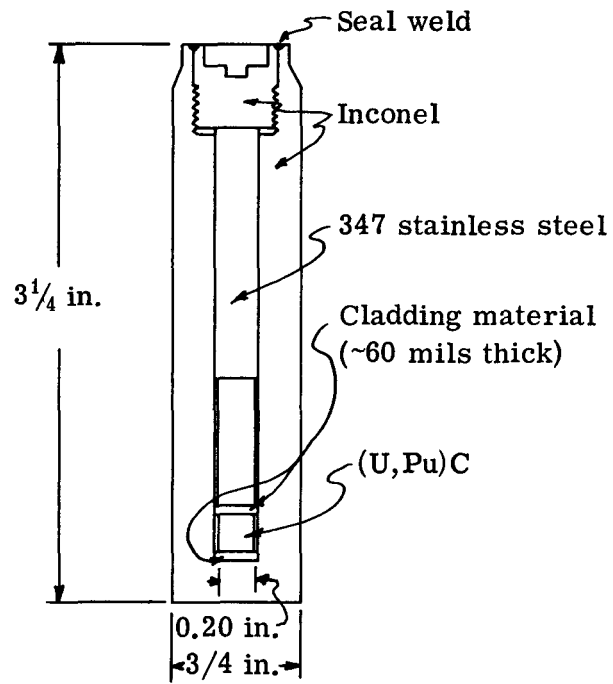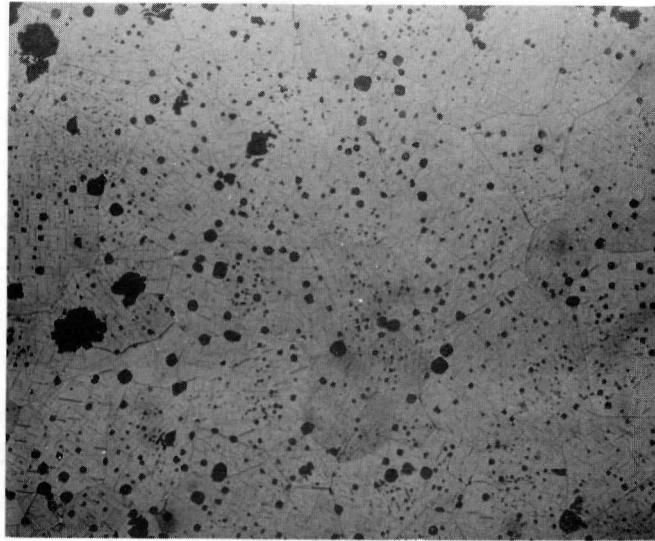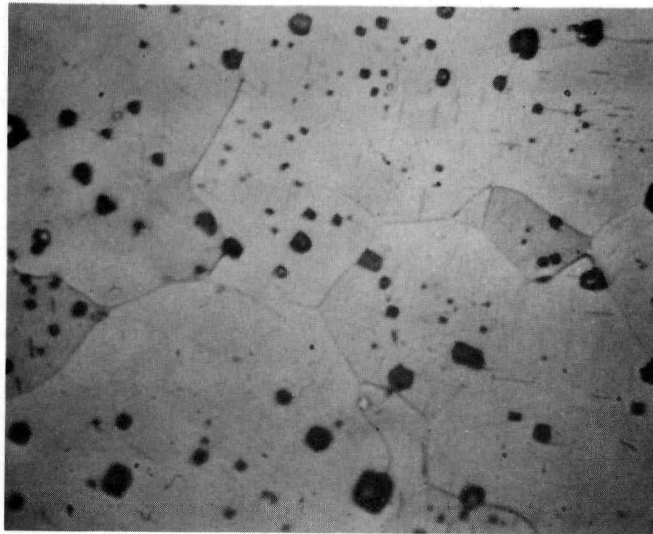(~60 mils thick)

(U,Pu)C

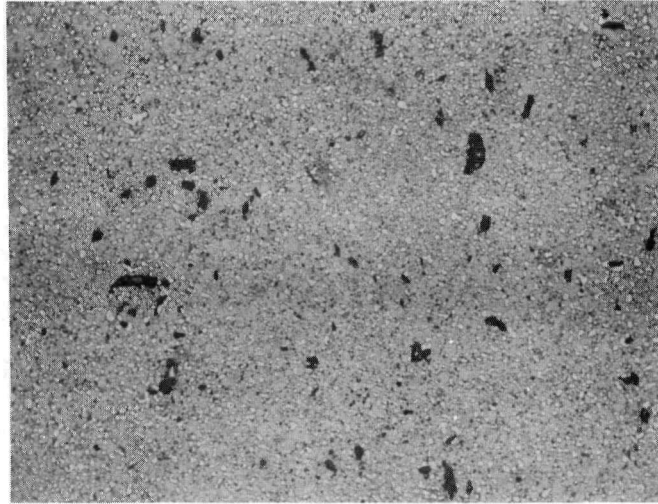$3\frac{1}{4}$ in.

0.20 in.

3/4 in.

Fig. 9 — Compatibility capsule

150×



600×

Fig. 10 — Microstructure of $(U_{0.8}Pu_{0.2})C_{0.95}$ — nitric acid-acetic acid-water etch.  Sintered 1950°C, 1 hr in helium.
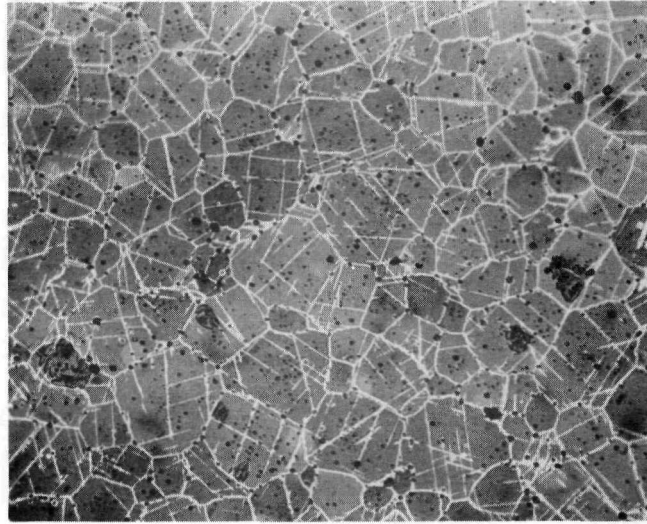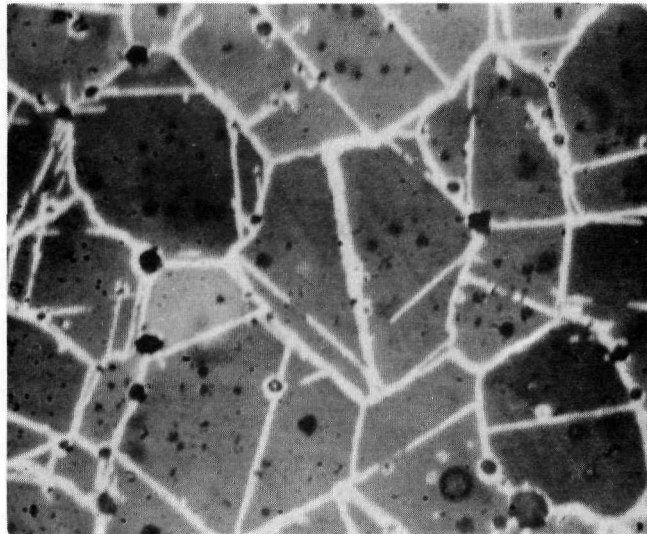
150×



600×

Fig. 11 — Microstructure of $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 w/o Ni — nitric acid-acetic acid-water etch. Sintered 1550°C, 1 hr in helium. X-ray analysis: major $(U,Pu)C$; faint $(U,Pu)_2C_3$.

150×



600×

Fig. 12 — Microstructure of $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 w/o Ni with grain boundary sesquicarbide — nitric acid-acetic acid-water etch. Sintered 1550°C, 1 hr in helium.

Type 316 Stainless Steel. There were no reactions between fuel and type 316 stainless steel samples, as shown in Table 17. A typical sample of steel which had been in contact with fuel is shown in Fig. 13. The carbide and sigma precipitation in the steel are a thermal effect, and not a product of interaction with the fuel.

Table 17 — Fuel-Type 316 Stainless Steel Compatibility

| Fuel | Temperature, °C (°F) | Time, hr | Remarks |
|------|----------------------|----------|---------|
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | 593 (1100) | 4000 | No reaction |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1% Ni | 593 | 4000 | No reaction |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | 816 (1500) | 1000 | No reaction |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1% Ni | 816 | 1000 | No reaction |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | 816 | 4000 | No reaction |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1% Ni | 816 | 4000 | No reaction (Fig. 13) |

$2\frac{1}{4}$ Cr-1 Mo Steel. There were no reactions between $(U_{0.8}Pu_{0.2})C_{0.95}$ and $2\frac{1}{4}$ Cr-1 Mo steel after 4000 hr at 816°C. The steel interface after testing is shown in Fig. 14.

Niobium, Niobium-1% Zirconium. There were no reactions between fuel and niobium, or niobium-1% zirconium alloy, as shown in Table 18. Typical niobium and niobium-1% zirconium samples which were in contact with fuel are shown in Figs. 15 and 16. The niobium was annealed by the test temperature, whereas the niobium-1% zirconium was not.

Table 18 — Fuel-Niobium, Niobium-1% Zirconium Compatibility

| Fuel | Clad | Temperature, °C (°F) | Time, hr | Remarks |
|---|---|---|---|---|
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | Nb | 593 (1100) | 4000 | No reaction |
|  | Nb-1% Zr |  |  | No reaction |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1% Ni | Nb | 593 | 4000 | No reaction |
|  | Nb-1% Zr |  |  | No reaction |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | Nb | 816 (1500) | 1000 | No reaction |
|  | Nb-1% Zr |  |  | No reaction |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1% Ni | Nb | 816 | 1000 | No reaction |
|  | Nb-1% Zr |  |  | No reaction |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | Nb | 816 | 4000 | No reaction (Fig. 15) |
|  | Nb-1% Zr |  |  | No reaction (Fig. 16) |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1% Ni | Nb | 816 | 4000 | No reaction |
|  | Nb-1% Zr |  |  | No reaction |

Interface with fuel

150×

600×
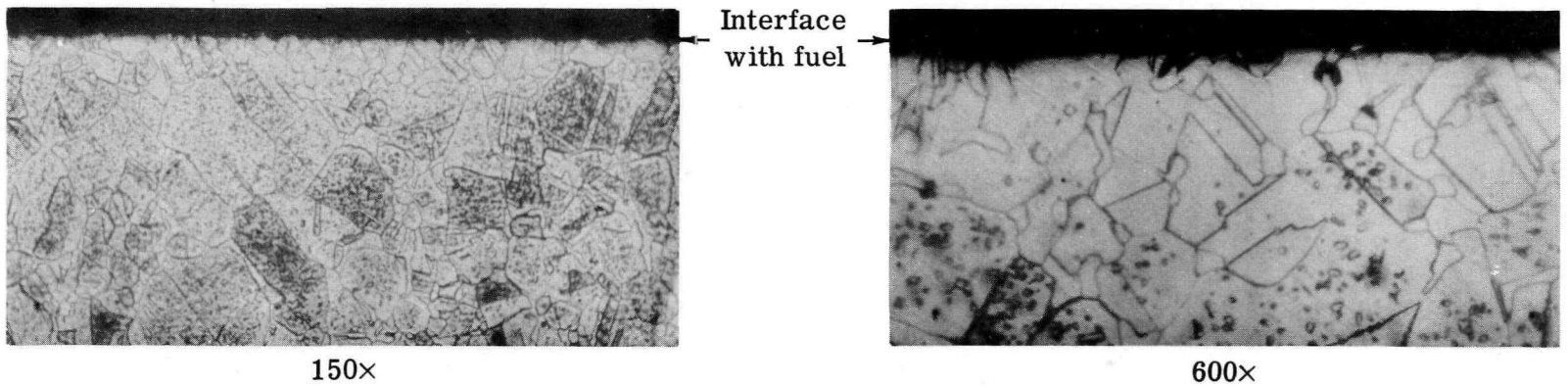
Fig. 13 — Type 316 stainless steel from compatibility test with $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 w/o Ni, 816°C (1500°F), 4000 hr

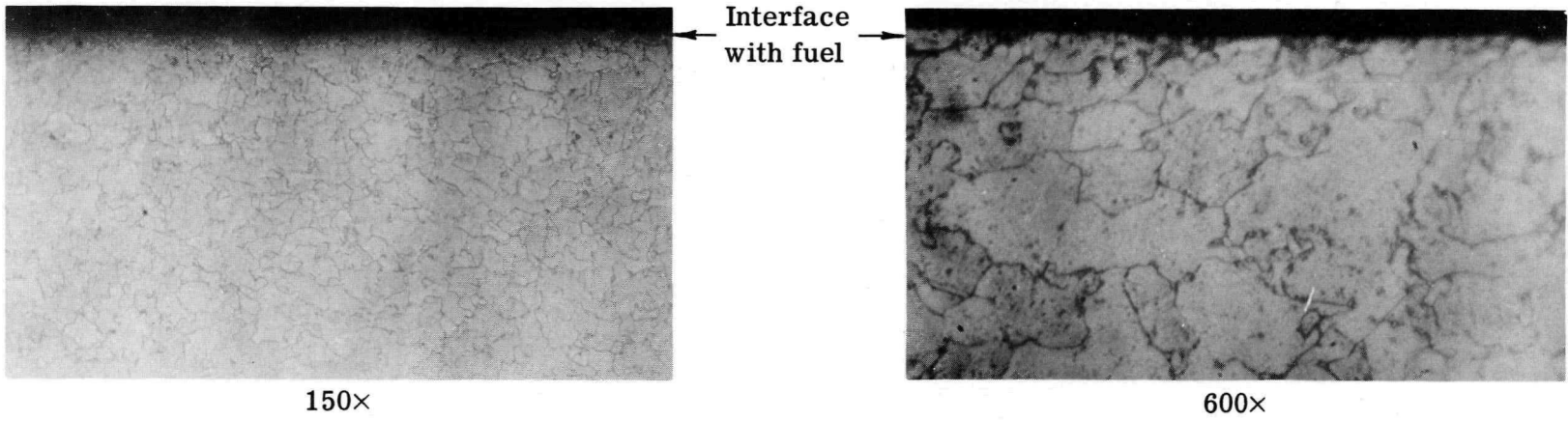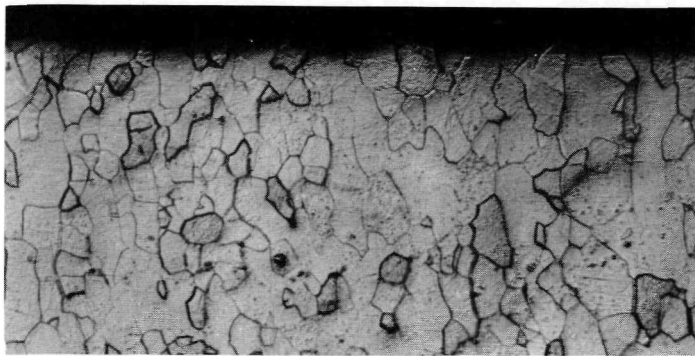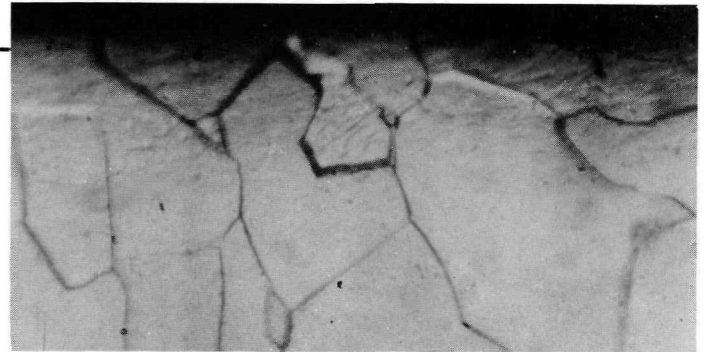Fig. 14 — $2\frac{1}{4}$ Cr-1 Mo steel from compatibility test with $(U_{0.8}Pu_{0.2})C_{0.95}$, 816°C (1500°F), 1000 hr

Fig. 15 — Niobium from compatibility test with $(U_{0.8}Pu_{0.2})C_{0.95}$, 816°C (1500°F), 4000 hr
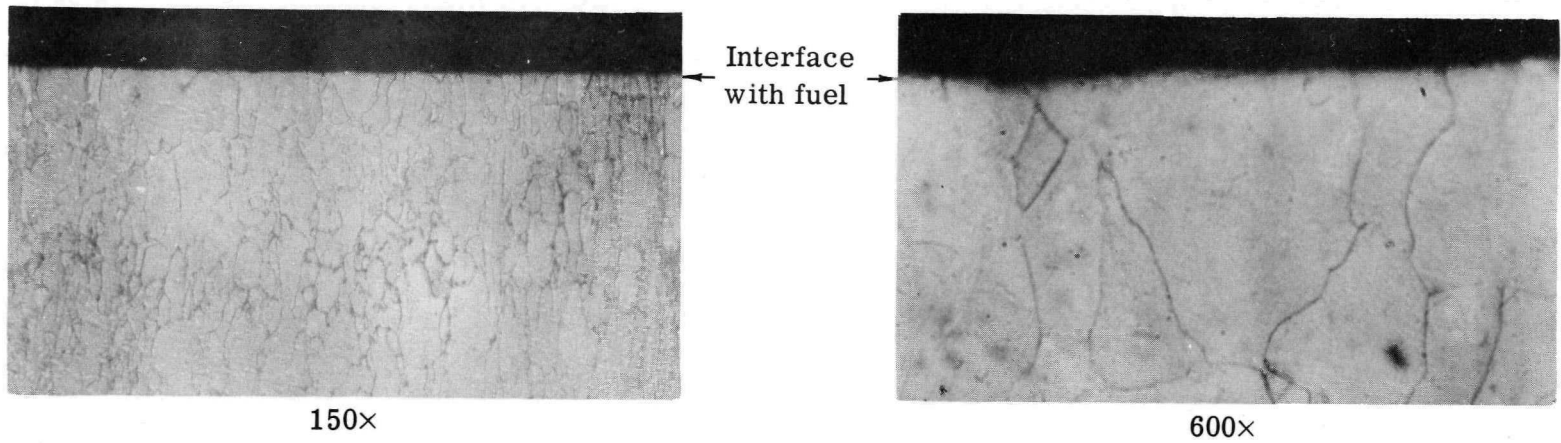
Interface with fuel →

150×        600×

Fig. 16 — Niobium-1% zirconium from compatibility test with $(U_{0.8}Pu_{0.2})C_{0.95}$, 816°C (1500°F), 4000 hr

Vanadium. There were no obvious reactions between fuel and vanadium. The results are given in Table 19. Some localized areas were observed which could be reaction products, but these were slight and could not be positively identified as reaction products. The "reaction product" in Fig. 17 was not attacked by etchants for carbide, vanadium, uranium, or plutonium. For this reason, it is not likely to be a reaction product, but may be an inclusion from an unidentified source. A duplicate sample did not show these inclusions as shown typically in Fig. 18.

Table 19 — Fuel-Vanadium Compatibility

| Fuel | Temperature, °C (°F) | Time, hr | Remarks |
|---|---|---|---|
| $(U_{0.8}Pu_{0.2})C_{0.95}$ | 593 (1100) | 1000 | No reaction |
| | 816 (1500) | 1000 | No reaction |
| | 816 | 4000 | No reaction (Fig. 17) Possible slight reaction (Fig. 18) |

Zircaloy-2. A reaction was noted between $(U_{0.8}Pu_{0.2})C_{0.95}$ and Zircaloy-2 in 1000 hr at 593 and 816°C. Fig. 19 shows a typical interface with the fuel. The reaction product has not been identified.

Inconel-X. There was no reaction between $(U_{0.8}Pu_{0.2})C_{0.95}$ and Inconel-X in 1000 hr at 593°C; however, there was a slight reaction in 1000 hr at 816°C. The extent of the reaction was not as great as that previously noted with UC.[12]
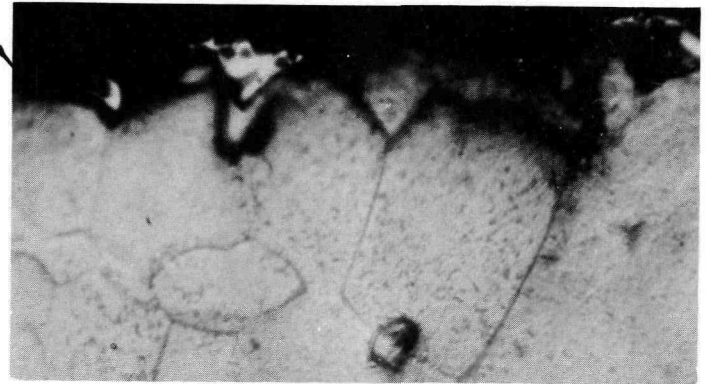
Fig. 17 — Vanadium from compatibility test with $(U_{0.8}Pu_{0.2})C_{0.95}$, with questionable reaction product — 816°C (1500°F), 4000 hr

150×

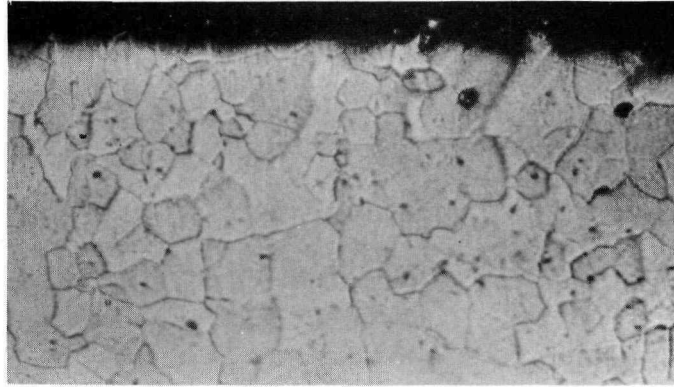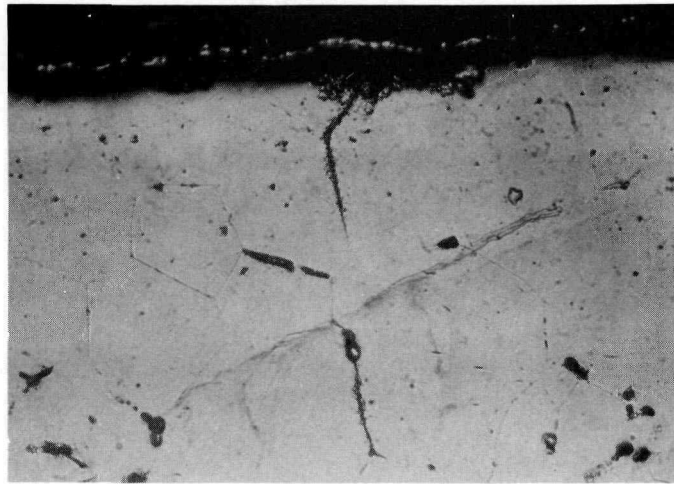Fig. 18 — Duplicate specimen of vanadium from compatibility test with $(U_{0.8}Pu_{0.2})C_{0.95}$, 816°C (1500°F), 4000 hr



150×

Fig. 19 — Zircaloy-2 from compatibility test with $(U_{0.8}Pu_{0.2})C_{0.95}$, 816°C (1500°F), 1000 hr

# 5. APPENDIX – CHEMICAL ANALYSIS

## 5.1 INTRODUCTION

Specimens of (U,Pu)C have been analyzed for nitrogen (colorimetry), oxygen (vacuum fusion), carbon (gravimetry), plutonium (alpha counting), uranium (fluorometry) and nickel (spectrophotometry). The nitrogen, oxygen, and plutonium analyses have been described in detail in UNC-5065.

The nickel analysis was performed by the Rocky Flats plant of the Dow Chemical Company. The standard spectrophotometric method with dimethyl glyoxime was used after removing the plutonium by anion exchange.

The remaining analyses, uranium and carbon, are described briefly in Sections 5.2 and 5.3.

## 5.2 URANIUM BY FLUOROMETRY

The fluorometric method was chosen for the analysis of uranium on the vapor pressure planchets, because it was the only method with sufficient sensitivity to analyze for microgram quantities. Such analyses had been made by previous investigators.[13]

The sample is dissolved in 8N nitric acid inside the glove box. The remainder of the analysis is completed in an open-face chemistry fume hood (see Fig. 20). Aliquots (λ quantities) are taken from the solution, tranferred to small platinum
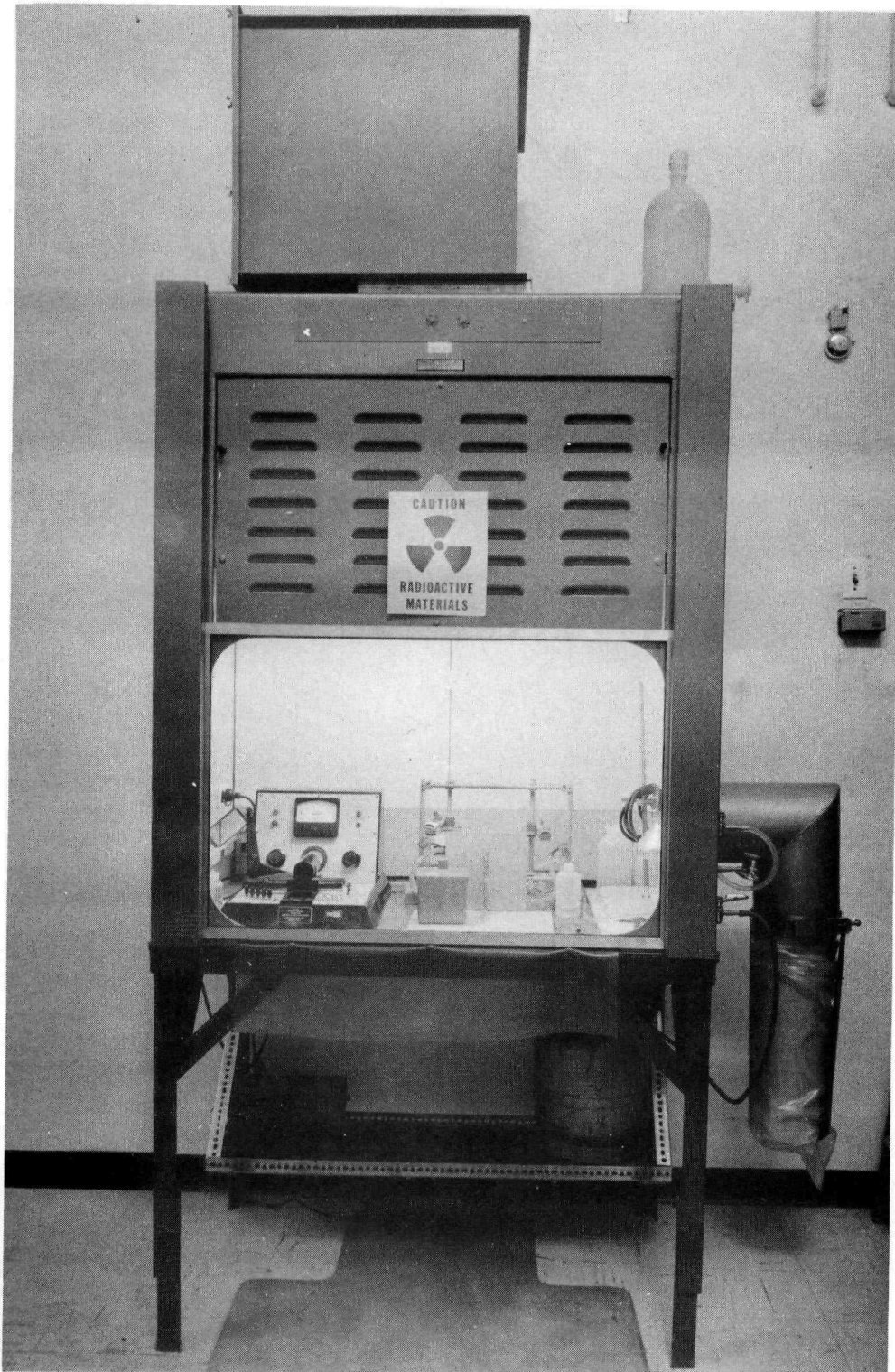
Fig. 20 — Chemistry fume hood in alpha laboratory

planchets, and evaporated to dryness. Pellets of the NaF-2% LiF are then placed on the planchets and heated with a propane burner until the flux is melted. The mixture is then fused for 1 min. After cooling, the flux containing the sample is removed from the planchet and read on the fluorometer. Uranium standards were used to establish calibration curves in two ranges: 0.02 to 0.10 $\mu$g uranium, and 0.10 to 1.00 $\mu$g uranium. Values for the samples were then obtained from the proper calibration curve. High ratios of plutonium-to-uranium did not affect the uranium values obtained.

## 5.3 CARBON BY GRAVIMETRY

Carbon is determined gravimetrically by combustion of the mixed carbides in an induction furnace using oxygen as the combustion gas. The ascarite collection bulb is located outside of the glove box and weighing of the bulb is done in the open laboratory. This standard method of analysis has been successful in analyzing standards of National Bureau of Standards sodium oxalate ($Na_2C_2O_4$), NBS, iron, and tungsten carbide with good reproducibility and accuracy. Analysis of mixed carbide samples also gave good reproducible and accurate results. Typical results are shown in Table 20.

Table 20 — Typical Carbon Analysis Results

| NBS $Na_2C_2O_4$ (Theo. carbon: 17.9%) | | NBS Iron (Theo. carbon: 4.39%) | | WC (Theo. carbon: 6.13%) | | $(U_{0.8}Pu_{0.2})C_{0.95}$ (Expansion Bar) | |
|---|---|---|---|---|---|---|---|
| Sample | Carbon, % | Sample | Carbon, % | Sample | Carbon, % | Sample | Carbon, % |
| 1 | 18.5 | 1 | 4.40 | 1 | 6.17 | 1 | 4.61 |
| 2 | 18.2 | 2 | 4.41 | 2 | 6.08 | 2 | 4.60 |
| 3 | 18.3 | 3 | 4.37 | 3 | 6.08 | | |
| 4 | 18.1 | 4 | 4.38 | 4 | 6.14 | | |
| | 18.3 avg | | 4.39 avg | | 6.12 avg | | 4.61 avg |

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ERRATA IN UNC-5074


In Report UNC-5074, Out-of-Pile Properties of Mixed Uranium-Plutonium Carbides, Final Report, dated December 6, 1963:

Page vi   Item 12 should read:

Microstructure of $(U_{0.8}Pu_{0.2})C_{0.95}$ with Grain Boundary Carbide

Page 48   Fig. 12 should read:

Microstructure of $(U_{0.8}Pu_{0.2})C_{0.95}$ with grain boundary carbide — nitric acid-acetic acid-water etch. Sintered 1550°C, 1 hr in helium.

Page 52   Fig. 14 should read:

$2\frac{1}{4}$ Cr-1 Mo steel from compatibility test with $(U_{0.8}Pu_{0.2})C_{0.95}$, 593°C (1100°F), 4000 hr