UNC-5065
UC-25, Metals, Ceramics and Materials
SPECIAL

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

## Progress Report

Period of February 6, 1962 to October 31, 1962

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September 18, 1963

Joint U. S.-Euratom Research and Development Program

Work Performed under UNC Project 2295
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# FOREWORD

The United States and the European Atomic Energy Community (Euratom), on May 29 and June 18, 1958, signed and 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 in Europe 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 mixed uranium-plutonium carbides is sponsored jointly by the USAEC and Euratom. The prime contractor is the United Nuclear Corporation, Development Division, and the subcontractor is The Carborundum Company. The United Nuclear Corporation is performing the property determinations and The Carborundum Company is preparing the fuel samples.

The report covers progress from the inception of the program on February 6, 1962 to October 31, 1962.

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

Results of this program are covered in:

| | |
|---|---|
| NDA 2140-2 | Carbide Fuel Development, Phase I Report (Oct. 15, 1959) |
| NDA 2145-6 | Carbide Fuel Development, Phase II Report (Nov. 6, 1960) |
| NDA 2162-5 | Carbide Fuel Development, Phase III Report (Sept. 30, 1961) |
| UNC-5003 | Carbide Fuel Development, Progress Report (Feb. 9, 1962) |
| UNC-5013 | Carbide Fuel Development, Progress Report (May 28, 1962) |
| UNC-5030 | Carbide Fuel Development, Progress Report (Aug. 10, 1962) |
| UNC-5055 | Carbide Fuel Development, Phase IV Report (Mar. 31, 1963) |
| UNC-5056 | Carbide Fuel Development, Progress Report (May 1, 1963) |

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# 1. INTRODUCTION

Fuels made of solid solutions of (U,Pu)C have a potential of reducing fuel cycle costs of plutonium-fueled power reactors. The fuel cycle cost reduction is anticipated because of increased burnup and increased power generation capability of (U,Pu)C, compared to presently available metallic fuels.

UC irradiation tests show that carbide fuels have considerably greater dimensional stability than metallic fuels. Because of the favorable behavior of UC there is expectation that (U,Pu)C fuels will behave similarly. 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 this program is to determine those out-of-pile properties of (U,Pu)C which have the most significant effect on the operational characteristics of the fuel.

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 exceeding temperatures for 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.

# 2. SUMMARY

## 2.1 FUEL SAMPLE FABRICATION

Fabrication studies to produce high density solid solutions of 80% UC-20% PuC, with reproducible structure, composition, and density, were completed. 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 1950°C;
2. $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 w/o Ni sintering aid, major monocarbide and minor amount of sesquicarbide pellets, with average densities of 13.1 g/cm$^3$ (96.5% of theoretical) sintered at 1550°C.

Bar-shaped thermal expansion specimens were fabricated of UC, prior to fabrication of similar (U,Pu)C specimens. UC pellets were fabricated for electropolishing and liquid-metal bonding studies.

Chemical analysis procedures were established, and checked, for plutonium, nitrogen, and oxygen. Chemical analysis procedures for carbon are being established.

## 2.2 PROPERTY DETERMINATIONS

The experimental setups for the measurement of coefficient of thermal expansion, thermal stability, melting point, and fuel cladding compatibility were completed.

Testing of thermal expansion, vapor pressure, and melting point standards was initiated. Agreement has been reached with a plutonium laboratory with existing apparatus to do thermal conductivity measurements.

UC-liquid metal-tantalum compatibility tests were completed, and (U,Pu)C-liquid metal-tantalum compatibility specimens were prepared. These tests are to help in choosing a liquid-metal bond for the thermal conductivity test.

The pre-installation tests for the safe performance of the high temperature measurements glove box were nearly completed.

# 3. FUEL SAMPLE FABRICATION

## 3.1 INTRODUCTION

The goal of the fabrication studies is to produce high density solid solutions of 80% UC-20% PuC, with reproducible structure, composition, and density. The material is to have a potential as an economically produced reactor fuel, and be suitable for testing. The development of powder fabrication techniques initiated on Contract AT(30-1)-2899 is being continued.

## 3.2 PELLET FABRICATION

### 3.2.1 General

Starting powder for the fabrication experiments was made on Contract AT(30-1)-2899, by the reaction of $UO_2$, $PuO_2$, and carbon to produce $(U_{0.8}Pu_{0.2})C_{0.95}$. The substoichiometric amount of carbon is used to produce single-phase material. The equilibrium relationships are apparently such that a stoichiometric amount of carbon promotes the formation of sesquicarbide. Fabrication of the powder is described in reports referenced in the Foreword. The resulting powder has a particle size estimated to be in the 1 to 10 micron range.

Sintering experiments were conducted with the $(U_{0.8}Pu_{0.2})C_{0.95}$ powder, both with and without nickel sintering aid. Past experience has shown that considerable improvements in density can be obtained by the use of small amounts of nickel sintering aid. Pellets with 1/4% Carbowax temporary binder dissolved in trichlorethylene were cold pressed at 30,000 psi, preheated to about 700°C in an open tantalum crucible to volatilize the binder, and sintered at the final temperature in a closed tantalum crucible. The size of the unsintered pellets was 0.224 in. diameter by 0.215 in. high. The furnace used is heated by a graphite resistance element and operates in the glove box helium atmosphere. The impurity content of the helium is measured continuously as about 2 to 3 ppm oxygen, and the nitrogen impurity is assumed to be about four times the oxygen impurity. The $H_2O$ content has been spot checked as less than 1 ppm.

### 3.2.2 $(U_{0.8}Pu_{0.2})C_{0.95}$

The investigation of the effect of sintering time and temperature on the density, structure, and composition of pellets without nickel sintering aid was continued. Previously, the best density obtained [on Contract AT(30-1)-2899] was 12.39 g/cm$^3$ by sintering at 1950°C for 1/4 hr. On this contract, pellets were sintered at 1950°C for 1 hr. Results are shown in Table 1. An average density of 12.83 g/cm$^3$ was obtained and judged to be sufficiently high for further evaluation.

A pilot batch of about 15 pellets was made to determine whether the densities are reproducible. The results are given in Table 2, and show that densities were reproducible. Previous indications* that plutonium losses may be excessive at high sintering temperatures were not correct, as shown by the plutonium analyses. The oxygen content was similar to that of UC made by the same process.

Metallographic examination showed essentially a single-phase structure (Fig. 1). Small amounts of Widmanstätten structure were noted in the majority of the pellets. Small amounts of free metallic phase were noted near the outside edges of a few of the pellets.

Approximately 55 g of $(U_{0.8}Pu_{0.2})C_{0.95}$ solid solution was prepared from the carbon reduction of $PuO_2$ and $UO_2$. This powder was used subsequently to prepare pellets scheduled for melting point, vapor pressure, and compatibility studies.

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*Contract AT(30-1)-2899.

Table 1 — Results of Sintering Experiments With $(U_{0.8}Pu_{0.2})C_{0.95}$ Compacts (no sintering aid)

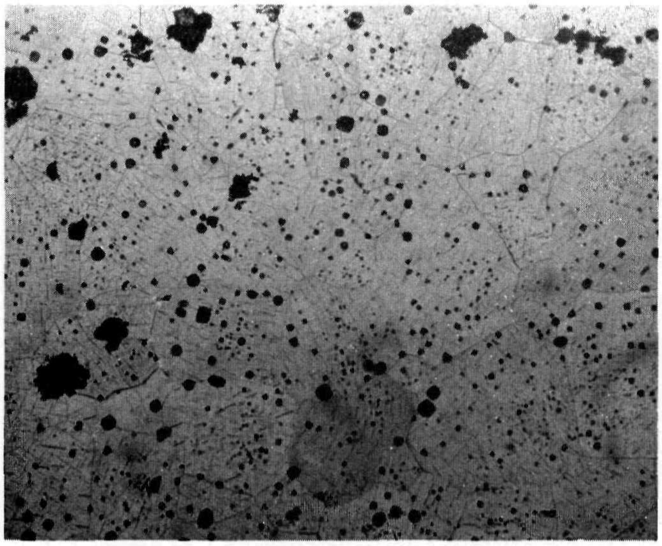
| Experiment No. | Temp and Hold Time | Avg. Density, g/cm$^3$ | X-Ray Analysis |
|---|---|---|---|
| 1 | 1950°C – 1/2 hr | 12.64 | Single-phase (U,Pu)C<br>$a_0 = 4.964 \pm 0.001$ Å |
| 2 | 1950°C – 1 hr | 12.83 | Single-phase (U,Pu)C<br>$a_0 = 4,982 \pm 0.001$ Å |

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

| Temp and Hold Time | Sintered Density, g/cm$^3$ | Chemical Analysis, % | Results of X-Ray Analysis |
|---|---|---|---|
| 1950°C – 1 hr, 15 pellets | 12.82 avg. (12.76-12.94) | 4.46 C*<br>18.8 Pu<br>19.1 Pu<br>200 ppm N<br>160 ppm N†<br>3140 ppm O†<br>1 ppm H† | Single-phase (U,Pu)C<br>$a = 4.961 \pm 0.003$ Å |
| 1925°C – 1 hr, 35 pellets | 12.70 avg. (12.58-12.83) | 4.66 C* | Single-phase (U,Pu)C<br>$a = 4.962 \pm 0.002$ Å |

*Theoretical carbon content is 4.56 w/o.

†By vacuum fusion at Rocky Flats Plant, Dow Chemical Co.



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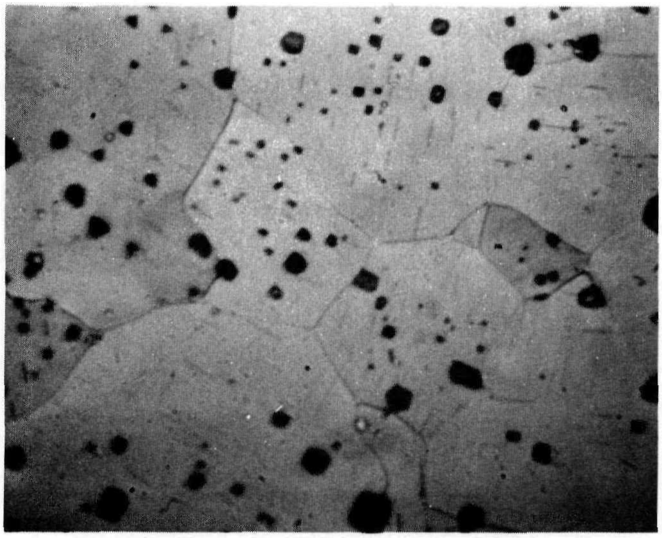

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Fig. 1 — Microstructure of 80% UC-20% PuC – nitric acid-acetic acid-water etch. Sintered 1950°C, 1 hr in helium – 12.8 g/cm$^3$, 4.5% $C_c$. X-ray analysis: single-phase (U,Pu)C, $a_0 = 4.961 \pm 0.003$ Å.

For synthesis, the batch constituents were blended by ball-milling for 24 hr in a rubber-lined mill using stainless steel balls. Chemical analysis for total carbon, on this material, gave 11.59%.

Reaction pellets, pressed from this material, were heated to 1625°C and held at temperature until the CO, present in the exhaust gas drawn from the heated furnace, decreased to 0.005%, indicating a complete reaction.

Chemical analysis, on the pulverized product, gave total carbon at 4.68%. X-ray analysis showed single-phase (U,Pu)C with a unit cell size, $a_0 = 4.966 \pm 0.001$ Å.

This carbide powder was subsequently ball-milled for 24 hr in a rubber-lined mill using stainless steel balls, and used to fabricate 35 pellets by cold pressing and sintering. The size of the cold pressed pellets was 0.224 in. in diameter by 0.215 in. high. These were pressed in the usual manner (30,000 psi, 1/4 w/o Carbowax). The cold pressed pellets were preheated to about 700°C in an open tantalum crucible to volatilize the binder; the final sintering was completed in a closed tantalum crucible at 1925°C with a hold time of 1 hr. The results are shown in Table 2. The densities reported in the table appear to be slightly lower than those of the pilot batch. However, the 35 pellets were not surface ground, since they will be used for property determinations. The microstructure was essentially the same as the pilot batch shown in Fig. 1.

Several sintering experiments were conducted with reprocessed $(U_{0.8}Pu_{0.2})C_{0.95}$ single-phase, solid solution powder. The pellets were fabricated in the standard manner. However, the efforts were only moderately successful as low density (12.6 g/cm$^3$), low carbon content (4.44%) pellets were obtained.

### 3.2.3 $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1% Ni

The investigation of the effect of sintering time and temperature on the density, structure, and composition of pellets with nickel sintering aid was continued. Previously, the best density obtained [Contract AT(30-1)-2899] was 13.00 g/cm$^3$

by sintering at 1550°C for 1 hr. On this contract, pellets were sintered at 1500 and 1550°C for 1/2 to 3½ hr. Results are shown in Tables 3, 4, and 5. An average density of 13.10 g/cm$^3$ was obtained and judged to be sufficiently high for further evaluation.

Metallographic examination showed a two-phase structure (Fig. 2). The major phase is monocarbide. The minor, light phase has been identified as the sesquicarbide by a combination of metallography and x-ray analysis. Sintering for 3½ hr instead of 1 hr causes some grain growth and agglomeration of the sesquicarbide (Fig. 3).

Initially there was a desire to lower sintering temperatures and shorten sintering times, due to apparent plutonium losses. Analytical procedures, improved since these sintering studies, showed that plutonium was not lost during synthesis or sintering.

The oxygen content of pellets without nickel sintering aid, sintered at 1950°C, was lower than those with nickel, sintered at 1550°C. Either some residual oxygen reacted with the (U,Pu)C at the higher temperatures to form U-Pu metal and CO, or the original powder batch had a lower oxygen content.

### 3.2.4 UC and UC + 0.1% Ni

Pellets of UC were fabricated for studies of electropolishing techniques and for screening-type compatibility tests with liquid metals. Fifteen pellets contained 0.12 w/o nickel sintering aid and 15 contained no sintering aid. Pellets were presintered at 1400°C to drive off the volatiles. UC pellets with nickel sintering aid were held for 1 hr at 1550°C, straight UC pellets were held for 1 hr at 1950°C. The results are shown in Table 6. Pellets with nickel (experiment No. 1), contained imperfections after surface grinding and an additional 15 pellets were fabricated. These are shown as experiment No. 3 in Table 6.

Table 3 — Results of Sintering Experiments at 1500°C With a 1-hr Hold Time

| Experiment No. | Composition of Pellet | Sintered Density, g/cm$^3$ | Total Carbon, % | X-Ray Analysis |
|---|---|---|---|---|
| 1 | $(U_{0.8}Pu_{0.2})C_{0.95}$ | 12.35* | 4.61 | Major (U,Pu)C<br>Faint $(U,Pu)_2C_3$<br>$a_0 = 4.965 \pm 0.001$ Å |
| 2 | $(U_{0.8}Pu_{0.2})C_{0.95}$<br>+ 0.12 w/o Ni | 12.96 | 4.64 | Major (U,Pu)C<br>Weak $(U,Pu)_2C_3$<br>$a_0 = 4.965 \pm 0.001$ Å |

*This unusually high density for a pellet without sintering aid, sintered at 1500°C, could not be reproduced in subsequent experiments.

Table 4 — Results of Sintering Experiments at 1500°C With a $3\frac{1}{2}$-hr Hold Time

| Experiment No. | Composition of Pellet | Sintered Density, g/cm$^3$ | Total Carbon, % | Weight Loss, % | X-Ray Analysis |
|---|---|---|---|---|---|
| 1 | $(U_{0.80}Pu_{0.20})C_{0.95}$ | 11.50 avg.<br>(11.48-11.56) | 4.66 | - | Single-phase (U,Pu)C<br>$a_0$ = 4.9653 ± 0.0008 Å |
| 2 | $(U_{0.8}Pu_{0.2})C_{0.95}$<br>+ 0.12 w/o Ni | 13.10 avg.<br>(13.09-13.11) | 4.77 | - | Major (U,Pu)C<br>Weak $(U,Pu)_2C_3$<br>$a_0$ = 4.9655 ± 0.0002 Å |
| 3* | $(U_{0.80}Pu_{0.20})C_{0.95}$<br>+ 0.12 w/o Ni | 13.04 | Not available | 0.72 | Major (U,Pu)C<br>Weak $(U,Pu)_2C_3$<br>a = 4.9652 ± 0.0008 Å |

*This pellet previously had been sintered at 1550°C with a 1/2-hr hold. Results of chemical analysis after this treatment gave total carbon at 4.68. X-ray analysis showed single-phase (U,Pu)C with a unit cell $a_0$ = 4.9844 ± 0.0003 Å.

Table 5 — Results of Sintering Experiments at 1550°C With a 1/2-hr Hold Time

| Experiment No. | Composition of Pellet | Avg. Density, g/cm$^3$ | Chemical Analysis, %* | X-Ray Analysis |
|---|---|---|---|---|
| 1 | $(U_{0.80}Pu_{0.20})C_{0.95}$ + 0.12 w/o Ni | 13.00 | 4.76 C<br>100 ppm N†<br>4920 ppm O†<br>1 ppm H† | Major (U,Pu)C<br>Weak $(U,Pu)_2C_3$<br>$a_0$ = 4.9640 ± 0.001 Å |
| 2 | As above – previous experiment | 12.90 | 4.68 C | Single-phase (U,Pu)C‡<br>$a_0$ = 4.9644 ± 0.0003 Å |

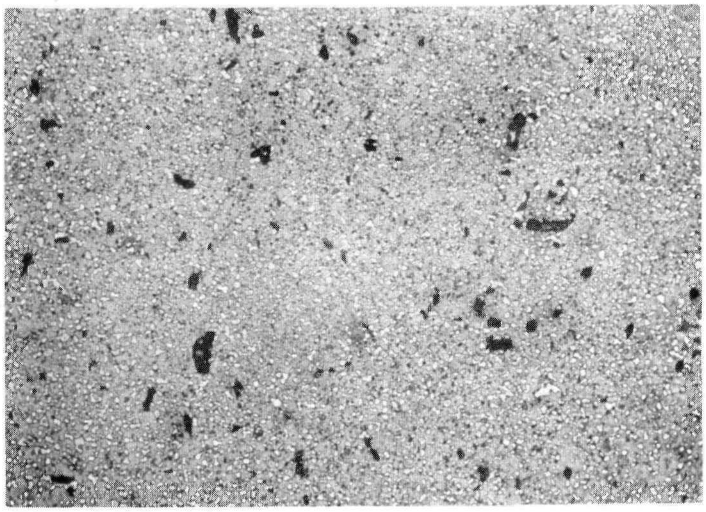
*Plutonium analyses of pellets made by a similar process on Contract AT(30-1)-2899 showed they contained the theoretical amount within experimental error. Nitrogen analyses gave 150-200 ppm.

†Average of 4 pellets analyzed by vacuum fusion at the Rocky Flats Plant, Dow Chemical Co.

‡Metallographic examination showed a two-phase structure. The sensitivity of the x-ray analysis is apparently limited to amounts of second-phase greater than present here.

Table 6 — Results of UC Sintering Experiments

| Experiment No. | Intended Composition | Temp and Hold Time | Sintered Density, g/cm$^3$ | Total Carbon, % | X-Ray Analysis |
|---|---|---|---|---|---|
| 1 | UC + 0.12 w/o Ni | 1550°C – 1 hr | 12.77 | — | — |
| 2 | UC | 1950°C – 1 hr | 12.14 avg.<br>(12.04-12.26) | 4.39 | Major UC<br>Faint $UO_2$ |
| 3 | UC + 0.12 w/o Ni | 1550°C – 1 hr | 13.20 avg.<br>(13.18-13.24) | 4.76 | Major UC<br>Weak $U_2C_3$<br>Faint/weak $UO_2$ |



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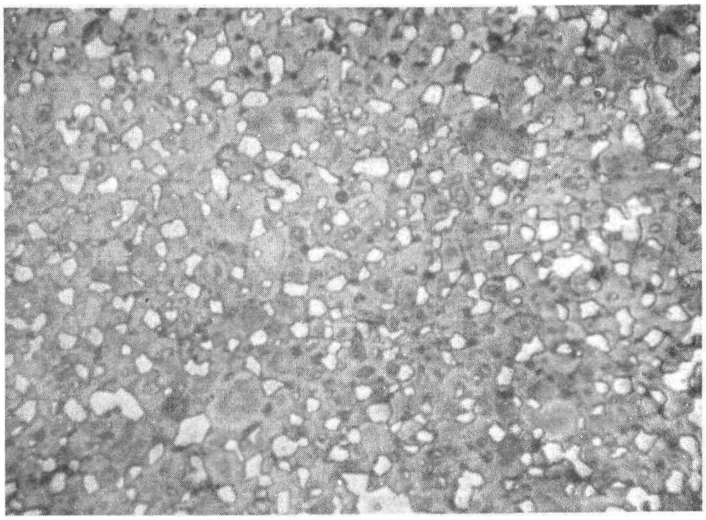

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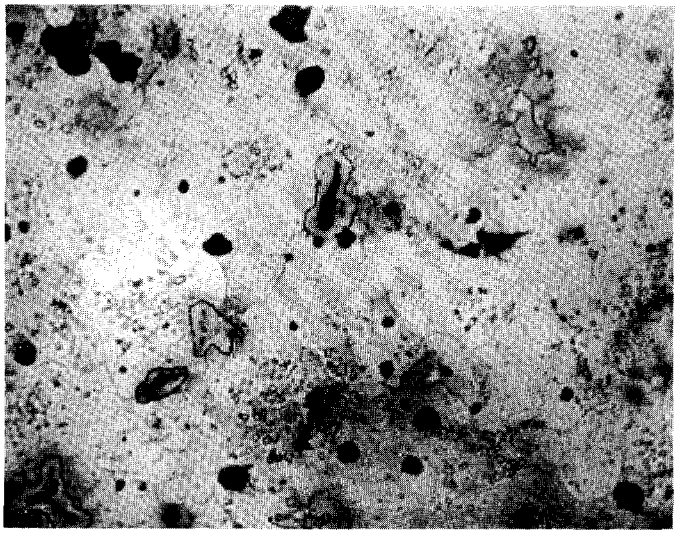
Fig. 2 — Microstructure of 80% UC-20% PuC-0.1% Ni – nitric acid-acetic acid-water etch. Sintered 1550°F, 1 hr in helium – 12.91 g/cm$^3$, 4.77% C. X-ray analysis: major (U,Pu)C; faint $(U,Pu)_2C_3$; $a_0 = 4.9644 \pm 0.0002$ Å



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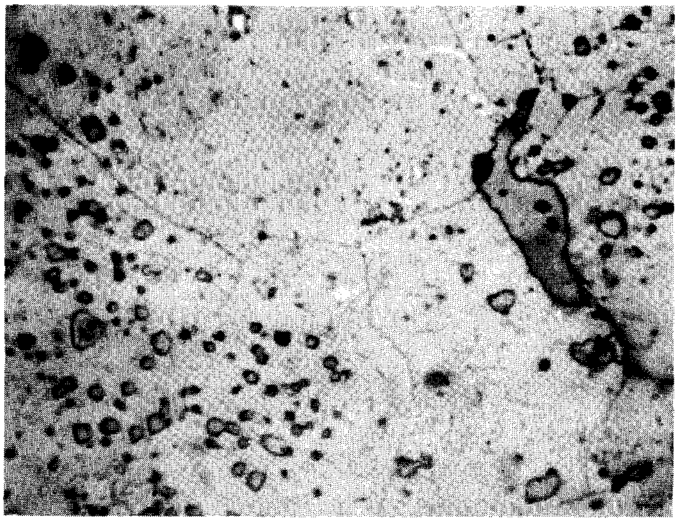

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Fig. 3 — Microstructure of 80% UC-20% PuC-0.1% Ni – nitric acid-acetic acid-water etch. Sintered 1500°C, 3½ hr in helium – 13.10 g/cm$^3$, 4.77% C. X-ray analysis: major (U,Pu)C; weak $(U,Pu)_2C_3$; $a_0$ = 4.955 ± 0.0002 Å

## 3.3 COEFFICIENT OF THERMAL EXPANSION BAR FABRICATION

Several UC test bars to be used for thermal expansion studies were prepared. The bar size was 2.000 ± 0.005 in. long by 0.205 ± 0.005 in. wide by 0.245 ± 0.005 in. high. The uranium monocarbide powder used to fabricate the specimens was prepared in vacuo, from the carbon reduction of $UO_2$. The temperature was 1850°C with a hold time of 1 hr. The reacted product was crushed, then ball-milled for 24 hr in a rubber-lined mill using stainless steel balls. Chemical and x-ray analyses are given in Table 7.

Six bars were fabricated from the milled UC powder. The temporary binder was 1/4 w/o Carbowax-6000 dissolved in trichlorethylene. The cold forming pressure was 30,000 psi. The bars were presintered in a tantalum-lined graphite container in argon at 1500°C to drive off the volatiles. The final sinter was completed in a vacuum furnace at 1950°C with a hold time of 1 hr. Three of the bars were ground to size. The densities were 11.71, 11.72, and 11.78 g/cm$^3$. Chemical and x-ray analyses of the bars are also given in Table 7.

## 3.4 DEVELOPMENT AND STANDARDIZATION OF CHEMICAL ANALYSIS PROCEDURES

### 3.4.1 Plutonium by Alpha Counting

Initial plutonium analyses were carried out by dissolving (U,Pu)C in a mixture of nitric and sulfuric acids, evaporating the solution on a standard planchet, fixing the plutonium on the planchet, counting, and comparing the counts to plutonium standards made by the AEC New Brunswick analytical laboratory. The results were consistently below theoretical, as shown in Table 8.

The New Brunswick laboratory made duplicate check analyses of the United Nuclear analyses by their own wet chemical analysis method,* based on ion exchange

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*C. Pietri and J. Baglio, "The Determination of Plutonium Based on NBS Potassium Dichromate," Vol. 6, pp. 159-166, Talanta, 1960.

## Table 7 — Analysis of UC Used for Thermal Expansion Bars

| | Chemical Analysis, w/o | X-Ray Analyses |
|---|---|---|
| Powder | | |
| Uranium | 95.12 | Major UC, faint $UO_2$ |
| Total carbon | 4.64 | |
| Free carbon | 0.06 | |
| Nitrogen | 0.02 | |
| Iron | < 0.01 | |
| Bar | | |
| Uranium | 95.18 | Major UC, faint $UO_2$ |
| Total carbon | 4.41 | $a_0 = 4.961 \pm 0.001$ Å |
| Free carbon | 0.03 | |
| Oxygen | 0.44 | |
| Nitrogen | Nil | |
| Iron | Nil | |

Table 8 — Plutonium Analysis Results (% Pu)

| Identification | Material | Theoretical | UNC Analysis (Alpha Counting – Original Technique) | UNC Analysis (Alpha Counting – Improved Technique) | New Brunswick Analysis (Titration) |
|---|---|---|---|---|---|
| - | $4\ UO_2 + 1\ PuO_2 + (0.95)15C$ powder | 15.6 | - | - | 15.5 |
| Lot 23 #2 | $(U_{0.8}Pu_{0.2})C_{0.95}$ powder synthesized at 1625℃, 2¼ hr | 19.1 | 15.8, 15.8 | 19.6 | 19.0, 19.5 |
| Lot 23 #1 | $(U_{0.8}Pu_{0.2})C_{0.95}$ powder synthesized at 1625℃, 6½ hr | 19.1 | 15.8, 15.9 | - | - |
| Lot 23 #3 | $(U_{0.8}Pu_{0.2})C_{0.95}$–0.1 w/o Ni sintered at 1550℃, 1 hr pellet | 19.1 | 15.0, 15.1, 15.1 | - | 19.4 |
| Lot 25 #3 | $(U_{0.8}Pu_{0.2})C_{0.95}$ +0.1 w/o Ni sintered at 1550℃, 1/2 hr | 19.1 | 15.5, 15.2 | - | - |
| Lot 25 #7 | $(U_{0.8}Pu_{0.2})C_{0.95}$ +0.1 w/o Ni sintered at 1550℃, 1/2 hr plus 1500℃, 3½ hr | 19.1 | 16.8, 17.2 | - | - |
| Lot 25 #6 | $(U_{0.8}Pu_{0.2})C_{0.95}$ green pellet | 19.1 | 16.0, 16.5 | - | - |
| Lot 27 #1 | $(U_{0.8}Pu_{0.2})C_{0.95}$ sintered at 1850℃, 1/4 hr | 19.1 | - | 18.7 | 18.0, 18.4 |
| Lot 29 #2<br>Lot 29 #3 | $(U_{0.8}Pu_{0.2})C_{0.95}$ sintered at 1950℃, 1 hr | 19.1 | - | 18.8<br>19.1 | - |

separation of U and Pu, and titration of Pu. Except for slight modifications in the decomposition procedure, the method was identical to that described in the reference. The results of analyses of (U,Pu)C checked the theoretical amount of Pu. A good check analysis of a standard, made by a mechanical mixture of $UO_2$-$PuO_2$-C, gave greater confidence in the New Brunswick results.

Since the analyses made by counting gave low but consistent results, the error was thought to be due to the planchet preparation method. A new set of standard planchets was made at United Nuclear from standard $Pu(NO_3)_4$ solution supplied by New Brunswick, and standard $UO(NO_3)_4$ solution added to simulate the 4/1 U/Pu ratio. The sample to be analyzed was also dissolved in $HNO_3$ rather than $HNO_3$-$H_2SO_4$ to eliminate any differences in procedure between the standard and the sample. All the planchets were fixed by heating on an electrical resistance heater. Good agreement was obtained between the improved counting technique, and the New Brunswick wet chemical technique as shown in Table 8.

The low results obtained by the initial counting technique were apparently due to the following factors.

1. Presence of uranium in the unknown was giving additional self shielding, compared to the standard which did not have uranium. This is contrary to data by Chalk River,* which state that uranium quantities larger than 280 $\mu g$ are needed for measurable self shielding. Only 0.5 $\mu g$ of uranium are present on the United Nuclear planchets.
2. The use of $H_2SO_4$ on steel planchets may have caused corrosion, and the Fe, Cr, or Ni may have added to the self shielding.
3. Flame fixing of the standards at New Brunswick probably caused more distortion of the planchet than electric resistance heater fixing at United Nuclear, giving different geometries for counting.

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*A. Aikin, T. Bruce, The Analysis for Plutonium by Counting Methods, CEI-58 (June 1953).

In addition to the improved counting technique for plutonium, the wet chemical analysis method is being set up at United Nuclear to provide a check plutonium analysis and a uranium analysis.

### 3.4.2 Nitrogen Colorimetrically

A micro-Kjeldahl method was set up under Contract AT(30-1)-2303, and is described in NDA 2145-6. Dissolution of UC samples in the $H_2SO_4$-$H_2O_2$ solution was satisfactory. However, contact of (U,Pu)C with the same solution produced a waxy substance which prevented further dissolution. The addition of 0.5 ml of HF to the 10 ml of 10% $H_2SO_4$ solution made the dissolution of (U,Pu)C possible. Subsequent nitrogen analyses of (U,Pu)C showed that only small amounts of nitrogen were present (150-200 ppm).

Nitrogen standards are not available; however, previous nitrogen analyses of the same sample of UC by Carborundum and United Nuclear gave results that checked.

### 3.4.3 Oxygen by Vacuum Fusion

Vacuum fusion oxygen analyses were made by the Rocky Flats plant of the Dow Chemical Co. Prior to analysis the carbide sample was electropolished to remove any oxide film. It was then wrapped in a tin capsule, placed in the apparatus, and dropped into a 2000°C molten platinum bath contained in a graphite crucible. Some oxygen contamination at this point was possible, since the pellet was handled in air. The CO and traces of $CO_2$ evolved were pumped into a sample bottle and analyzed by a mass spectrometer. The reproducibility of this method is within 2%. However, a series of analyses of UC samples from the same batch by three laboratories gave results that checked well, as shown in Table 9.

The results show there was little change in oxygen content during processing from clinker to pellet. The pellet with nickel was pressed from a batch of powder different from the one that was analyzed, possibly accounting for the higher oxygen content.

Table 9 — Oxygen Analysis Results (ppm)

| | X-Ray Analysis | Total Carbon, % | Dow | National Research | Carborundum |
|---|---|---|---|---|---|
| UC, as Synthesized Clinker | Major UC<br>Faint $UO_2$ | 4.76 | 1150<br>1110<br>1130 | - | 1100 |
| UC, as Synthesized Clinker | Major UC<br>Faint $UO_2$ | 4.62 | 4970<br>5220<br>4870 | 4700 | 4700 |
| 80% UC-20% PuC as Synthesized Clinker<br>Exp. 8 } Table 1, UNC-5030<br>Exp. 10 } | Single-phase (U,Pu)C | 4.67<br>4.52 | 3610<br>3400 | - | - |
| 80% UC-20% PuC pellet<br>Exp. 1, Table 2 this report | Single-phase (U,Pu)C | 4.46 | 3140 | - | - |
| 80% UC-20% PuC-0.1% Ni pellet<br>Exp. 1, Table 4, this report | Major (U,Pu)C<br>Weak $(U,Pu)_2C_3$ | 4.76 | 4680<br>5130<br>4940<br>4950 | - | - |

### 3.4.4 Carbon by Titration and Gravimetrically

Carbon was determined by combustion of the carbide in oxygen.

At the Carborundum Co. the resulting $CO_2$ was measured gravimetrically by absorption in Ascarite. A previously analyzed lot of UC was used as a standard.

At United Nuclear initial development work concentrated on absorbing the $CO_2$ in potassium hydroxide or benzylamine solutions, then titrating to determine the carbon content. This method has the advantage of doing the entire measurement in one box. Gravimetric analysis would have required numerous time consuming transfers of the Ascarite bulb to the balance box. The titration technique did not give sufficiently good reproducibility and was abandoned. The standard gravimetric technique will be set up now, with the Ascarite bulb outside the glove box. The Ascarite bulb will be weighed on a balance in the open laboratory, eliminating any transfer between boxes. It is expected that this technique will be simpler and more reproducible than the titration.

# 4. PROPERTY DETERMINATIONS

## 4.1 COEFFICIENT OF THERMAL EXPANSION

The dilatometer, dilatometer furnace, and glove box were designed and constructed under Contract AT(30-1)-2899. The differential dilatometer consists of high purity, high density tubular alumina elements (Figs. 4 and 5). The difference in expansion between the alumina and the specimen is sensed by both a dial gage and a linear variable differential transformer. The novel feature of this dilatometer is that the transformer is located inside the vacuum chamber and the dial gage is located outside the chamber with the extension transmitted to the gage through a bellows seal. Temperature is measured by two W-W/26% Re thermocouples located next to the sample.

The dilatometer assembly is surrounded by a closed end alumina protection tube in the furnace, and can contain a moderate vacuum or an inert atmosphere. The temperature limit is represented by the ability of this tube to hold an atmosphere. The dilatometer assembly is placed in a horizontal silicon carbide resistance element furnace capable of operation to 1800°C (3272°F). The furnace is located in a horizontal well on one end of the glove box (Fig. 12). The resistance elements operate in the nitrogen atmosphere of the box and for this reason can operate at higher temperatures than they would in air. The heating element assembly was modified mechanically (under this contract) to provide easier replacement as a unit.

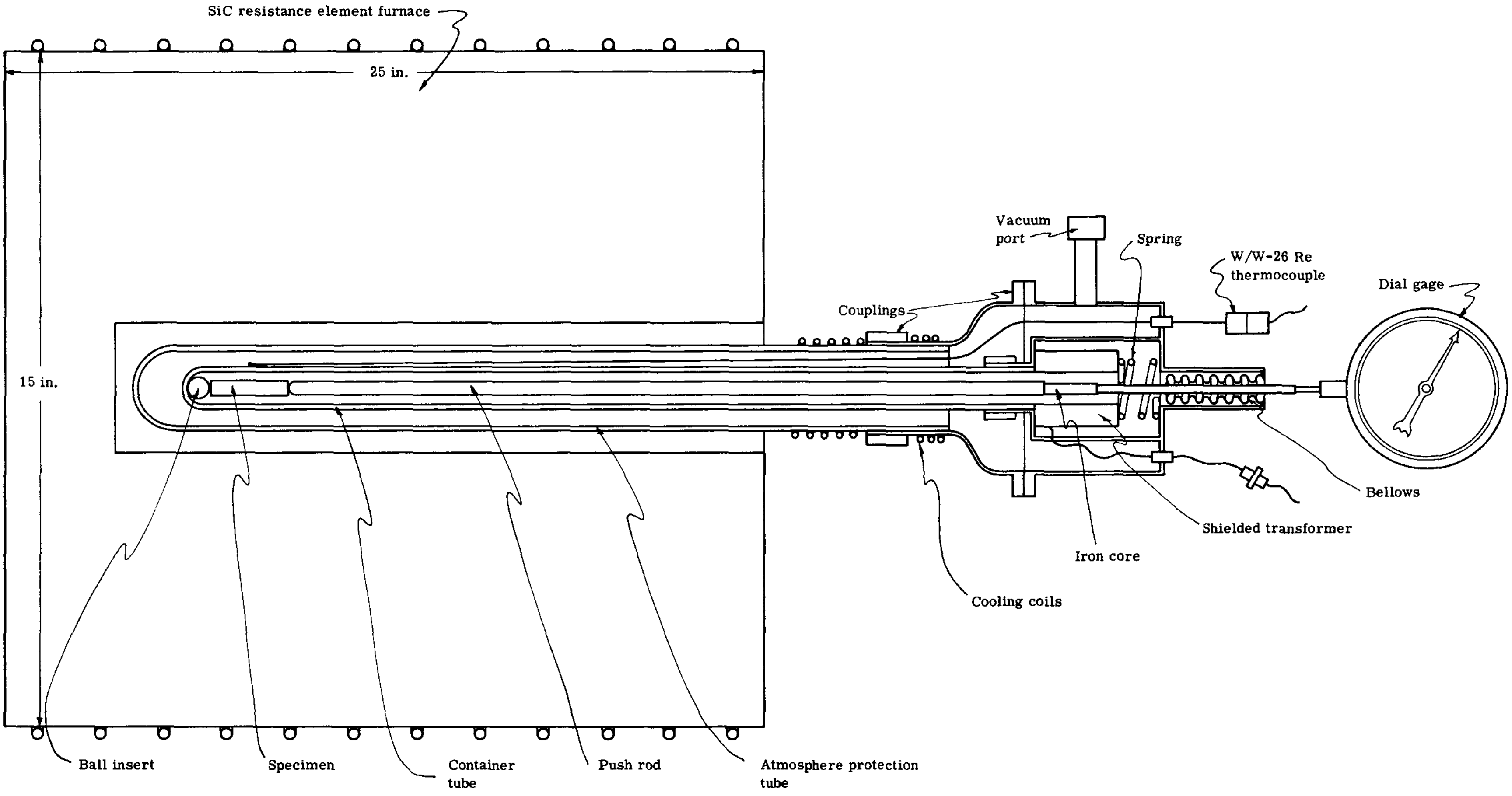

Fig. 4 — Schematic of dilatometer

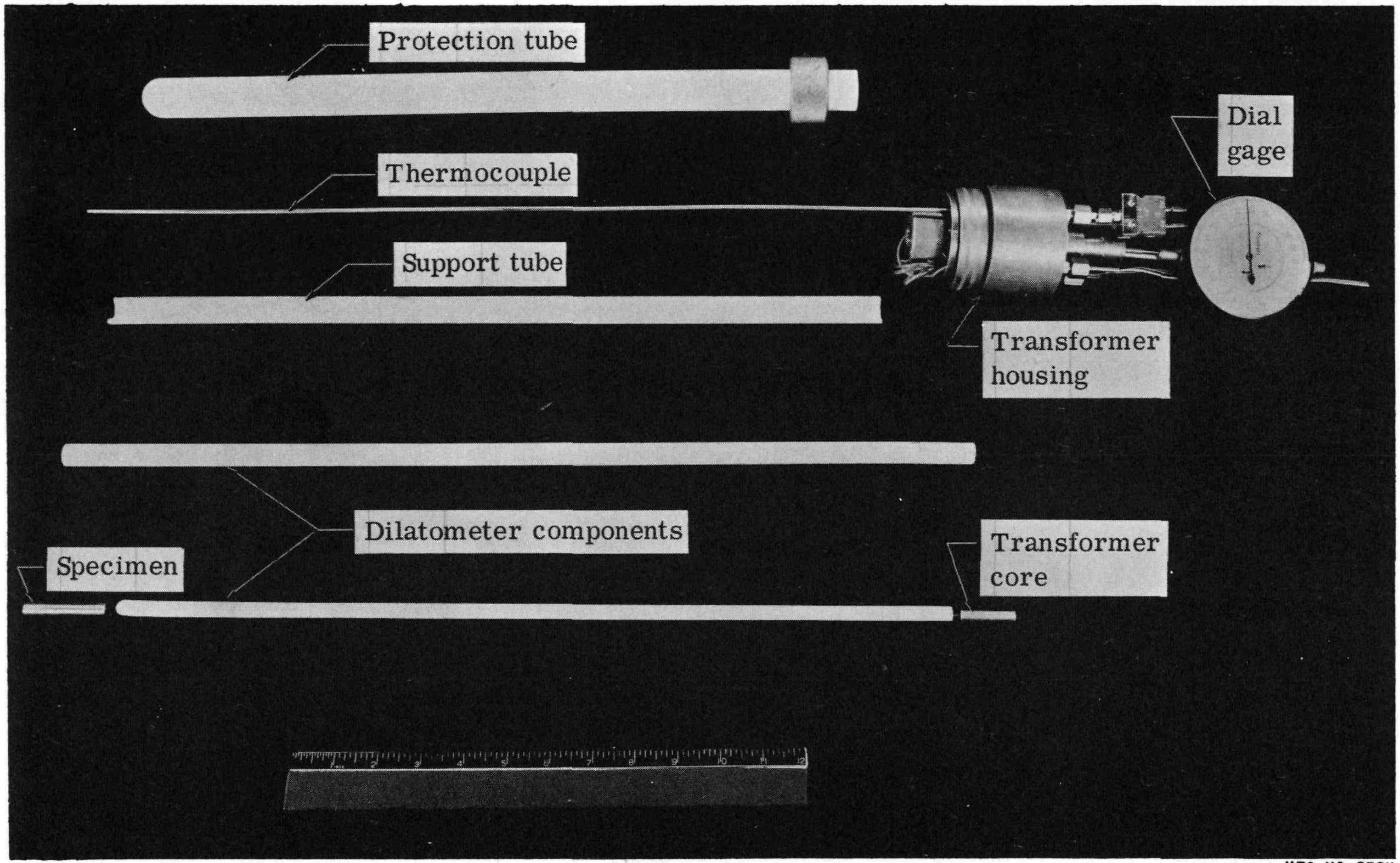

Fig. 5 — Photograph of dilatometer components

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%.

UC specimens are being tested currently to provide experimental checks of the dilatometer on a material with a coefficient of expansion likely to be similar to (U,Pu)C. UC specimens were fabricated by The Carborundum Company, by cold pressing in the die to be used for (U,Pu)C, and subsequently sintered (see Section 3.3). The coefficient of expansion of similar UC bars had been measured previously at Carborundum on a silicon carbide differential dilatometer. A second type of UC specimen was fabricated by arc casting at United Nuclear, and its coefficient of expansion measured on a Leitz interferometer dilatometer under USAEC Contract AT(30-1)-2374.

Preliminary measurements by United Nuclear and average values of The Carborundum Co.* are shown in Table 10 for the specimen prepared by Carborundum. The results are in fair agreement within experimental error. Preliminary data on arc cast UC are also shown in the table.

Table 10 — The Coefficient of Linear Expansion of UC

| Temperature, °C | Sintered UC, Carborundum Co., $10^{-6}$/°C | Sintered UC, United Nuclear, $10^{-6}$/°C | Arc Cast UC, United Nuclear, $10^{-6}$/°C |
|---|---|---|---|
| 25 to 400 | 10.3 | 8.10 | 9.70 |
| 25 to 600 | 10.7 | 9.13 | 10.9 |
| 25 to 800 | 11.0 | 10.0 | 12.1 |
| 25 to 1000 | 11.2 | 10.8 | 12.6 |
| 25 to 1200 | 11.4 | 11.3 | 12.9 |

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*K. Taylor and C. McMurtry, Synthesis and Fabrication of Refractory Uranium Compounds, ORO-400 (Feb. 1961).

## 4.2 THERMAL STABILITY

The design and construction of the experiment to study the high temperature vaporization of (U,Pu)C was completed. The experimental setup was adapted to a commercial tantalum resistance furnace, available in a glove box from Contract AT(30-1)-2899 (see Fig. 6).

The Knudsen effusion method will be used. A schematic of the experimental setup is shown in Fig. 7. The effusion cell is a carburized tantalum cup, 3/8 in. in diameter, and 1/2 in. deep, with a 0.0007-in. thick lid and a 0.010-0.040 in. hole. The cell is centered within the heating element on a tantalum pedestal.

The pedestal contains a W-W/26% Re thermocouple. A beam of vapor is isolated by perforations in the tantalum heat shields and the vapor is condensed on a standard counting planchet cooled by contact with a water-cooled copper block. Eight planchets are located on a rotating disc, and may be successively lined up with the vapor beam without breaking the vacuum. The deposit on the planchets will be analyzed for plutonium by alpha counting and for uranium by fluorimetry. An attempt will be made to determine the structure of the condensed vapor by x-ray diffraction. The weight loss of the effusion cell will be checked against the weight loss calculated from the planchet weight gains.

Initial vaporization tests were made on a silver standard, to calibrate the equipment. The cell containing silver (99.999%) was heated for various times at temperatures ranging from 1160 to 1400°K. The weight of silver deposited on the planchets was determined by chemical means. The Knudsen equation was then employed to yield the fraction of vapor collected. This value of 2.2% was not in agreement with the geometrically calculated amount, 1.2%, and further analysis is planned.

Development of a carburized tantalum effusion cell is in progress. Tantalum cups were deep drawn from sheet, by a commercial fabricator. A carburized layer is required on the inside of the cell, to prevent reaction between the car-

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Fig. 6 — High-temperature-measurements box

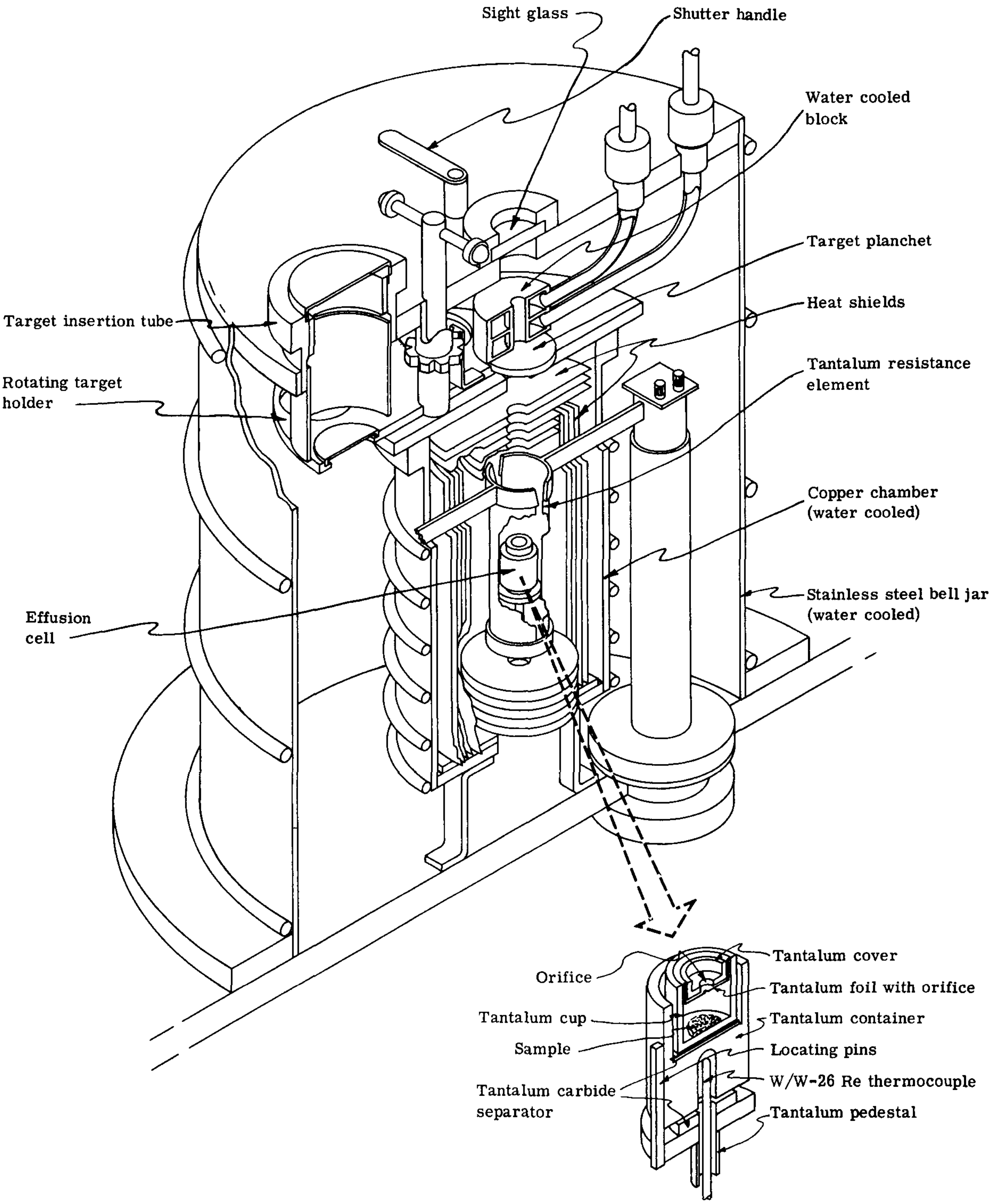

Fig. 7 — Schematic of thermal stability experiment

bide sample and tantalum metal. The reaction would result in the formation of free uranium and plutonium metal whose vapor would interfere with the carbide vaporization measurement. A tantalum carbide layer is also desirable because its vapor pressure is lower than that of tantalum. This prevents a possible chemical reaction of tantalum vapor with the vapor from the fuel carbide.

Tantalum sheet was carburized by heating it in contact with carbon powder, graphite powder, and graphite block at various temperatures and times. The best results were obtained at 1900°C for 1/2 hr with each of the carburizing agents. The carburized layer is shown in Fig. 8. Carburization tests of the drawn cups are in progress. Initial tests show that the cold worked structure of the cups carburizes under different conditions than the annealed sheet. The cups will be annealed prior to additional tests.

## 4.3 MELTING POINT

The design and construction of the equipment to measure melting points of (U,Pu)C was completed and calibration of the temperature readings was initiated.

The tantalum resistance element furnace to be used for the vaporization studies is being used for melting point determinations. A typical melting point specimen is shown in Fig. 9. The specimen has a black body hole for optical temperature measurements. Melting is observed in sharp notches in the specimen OD, and in the black body hole itself. The specimen is contained in a disposable tantalum crucible identical to the effusion cell cup. The cup is centered within the heating element on a tantalum pedestal. The pedestal contains a W-W/26% Re thermocouple. Optical temperature measurements are made through a sight glass on the top of the bell jar.

Temperature corrections required for the optical temperature measurements due to absorption by the sight glass, prism, and glove box window, were measured by the interposition of additional samples of sight glass, prism, and glove box window.

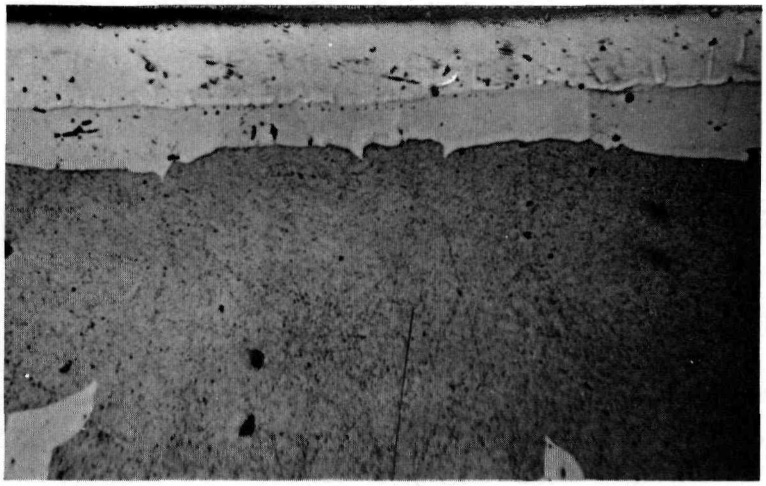

Fig. 8 — Tantalum carbide coating on tantalum; ~0.0015 in. coating thickness – 500×.

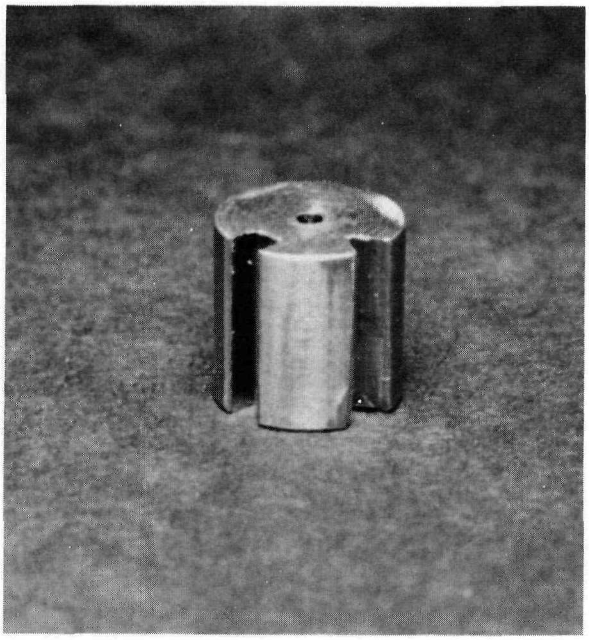

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Fig. 9 — Typical melting point specimen

The final calibration curve will be based on melting point standards:

| Material | Melting Point, °C |
|---|---|
| 99.9 + % copper | 1083 ± 0.1 |
| 99.9 + % titanium | 1668 ± 10 |
| 99.9 + % alumina (sapphire) | 2040 ± 10 |
| 99.9 + % niobium | 2468 ± 10 |

To date, the copper and titanium standards were tested. The corrected optical pyrometer readings were lower than the standards, and the thermocouple readings were higher. The deviations were consistent and reproducible.

## 4.4 THERMAL CONDUCTIVITY

Agreement was reached among the USAEC, the Monsanto Research Corp.'s Mound Laboratories, and United Nuclear Corporation, to have Mound Laboratories measure thermal conductivity of (U,Pu)C specimens and a UC standard prepared by United Nuclear and Carborundum.

The Mound Laboratory apparatus is a calorimeter capable of obtaining thermal diffusivity and specific heat to about 700°C. The sample to be measured is totally enclosed in a cylindrical metal container. Temperature is measured by thermocouples in the center and on the outside wall of the container. The specimen is held until the two thermocouples record the same temperature. The temperature of the furnace is then increased, or decreased, a few degrees so that an unbalance occurs between the two thermocouples. The thermal diffusivity of the sample is then calculated from the total time integral of the transient temperature unbalance of the two couples in going from the initial to the final temperature. The thermal conductivity is then calculated from specific heat, thermal diffusivity, and density.

To date, the apparatus has been used by Mound Laboratories to measure thermal conductivity of molten plutonium alloys. Two major differences exist between the previous and proposed measurements. (U,Pu)C probably has a higher thermal conductivity than molten plutonium alloys, and the contact resistance between the solid (U,Pu)C and the container will be greater than the contact resistance between the molten alloys and the container. Because of these differences, modifications to the specimen design were considered, which will help in obtaining reliable thermal conductivity values. 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.

The compatibility and wetting capabilities of liquid metals with fuel and container were studied next. Liquid metals were chosen on the basis of their:

1. low melting point, for ease of assembly;
2. low specific heat, to maximize heat transfer rate outside the fuel;
3. high thermal conductivity, to minimize the thermal resistance outside fuel;
4. good compatibility with Ta and fuel.

A comparison of properties is given in Table 11.

Gallium, tin, cadmium, and lead were chosen for screening tests with UC. Sodium and NaK were eliminated, because the time and cost for setup in a glove box for a few samples were prohibitive. Bismuth and thallium were eliminated because of their lower thermal conductivity.

Eight individual tantalum capsules containing one fuel sample with one type of liquid metal were tested for 100 hr at 700°C. The highest purity liquid metals commercially available were used. The fuel surfaces were electropolished prior to the test. The results are summarized in Table 12.

Tin and gallium were chosen for further tests with (U,Pu)C.

Table 11 — Possible Liquid-Metal Bonds for Thermal Conductivity Specimen

| | Ga | Na | Sn | Bi | Tl | Cd | Pb |
|---|---|---|---|---|---|---|---|
| Melting Point, °C | 30 | 208 | 231 | 271 | 303 | 321 | 327 |
| Specific Heat, cal/cm$^3$-°K | 0.46 | 0.25 | 0.48 | 0.4 | 0.4 | 0.5 | 0.37 |
| Thermal Conductivity, w/cm-°C | 0.346 | 0.761 | 0.346 | 0.156 | 0.242 | 0.415 | 0.415 |
| 700°C Compatibility with Ta | O.K. | O.K. | ? | O.K. | ? | ? | O.K. |
| Compatibility and Wetting with (U,Pu)C | ← Unknown → | | | | | | |

Table 12 — Results of UC-Liquid Metal Screening Tests (700°C, 100 hr)

| | | Wetting | | Metallography | |
|---|---|---|---|---|---|
| Fuel | Liquid Metal | Fuel | Tantalum | Fuel | Tantalum |
| UC | Ga | Good | Good | Considerable interaction | Slight "erosion" |
| UC + 0.1% Ni | Ga | Excellent | | Interaction | |
| UC | Sn | Good, but not as good as Ga | | No interaction, slight infiltration | Very slight "erosion" |
| UC | Pb | Did not wet | | No examination made | |
| UC | Cd | | | | |

## 4.5 FUEL-CLAD COMPATIBILITY TESTS

The compatibility of (U,Pu)C with the potential cladding materials shown in Table 13 will be studied under conditions similar to those that would prevail in a fuel element. (U,Pu)C will be held in contact with the cladding materials in capsules similar to the one shown in Fig. 10. Continued contact between fuel and cladding samples at elevated temperatures is assured since the stainless steel insert has a higher coefficient of thermal expansion than the Inconel container. Most capsules will contain only one type of cladding material. The capsules will be 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 furnace. The furnace itself stands in a hood in the plutonium facility (see Fig. 11).

After the test the samples will be sectioned and examined metallographically.

All of the compatibility capsules, cladding samples, and fuel pellets have been fabricated. Assembly of the capsules for the 1500°F test is nearly complete. Prior to assembly, the fuel was electropolished to remove any oxide film.

Table 13 — Proposed Fuel-Clad Compatibility Tests

| | 816°C (1500°F) | | 593°C (1100°F) | |
|---|---|---|---|---|
| | 1000 hr | 4000 hr | 1000 hr | 4000 hr |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ vs: | | | | |
| Type 316 SS | x | x | – | x |
| Nb | x | x | – | x |
| Inconel-X | x | – | x | – |
| Zircaloy-2 | x | – | x | – |
| $2\frac{1}{4}$ Cr-1 Mo | – | x | – | x |
| $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1% Ni vs: | | | | |
| Type 316 SS | x | x | – | x |
| Nb | x | x | – | x |

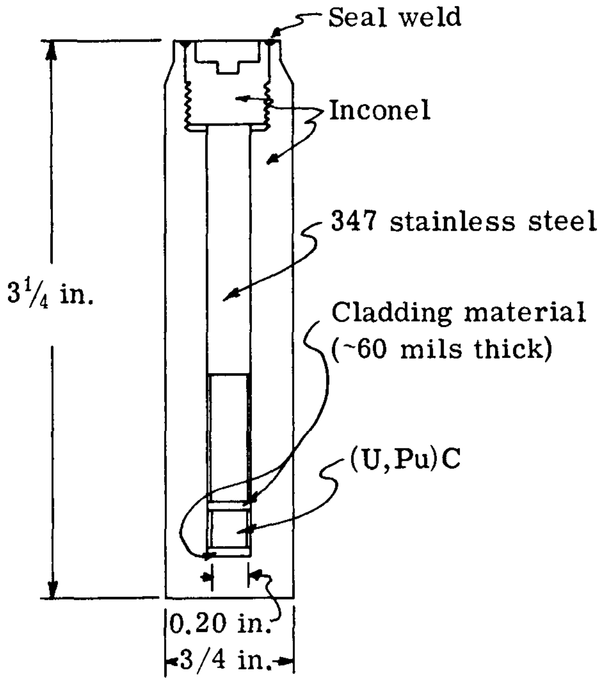

Fig. 10 — Compatibility capsule

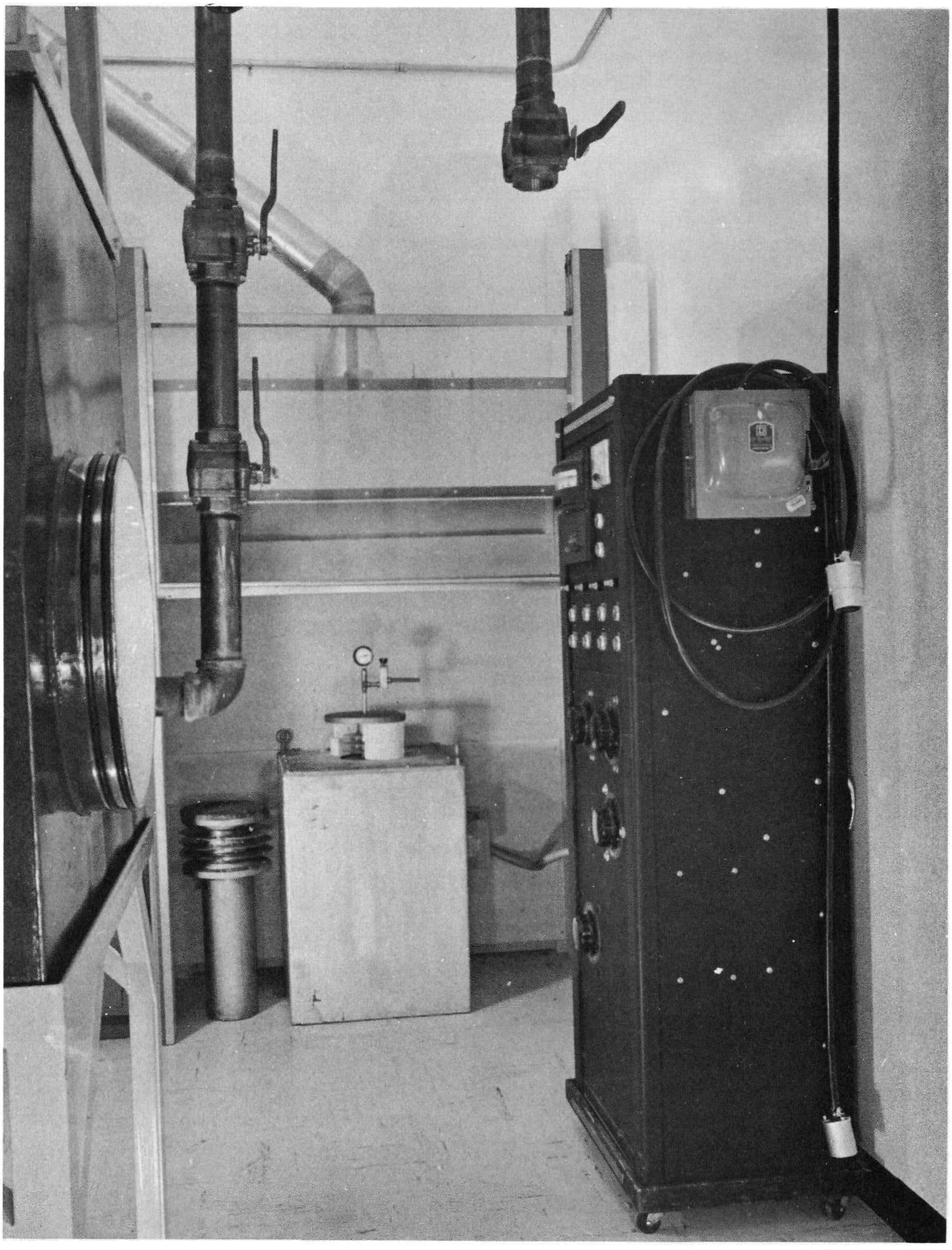

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Fig. 11 — Compatibility furnace and control console

## 4.6 HIGH-TEMPERATURE-MEASUREMENTS GLOVE BOX PERFORMANCE TEST

The high-temperature-measurements glove box, containing the dilatometer and vacuum furnace and its associated cooling system (Fig. 12) has been tested for safe performance prior to its installation at the plutonium facility in Pawling, N.Y.

Pre-installation performance tests consisted of:

- helium mass spectrometer leak test of box
- check of excess box vacuum safety cut-off
- check of operation of water system (leakage, relief valves, level control, low flow safety devices, flow rates through all systems)
- check of box atmosphere and water temperatures at simultaneous operation of both furnaces at maximum operating temperature.

After the tests were completed, the box was disassembled, repainted, and shipped to Pawling. The nitrogen, helium, air, water, control, and sampling lines were installed and the post-installation safety test was begun. Fig. 13 shows the high-temperature-measurements glove box and instrument cabinet located in the Alpha Laboratory.

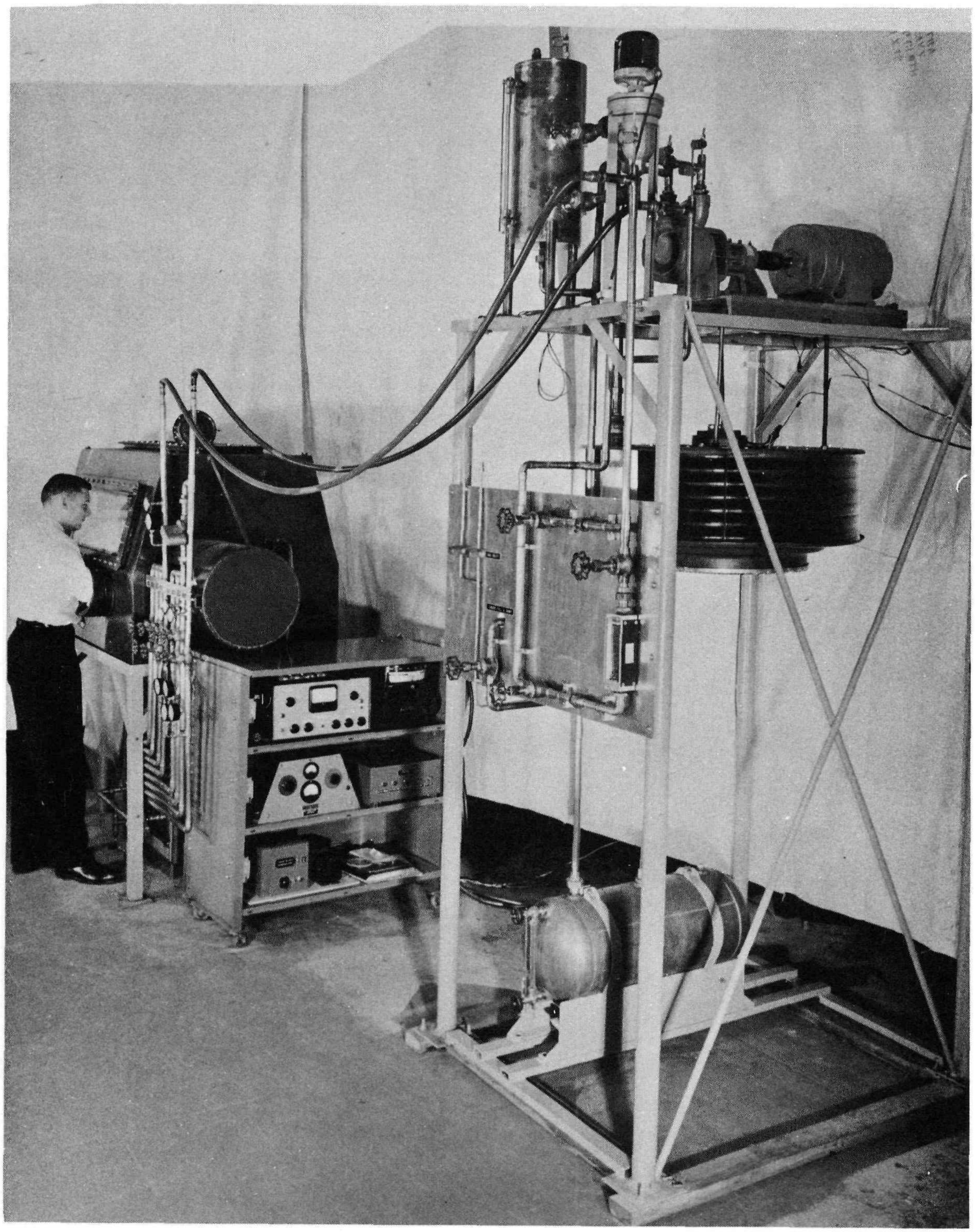

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Fig. 12 — High-temperature-measurements box and cooling system in a cold laboratory.

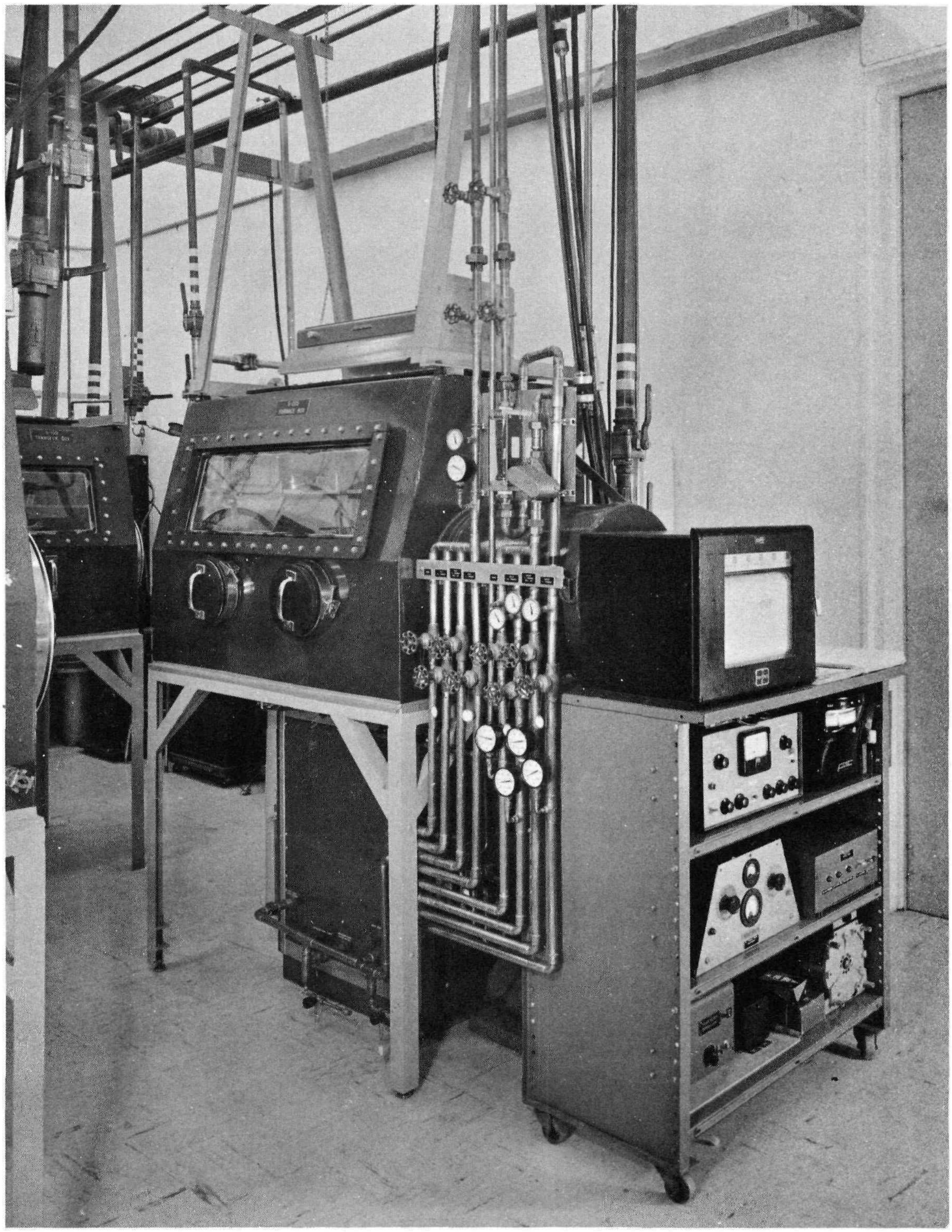

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Fig. 13 — High-temperature-measurements box in Alpha Laboratory

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