# TABLE OF CONTENTS

# DISCLAIMER

# AN EVALUATION OF DATA ON NUCLEAR CARBIDES

Frank A. Rough and Walston Chubb

*Available data on the physical and mechanical properties, constitution, compatibility, and radiation behavior and on fabrication methods for uranium, thorium, and plutonium carbides were reviewed. Very incomplete data on thorium and plutonium carbides were located.*

*Only limited data on the physical and mechanical properties of uranium carbides were discovered. No information on high-temperature mechanical properties was found. Considerable information concerning the constitution of the carbides was obtained, however, and ternary diagrams were constructed. The incomplete data on the compatibility and corrosion behavior of the carbides that were found in the literature were supplemented by thermodynamic calculations for various possible reactions with coolants and claddings.*

*Available information on preparation of bulk carbides was reviewed and data on thermodynamics, preparation by chemical reactions, melting and casting, solid-phase fabrication, and storage and handling were assembled. Some information on the effects of irradiation of cast uranium monocarbide to burnups of up to 1.7 a/o of the uranium was collected and evaluated.*

*The results of the survey indicate that commercial production of bulk uranium carbide is feasible and that, on the basis of its radiation behavior, this material has excellent potential as a reactor fuel.*

## INTRODUCTION

As a result of promising irradiation results and favorable physical characteristics, uranium monocarbide has been revealed as a promising prospect for the fuel to be used in various types of reactors. At present, the Reactor Development Division of the U. S. Atomic Energy Commission is supporting several programs intended to further develop and evaluate bulk uranium carbides as fuels. Because of this current effort on carbides, it must be expected that any literature review will be quickly outdated. Nonetheless, a review and evaluation of the literature is needed as a basis for this research. In carrying out the review, no attempt was made to review research in progress, although the authors have drawn considerably upon Battelle research and experience for the details needed to give the report some depth.

For a summary of current research, the reader is referred to TID-7589, "Progress in Carbide Fuels", May, 1960, which contains summaries of the research being conducted at various laboratories.

While considerable information is compiled in this report for uranium carbides, very little information is available for thorium and plutonium carbides. The information that was found is reported with the uranium carbide data. No attempt was made to include information on fuel types other than bulk carbides, such as dispersions and cermets.

Considerable information is available on the constitution of the carbides, and, wherever possible, the corresponding ternary diagrams have been constructed. Very limited data are reported on the physical and mechanical properties of uranium carbides. Additional research is needed to establish and understand the effects of composition, impurities, and fabrication history upon the temperature dependence of thermal conductivity. High-temperature mechanical-property data are completely lacking. Incomplete data on the compatibility and corrosion behavior of carbides have been assembled. These data are supplemented by thermodynamic calculations for various possible reactions with coolants and claddings.

Information available on methods of preparation of uranium carbides is reviewed. In general only the results of laboratory-scale experiments are available. Thermodynamic data relating to the various methods of preparation have been assembled and are presented. Serious effort on methods for the commercial preparation of uranium carbide as powder and also in forms suitable for feed for arc-melting processes is needed.

Information is available upon several methods of fabricating bulk uranium carbide into pellets or cast slugs. With respect to powder methods of forming, additional effort is needed in a few of the more promising areas. Unfortunately, discernment of any promising areas depends, in turn, upon advancement of the technology of production of powders. Preparation of uranium carbides by casting techniques has received considerable study, and pilot-plant operations to establish production procedures and estimates of expected costs are in order. Commercial feed material is needed even for the latter process.

The effects of irradiation on uranium carbide are reviewed, and, although only a limited number of tests have been performed, almost exclusively on high-density as-cast slugs of uranium monocarbide, the results are promising. The tests represent burnups of up to 1.7 a/o uranium (10,000 MWD/T of uranium) at modest temperatures. Much additional testing is required to evaluate carbides for various specific applications.

# PROPERTIES OF NUCLEAR CARBIDES

W. M. Phillips

## Physical Properties

The melting points, crystal structures, specific heats, and electrical resistivities of uranium, thorium, and plutonium carbides, insofar as they are presently available, are summarized in Table 1(1-13) and are discussed briefly below. Thermal conductivities, thermal-expansion coefficients, and the mechanical properties are also summarized in this section.(14-18) Thermodynamic properties, however, appear in the section of this report on preparation and fabrication of nuclear carbides.

The melting-point data are, in general, mean values of several published values which are all within ±100 C of the values listed. The crystal-structure and lattice-parameter data for the uranium and thorium carbides were obtained by X-ray and neutron-diffraction techniques(5,9). Those for the plutonium carbides were determined by X-ray diffraction techniques only.

Analysis of the interatomic distances in uranium carbides reveals considerable information about the nature of the bonding.(9) The interatomic distances in uranium carbides are shown in Table 2. In uranium monocarbide, four of the valence electrons of uranium appear to be involved in covalent bonding with the uranium and carbon atoms. The remaining two valence electrons are available for metallic bonding, accounting for the high thermal conductivity and other metallic characteristics of uranium monocarbide. In $U_2C_3$, the bond between the uranium and carbon atoms is not quite as strong, and covalent bonds are found between adjacent carbon atoms, perhaps accounting for the higher hardness of $U_2C_3$. In $UC_2$, most of the uranium-carbon bonds are quite weak, and strong, covalent bonding between carbon atoms is indicated.(9)

The electrical resistivity of uranium carbide has been reported for both sintered specimens and cast specimens (Table 1). The unusually high value of 100 microhm-cm for the sintered material, which had a density of 10.82 g per cm$^3$, is probably related to the low density. The resistivities of about 100 cast specimens, ranging in composition from 4.8 to 5.0 w/o carbon, have been measured. The resistivities obtained ranged from 35 to 45 microhm-cm; the mean value being about 40 microhm-cm. Earlier work produced values of 33, 44,(13) and 99 microhm-cm(19). The latter high value may have been the result of deterioration or cracking of the sample from exposure to moisture during handling. Recent experience(18) has shown that impurity variations of less than 800 ppm of iron, nickel, silicon, and tungsten have no significant effect upon the resistivity of cast carbides. The impurities in typical as-cast material amount to about 200 ppm of which about 100 to 110 ppm is oxygen.

The available data for the thermal conductivities of uranium monocarbide and uranium dicarbide are shown in Table 3 and in Figure 1. These data seem to indicate that a carbon content in the range of 4.8 to 5.3 w/o does not have a significant effect upon thermal conductivity. The temperature dependence of thermal conductivity in this range of composition is not clear.

Thermal-expansion data for uranium monocarbide are shown in Figure 2. The most reliable data are believed to be those for the cast material.(14) Significantly

TABLE 1. PHYSICAL PROPERTIES OF URANIUM, THORIUM, AND PLUTONIUM CARBIDES(1-13)

| | UC | $U_2C_3$ | $UC_2$ | PuC | $Pu_2C_3$ | ThC | $ThC_2$ |
|---|---|---|---|---|---|---|---|
| Melting Point, C | 2400 | Decomposes at 1775 C | 2400 | 1850 | 1900 | 2625 | 2655 |
| Crystal Structure | Fcc, NaCl type | Bcc | Bct, $CaC_2$ type | Fcc, NaCl type | Bcc | Fcc, NaCl type | Monoclinic |
| Lattice Parameters, A | a = 4.9598 ± 0.0003 | a = 8.0885 ± 0.0005 | a = 3.509 ± 0.003,<br>c = 5.980 ± 0.005 | a = 4.97 | a = 8.129 | a = 5.34 | a = 6.53, b = 4.24,<br>c = 6.56; $\beta = 104°$ |
| Theoretical Density, g per $cm^3$ | 13.63 | 12.88 | 11.68 | 13.6 | 12.7 | -- | -- |
| Specific Heat, cal/(g)(C) | 0.048 ± 0.003 (125 C),<br>0.053 ± 0.003 (250 C) | -- | -- | -- | -- | -- | -- |
| Electrical Resistivity, microhm-cm | 100 ± 4 (sintered; density, 10.82 g per $cm^3$)<br>40 (as cast; density, 98 per cent) | -- | -- | -- | -- | -- | -- |

TABLE 2. INTERATOMIC DISTANCES IN URANIUM CARBIDES(9)

| Compound | Atom | Adjacent Atoms Number | Adjacent Atoms Type | Interatomic Distance, A |
|---|---|---|---|---|
| UC | Uranium | 12 | Uranium | 3.50 |
| | Uranium | 6 | Carbon | 2.48 |
| | Carbon | 12 | Carbon | 3.50 |
| $U_2C_3$(a) | Uranium | 3 | Uranium | 3.34 |
| | Uranium | 2 | Uranium | 3.48 |
| | Uranium | 6 | Uranium | 3.48 |
| | Uranium | 3 | Carbon | 2.50 |
| | Uranium | 3 | Carbon | 2.56 |
| | Uranium | 3 | Carbon | 2.82 |
| | Carbon | -- | Carbon | 1.295 |
| $UC_2$ | Uranium | 8 | Uranium | 3.90 |
| | Uranium | 4 | Uranium | 3.54 |
| | Uranium | 2 | Carbon | 2.325 |
| | Uranium | 8 | Carbon | 2.59 |
| | Carbon | -- | Carbon | 1.34 |

(a) For $X_U = 0.050$ and $X_C = 0.295$.

TABLE 3. THERMAL CONDUCTIVITY OF UC AND $UC_2$

| | Thermal Conductivity of Material Shown, cal/(cm)(sec)(C) | | | | | |
|---|---|---|---|---|---|---|
| Temperature, C | Arc-Cast U-5.2 w/o C [Reference (14)] | Arc-Cast U-4.9 w/o C [Reference (17)] | Arc-Cast U-5.3 w/o C [Reference (17)] | Sintered U-4.8 w/o C [Reference (11)] | Sintered U-4.8 w/o C [Reference (1)] | Sintered(a) $UC_2$ [Reference (15)] |
| 20 | -- | -- | -- | -- | 0.078 | -- |
| 45 | -- | -- | -- | -- | -- | 0.079 |
| 60 | -- | -- | -- | 0.080 | -- | -- |
| 100 | 0.060 | -- | -- | -- | -- | -- |
| 115 | -- | -- | -- | 0.074 | -- | -- |
| 145 | -- | -- | -- | 0.061 | -- | -- |
| 200 | 0.056 | 0.056 | 0.056 | -- | -- | -- |
| 265 | -- | -- | -- | 0.050 | -- | -- |
| 300 | 0.054 | 0.053 | 0.055 | -- | -- | -- |
| 400 | 0.053 | 0.051 | 0.054 | -- | -- | -- |
| 500 | 0.053 | 0.050 | 0.054 | -- | -- | -- |
| 600 | 0.057 | 0.049 | 0.054 | -- | -- | -- |
| 700 | 0.060 | 0.049 | 0.054 | -- | -- | -- |
| 800 | -- | 0.049 | 0.054 | -- | -- | -- |
| 900 | -- | 0.048 | 0.054 | -- | -- | -- |
| 1000 | -- | 0.048 | 0.055 | -- | -- | -- |
| 1020 | -- | 0.048 | -- | -- | -- | -- |

(a) Sintered to a density of 10 g per $cm^3$.

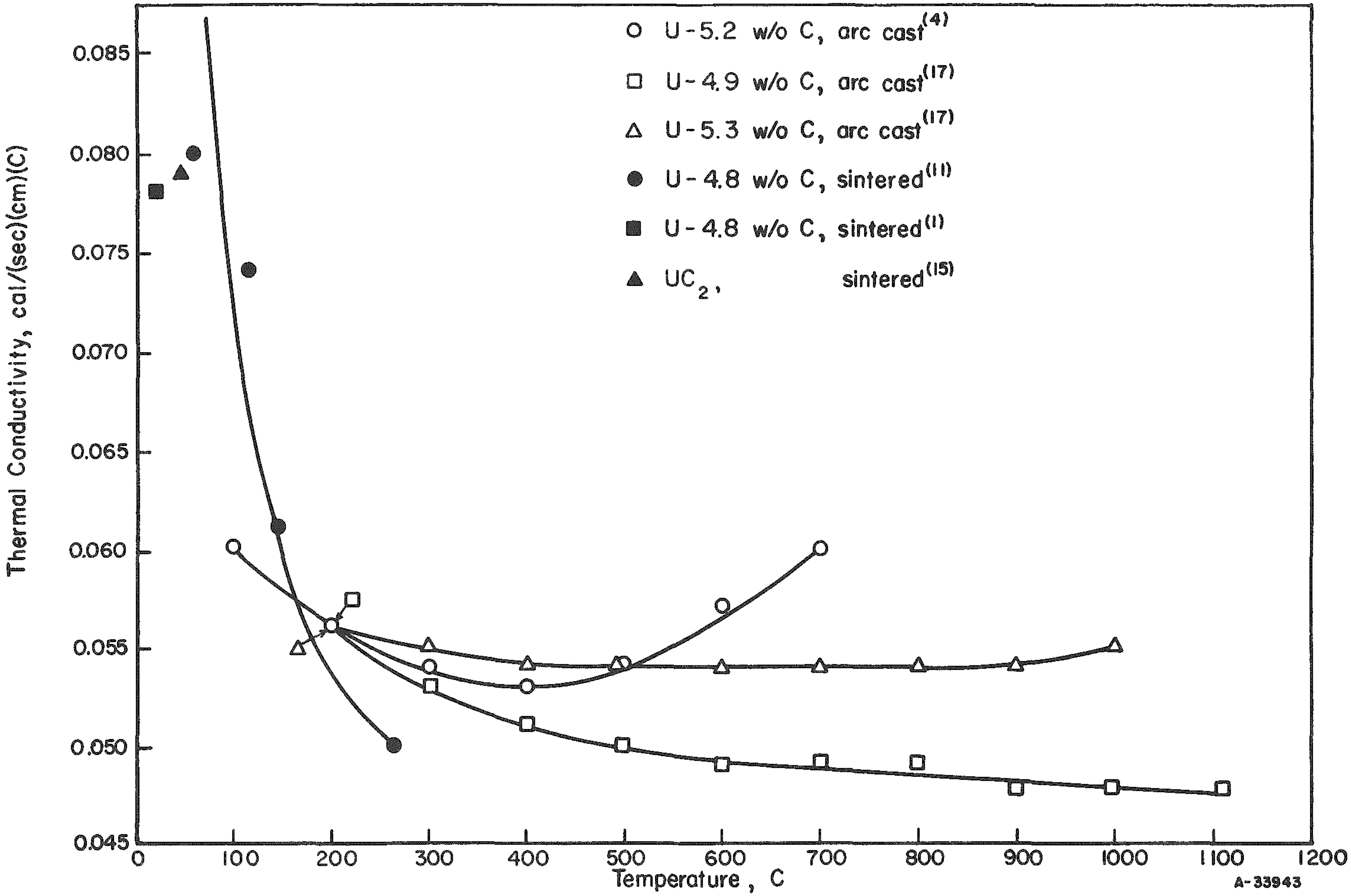

FIGURE 1. THERMAL CONDUCTIVITY OF UC AND $UC_2$

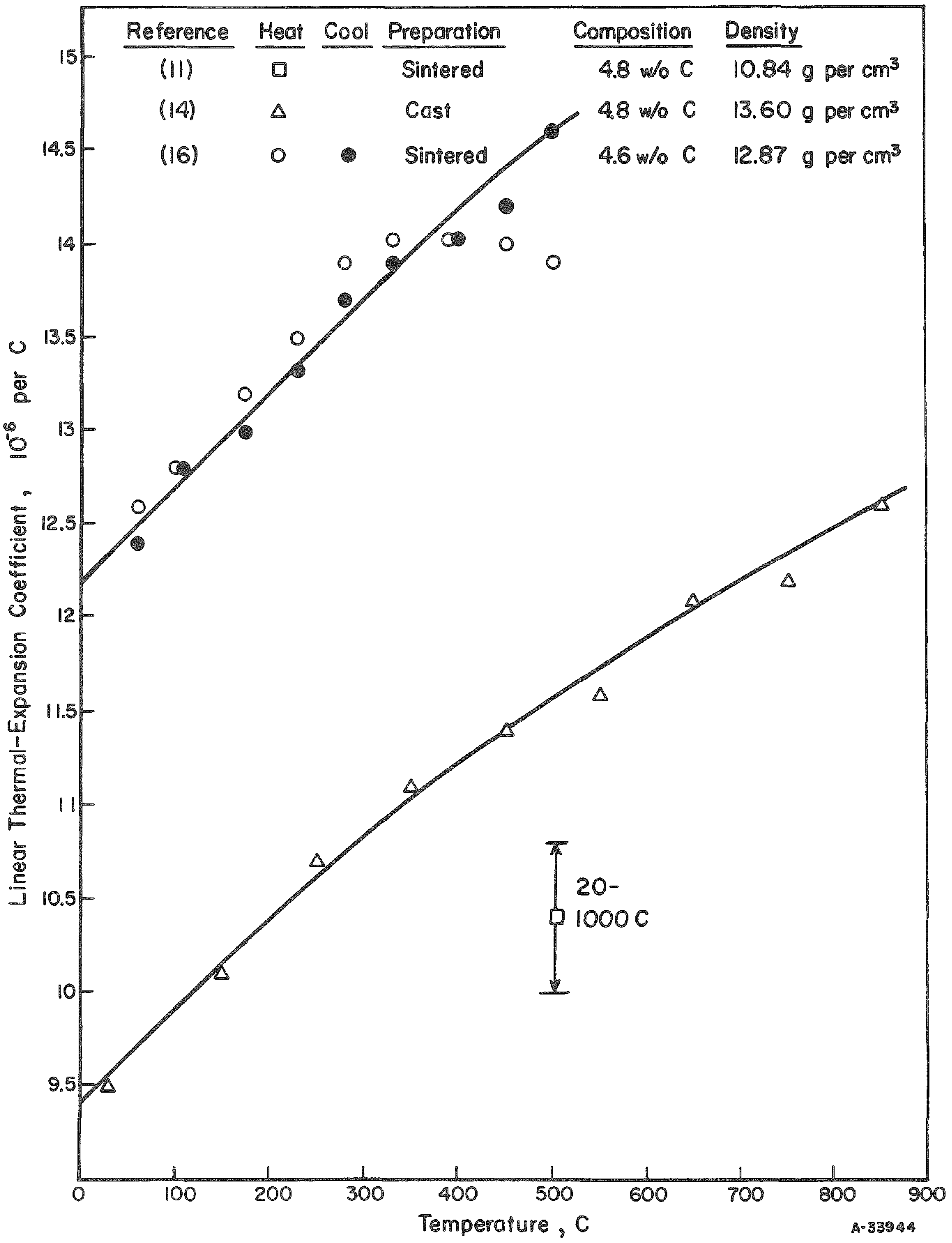

FIGURE 2. THERMAL-EXPANSION COEFFICIENTS OF URANIUM MONOCARBIDE

higher and lower values have been obtained on sintered products. The higher values are believed to be the result of free uranium in the sintered product, but the reason for the lower mean value of $10.4 \times 10^{-6}$ per C for 20 to 1000 C is not evident.

## Mechanical Properties

In general, data on mechanical properties, such as hardness, rupture strength, ductility, etc., are available only on carbides near UC in composition. Because of its covalent bonding and high melting point, uranium monocarbide should exhibit high strength at elevated temperatures. However, it is known to be ductile at 1800 C(20) and can be expected to show slight ductility at about 1300 C (approximately 0.6 times its melting point on the absolute temperature scale) while retaining high strength. The room-temperature properties of uranium monocarbide are those one expects of a brittle material. The hardness of uranium carbide samples depends upon fabrication, heat treatment, and other variables, but it generally ranges from 560 to 800 VHN as shown in Table 4. Available data on the strength and modulus of elasticity of uranium monocarbide are also given in Table 4.

TABLE 4. SOME MECHANICAL PROPERTIES OF URANIUM-CARBON ALLOYS

| Material | Vickers Hardness, kg per mm$^2$ | Rupture Strength, psi | | Elastic Modulus, $10^6$ psi | Reference |
|---|---|---|---|---|---|
| | | Transverse | Compressive | | |
| Cast U-4.6 w/o C | 900 | 9,600 | -- | -- | (18) |
| Cast U-5.2 w/o C | | | | | |
| As cast | 600 | -- | 54,500 | 31.5 | (14) |
| Annealed 1 hr at 1000 C | 560 | -- | -- | -- | (14) |
| Annealed 1 hr at 1500 C | 760 | -- | -- | -- | (14) |
| Cast U-7 w/o C | 850 | 13,000 | -- | -- | (18) |
| Sintered UC | 750-800 | 40,000-55,000 | -- | -- | (2) |
| Sintered UC | | | | | |
| Density, 10.84 g per cm$^3$ | 700 ± 150 | -- | 42,500 ± 5,500 | -- | (11) |
| Density, 10.2 g per cm$^3$ | 550 ± 150 | -- | -- | -- | (11) |

In general, $U_2C_3$ and $UC_2$ are also quite brittle, since both have covalent uranium-carbon and carbon-carbon bonding. Uranium sesquicarbide appears to be harder than UC, having a hardness of about 1100 Knoop.(18) Uranium dicarbide is believed to have a hardness of about 500 Knoop.(18) Neither $U_2C_3$ nor $UC_2$ is expected to compare with UC in mechanical strength at high temperatures, since $U_2C_3$ decomposes peritectoidally at about 1775 C, and tetragonal $UC_2$ is stable only to about 1800 C.

Additions of 1 w/o of the soluble carbides (VC, NbC, TiC, ZrC, and TaC) have been made to UC by melting and casting.(18) The resultant hardnesses were about 700 Knoop as compared with 600 Knoop for unalloyed, cast UC. Carbide castings containing additions of 10 w/o of the same carbides possessed hardnesses of 1200 to 1400 Knoop and demonstrated up to 50 per cent increases in the modulus of rupture.

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# URANIUM, THORIUM, AND PLUTONIUM CARBIDE SYSTEMS

W. Chubb

## INTRODUCTION

### Diagrams

Constitutional diagrams are presented only for those systems where diagrams are reported in the literature or where there are sufficient data to justify construction of an isothermal ternary section. Because many of these sections are constructed from fragmentary data, they must be considered as tentative. The sections are generally constructed at a temperature near 1000 C.

### Symbols

All binary diagrams are presented with weight per cent (w/o) and atomic per cent (a/o) scales. All ternary diagrams are presented with atomic per cent (a/o) scales. All quaternary diagrams and pseudoternary diagrams are presented with mole per cent scales.

Greek letters are used only to describe those phases for which usage has established a clear precedent, as for example, "gamma" iron and "gamma" uranium. Intermetallics are shown in terms of their chemical stoichiometry or in terms of their crystal stoichiometry, if the latter is known.

No data are presented on the crystallography of phases in the binary metallic systems.

### References

While pertinent references are cited in the discussions of the individual systems, the following publications were found extremely useful in compiling much of the information presented throughout this section:

#### Uranium and Thorium

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Carbides

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Plutonium

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## THE URANIUM-CARBON BINARY SYSTEM

### Constitution

The melting point of UC in contact with tungsten was determined to be 2280 C by Newkirk and Bates(1). The melting point of UC was determined by Brownlee(2) by focusing an optical pyrometer on the liquid-solid interface of an arc melt and found to be 2520 C. Chiotti(3) found the melting point of UC to be 2590 C. Mallett, Gerds, and Nelson(4) found the melting point of UC to be 2390 C and the melting point of $UC_2$ to be 2480 C. Chubb and Phillips(5) have found metallographic evidence of a eutectic between 6.2 and 6.6 w/o carbon in cast samples of uranium-carbon alloys. Chubb and Phillips(5) also indicate a miscibility gap between UC and $UC_2$ above 2200 C in agreement with the suggestion of Hansen and Anderko(6). Chubb and Phillips(5) found evidence that the homogeneity range of cubic $UC_2$ at about 1800 C was from 7 to 9 w/o carbon; a eutectoid at 7 w/o carbon was indicated. This eutectoid results in the formation of UC and tetragonal $UC_2$. The allotropy of $UC_2$ was discovered by Wilson(7) using a high-temperature X-ray camera.

Mallett, et al.,(4,8) indicates that uranium sesquicarbide ($U_2C_3$) is stable below 1775 C, forming by a sluggish or stress-sensitive nucleation process. The fact that the eutectoid at 7 w/o carbon and 1800 C produces UC and $UC_2$ rather than $U_2C_3$ and the fact that $UC_2$ precipitates from UC containing 4.9 to 5.5 w/o carbon on cooling from high temperatures suggest that the temperature for peritectoid formation of $U_2C_3$ should be well below the eutectoid at 1800 C and probably below 1775 C. Chubb and Phillips(5) have produced equilibrium amounts of $U_2C_3$ in cast samples containing 5.7 to 7.8 w/o carbon by reheating to 1550 C for 1 hr.

Blumenthal(9) has obtained data indicating a eutectic at 0.05 w/o carbon and 1117 C between UC and gamma uranium containing 0.015 w/o carbon. The solubility of carbon in liquid uranium is 0.1 w/o at 1300 C and 0.15 w/o at 1400 C.

The uranium-carbon constitutional diagram is presented in Figure 3.

## Crystallography(10)

UC: fcc (NaCl, B1 type), a = 4.9598 A, four molecules per unit cell; density = 13.6 g per $cm^3$.

$U_2C_3$: bcc (space group $I\bar{4}3d$), a = 8.0885 A, eight molecules per unit cell; density = 12.5 g per $cm^3$.

$UC_2$ (below 1800 C): tetragonal ($CaC_2$, C11a type), a = 3.509 A, c = 5.980 A, two molecules per unit cell; density = 11.7 g per $cm^3$.

$UC_2$ (above 1800 C): fcc ($CaF_2$, C1 type), a = 5.47 A (at 1820 C), four molecules per unit cell.

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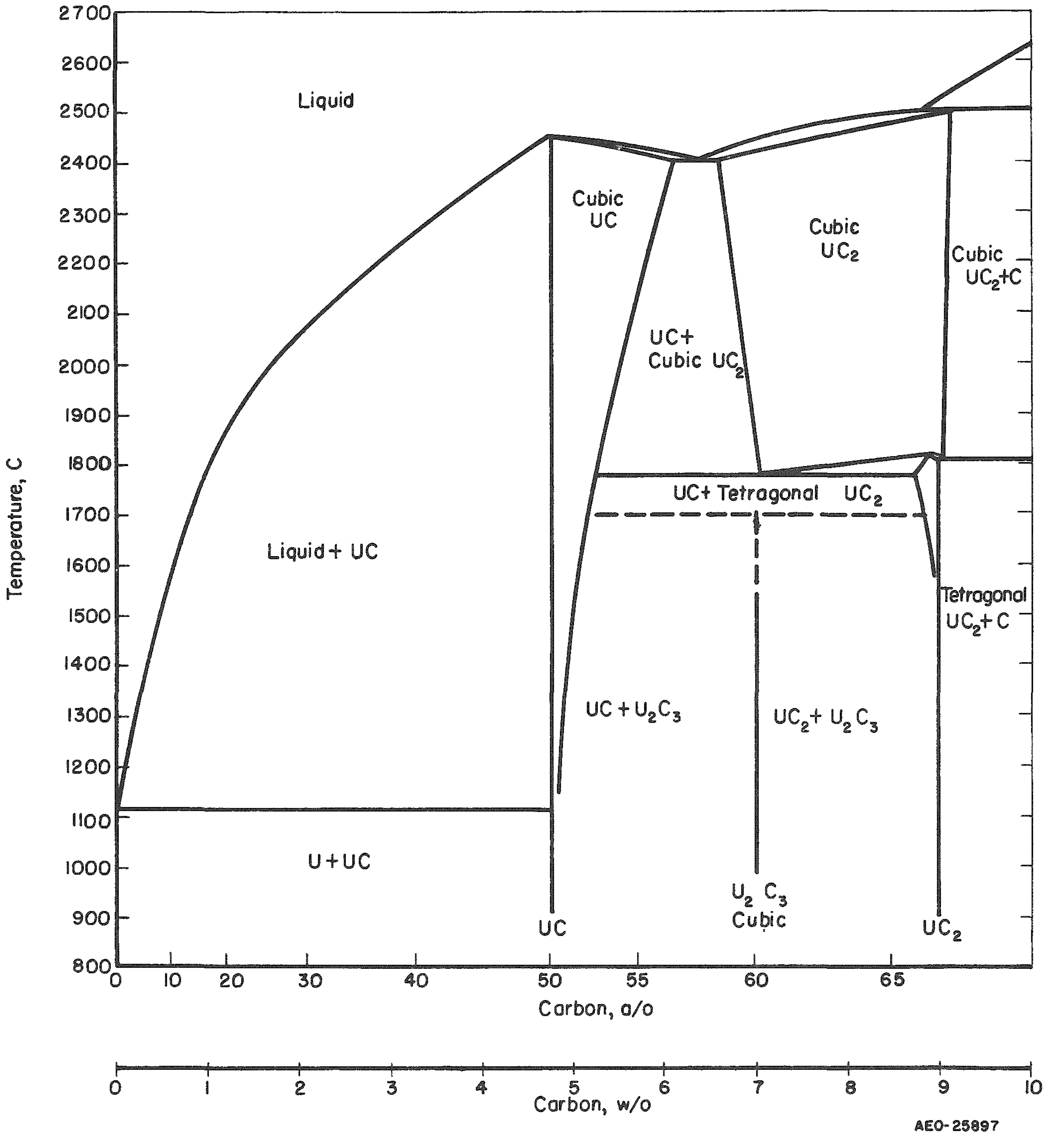

FIGURE 3. URANIUM-CARBON CONSTITUTIONAL DIAGRAM

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## URANIUM-CARBON TERNARY SYSTEMS

### Aluminum

#### Constitution

The ternary section shown in Figure 4 is based on statements by Thurber and Beaver(1) to the effect that UC reacts with aluminum to produce $UAl_3$ and $UAl_4$; and that some $UAl_3$ or $UAl_4$ was detected by X-ray in samples of uranium-carbon alloys containing more than 7 w/o carbon after being in contact with aluminum for 24 hr at 620 C. They found that $UC_2$ showed negligible reaction with aluminum, suggesting a pseudobinary between $UC_2$ and aluminum.

The melting point of $Al_4C_3$ is above 2800 C.

#### Crystallography

$Al_4C_3$: rhombohedral (D7 type), a = 8.55 A, $\alpha = 22°18'$, one molecule per unit cell; density = 2.99 g per $cm^3$.

#### Reference

(1) Thurber, W. C., and Beaver, R. J., "Dispersions of Uranium Carbides in Aluminum Plate-Type Research Reactor Fuel Elements", ORNL-2618 (November, 1959).

## Beryllium

### Constitution

Burdick, Parker, Roth, and McGandy(1) indicate that there is no solubility of UC or $UC_2$ in $Be_2C$, but that UC dissolves 40 and 20 mole per cent $Be_2C$ at 1900 and 1700 C, respectively. The solubility of $Be_2C$ in UC decreases to 6 mole per cent at temperatures below 1700 C. No ternary phases were found between UC, $UC_2$, and $Be_2C$. The solubility of $Be_2C$ in $UC_2$ is negligible.

Ivanov and Badayeva(2) report that pseudobinary sections exist between UC and $UBe_{13}$, between $UBe_{13}$ and $Be_2C$, and between UC and $Be_2C$. Eutectics are found in the UC-$Be_2C$ and in the $UBe_{13}$-UC sections. No ternary compounds are formed.

The ternary section shown in Figure 5 is based on information provided by both the above sources.

The $Be_2C$ phase decomposes at about 2200 C.

### Crystallography

$Be_2C$: fcc ($CaF_2$, C1 type), a = 4.34 A, four molecules per unit cell; density = 2.44 g per $cm^3$.

### References

(1) Burdick, M. D., Parker, H. S., Roth, R. S., and McGandy, E. L., "An X-Ray Study of the System: UC, $UC_2$, $Be_2C$", J. Research Natl. Bur. Standards, 54, 217-29 (April, 1955).

(2) Ivanov, O. S., and Badayeva, T. A., "Phase Diagrams of Certain Uranium and Thorium Systems", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Vol 6, A/Conf. 15/P/2043, p 139.

## Chromium

### Constitution

Nowotny, Kieffer, and Benesovsky(1) report that UC and $Cr_3C_2$ are not soluble in one another. Ivanov and Badayeva(3) report no solubility between UC and chromium. A ternary section is presented in Figure 6.

$Cr_3C_2$ melts at about 1900 C.

$Cr_7C_3$ melts at about 1700 C.

$Cr_{23}C_6$ decomposes peritectically at about 1550 C.

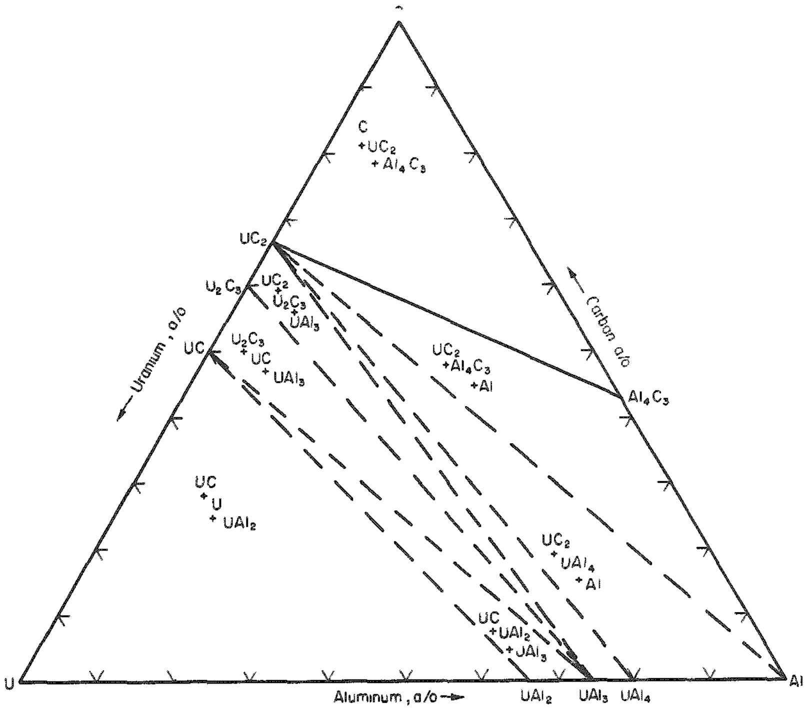

FIGURE 4. URANIUM-CARBON-ALUMINUM TERNARY SECTION AT 600 C

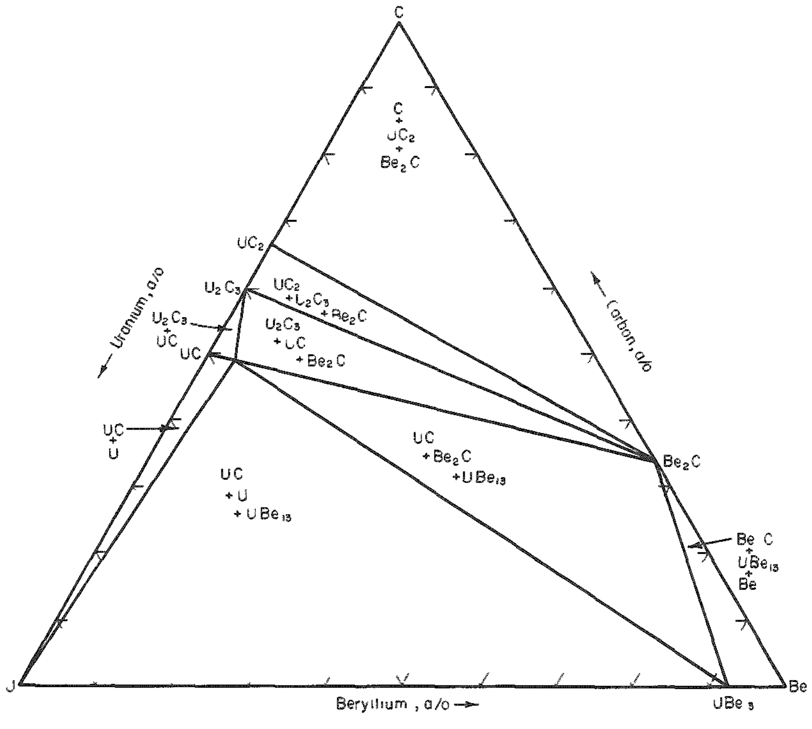

FIGURE 5. URANIUM-CARBON-BERYLLIUM TERNARY SECTION AT 1000 C

### Crystallography

$Cr_3C_2$: orthorhombic ($D5_{10}$ type), a = 2.82 A, b = 5.52 A, c = 11.46 A, four molecules per unit cell; density = 6.7 g per $cm^3$.

$Cr_7C_3$: hexagonal, a = 14.00 A, c = 4.52 A, eight molecules per unit cell; density = 6.9 g per $cm^3$.

$Cr_{23}C_6$: fcc ($D8_4$ type), a = 10.64 A, four molecules per unit cell; density = 7.0 g per $cm^3$.

### References

(1) Nowotny, H., Kieffer, R., and Benesovsky, F., "Preparation of UC and Its Relation to the Carbides of Refractory Transition Metals", Rev. met., 55, 453-58 (May, 1958); see also Reference (2).

(2) Nowotny, H., Kieffer, R., Benesovsky, F., and Laube, E., "Contribution to the Knowledge of the Partial Systems: UC with TiC, ZrC, VC, NbC, TaC, $Cr_3C_2$, $Mo_2C$, and WC", Monatsh. Chem., 88, 336-43 (June, 1957).

(3) Ivanov, O. S., and Badayeva, T. A., "Phase Diagrams of Certain Uranium and Thorium Systems", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Vol 6, A/Conf. 15/P/2043, p 139.

## Cobalt

### Constitution

Bowman(1) reports that cobalt may be added to UC to aid sintering at 2000 to 2200 C and removed later by vacuum treatment at these temperatures. This would indicate a pseudobinary of the UC-chromium type between UC and cobalt at least up to 2200 C. A uranium-carbon-cobalt ternary section is shown in Figure 7.

### Crystallography

The compounds $Co_2C$ and $Co_3C$, if they exist, apparently decompose at temperatures above about 300 C.

### Reference

(1) Bowman, M. G., "Bonding Uranium Carbide to Tantalum", AECU-4303 (May, 1959).

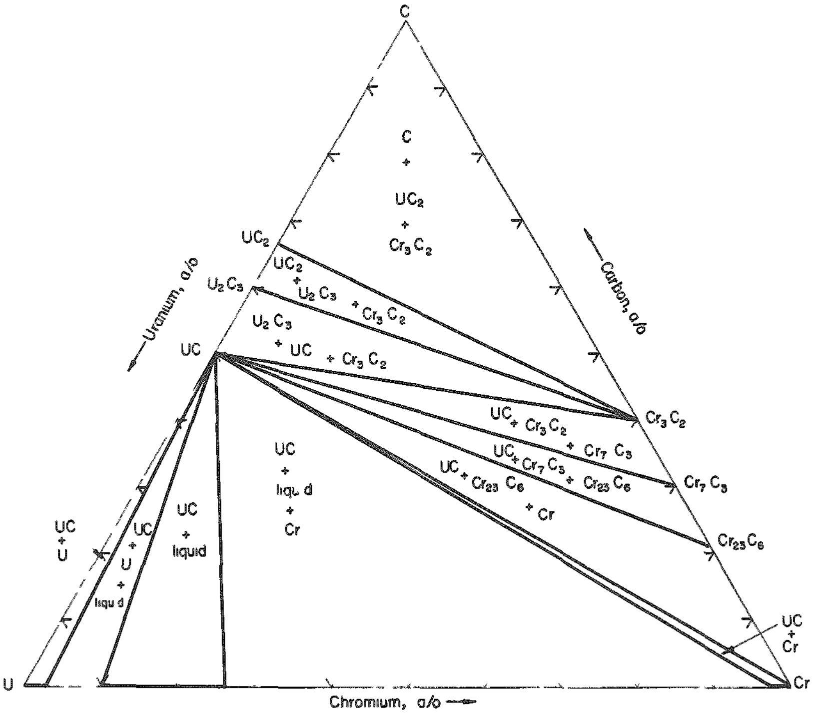

FIGURE 6. URANIUM-CARBON-CHROMIUM TERNARY SECTION AT 1000 C

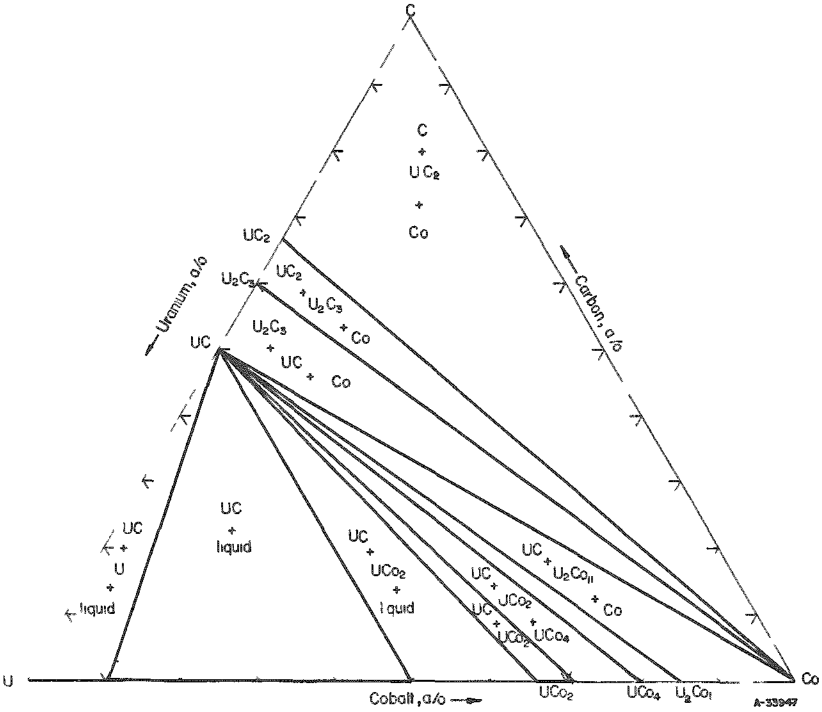

FIGURE 7. URANIUM-CARBON-COBALT TERNARY SECTION AT 1000 C

## Copper

### Constitution

Bowman(1) reports that copper may be added to UC to aid sintering at 2000 to 2200 C and removed later by vacuum treatment at these temperatures. This would indicate a pseudobinary of the UC-chromium type between UC and copper at least up to 2200 C. A ternary section is shown in Figure 8.

### Crystallography

The carbides of copper are reported by Meerson and Umanskii(2) to be unstable to the point of explosiveness.

### References

(1) Bowman, M. G., "Bonding Uranium Carbide to Tantalum", AECU-4303 (May, 1959).

(2) Meerson, G. A., and Umanskii, I. S., "On the Hardness of Refractory Carbides", Izvest. Sektora Fiz. Khim. Anal., 22, 104 (1953).

## Hafnium

### Constitution

The nature of the uranium-hafnium binary system has been reported recently by Peterson and Beerntsen(1). Since the unit-cell size of HfC is only 7 per cent smaller than that of UC, complete solubility between UC and HfC is to be expected. While HfC exists over a range of compositions, the composition limits have not been reported.

Although it is not known, the ternary section of the uranium-carbon-hafnium system is expected to resemble the uranium-carbon-thorium system section at 1000 C.

HfC melts at about 3900 C.

### Crystallography

HfC: fcc (NaCl, B1 type), a = 4.64 A, four molecules per unit cell; density = 12.2 g per cm$^3$.

### Reference

(1) Peterson, D. T., and Beerntsen, D. J., "The Uranium-Hafnium Equilibrium System", Trans. ASM, 52, 763-80 (1960).

## Iron

### Constitution

Bowman(1) reports that iron may be added to UC to aid sintering at 2000 to 2200 C and then removed by vacuum treatment at these temperatures. This would indicate a pseudobinary of the UC-chromium type between UC and iron up to about 2200 C.

$Fe_3C$ is metastable and decomposes rapidly at temperatures above 1200 C.

The uranium-carbon-iron diagram at 1000 C is shown in Figure 9.

### Crystallography

$Fe_3C$: orthorhombic, a = 4.52 A, b = 5.08 A, c = 6.74 A; density = 7.67 g per $cm^3$.

$Fe_2C$: hexagonal or orthorhombic; density = 7.2 g per $cm^3$.

### Reference

(1) Bowman, M. G., "Bonding Uranium Carbide to Tantalum", AECU-4303 (May, 1959).

## Molybdenum

### Constitution

The ternary section shown in Figure 10 is based on statements by Phillips(1) and Nowotny, Kieffer, and Benesovsky(2) to the effect that UC and $Mo_2C$ do not dissolve in one another, and by Bowman(3) to the effect that UC reacts with molybdenum to form $Mo_2C$.

The melting point of MoC is about 2650 C. It decomposes or transforms below about 1900 C.

$Mo_2C$ decomposes peritectically at about 2400 C.

### Crystallography

MoC: hexagonal (WC type), one molecule per unit cell, a = 2.901 A, c = 2.768 A; density = 8.5 g per $cm^3$.

$Mo_2C$: hcp ($W_2C$ type), one molecule per unit cell, a = 2.994 A, c = 4.722 A; density = 8.9 g per $cm^3$.

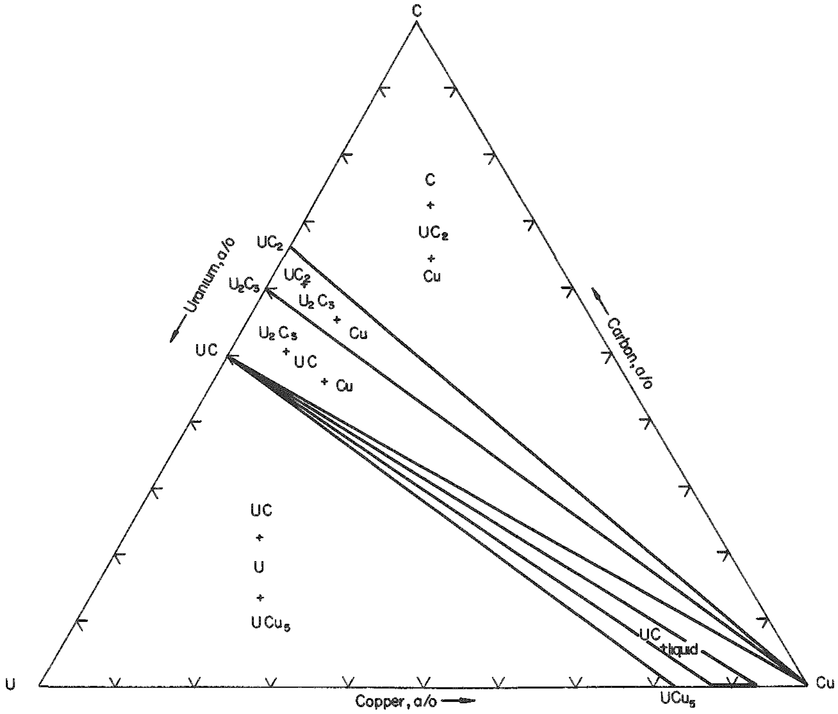

FIGURE 8. URANIUM-CARBON-COPPER TERNARY SECTION AT 1000 C

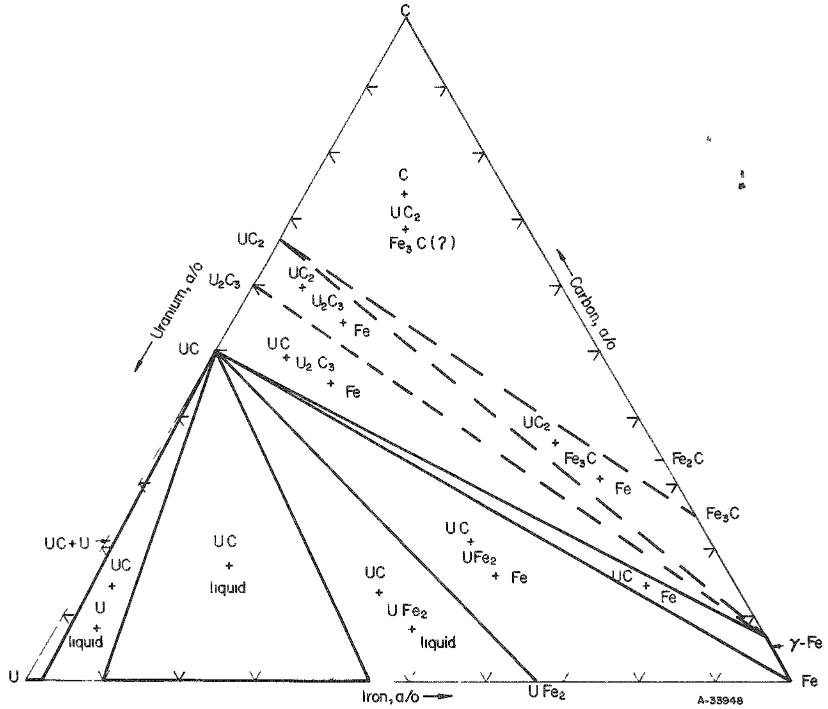

FIGURE 9. URANIUM-CARBON-IRON TERNARY SECTION AT 1000 C

### References

(1) Phillips, W. M., BMI, Private Communication (November, 1959).

(2) Nowotny, H., Kieffer, R., and Benesovsky, F., "Preparation of UC and Its Relation to the Carbides of Refractory Transition Metals", Rev. met., 55, 453-58 (May, 1958); see also Reference (4).

(3) Bowman, M. G., LASL, Private Communication (August, 1959).

(4) Nowotny, H., Kieffer, R., Benesovsky, F., and Laube, E., "Contribution to the Knowledge of the Partial Systems: UC with TiC, ZrC, VC, NbC, TaC, $Cr_3C_2$, $Mo_2C$, and WC", Monatsh. Chem., 88, 336-43 (June, 1957).

## Nickel

### Constitution

Bowman(1) reports that nickel may be added to UC to aid sintering at 2000 to 2200 C and removed later by vacuum treatment at these temperatures. This would indicate a pseudobinary of the UC-chromium type between UC and nickel up to at least 2200 C.

Boettcher and Schneider(2) report that nickel reacts with UC at 1000 C to form $U_6Ni$. Since $U_6Ni$ normally decomposes to liquid above 790 C, Boettcher and Schneider probably had a liquid layer in their sample at 1000 C.

$Ni_3C$ probably is stable only in a narrow temperature range from 2000 to 2500 C.

The uranium-carbon-nickel diagram at 1000 C is presented in Figure 11.

### Crystallography

$Ni_3C$: orthorhombic ($Fe_3C$ type); density = 7.96 g per $cm^3$.

$Ni_6C$ has been reported but may exist only as a ternary compound of the $Fe_3W_3C$ type.

### References

(1) Bowman, M. G., "Bonding Uranium Carbide to Tantalum", AECU-4303 (May, 1959).

(2) Boettcher, A., and Schneider, G., "Some Properties of Uranium Monocarbide", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Vol 6, A/Conf. 15/P/964, pp 561-63.

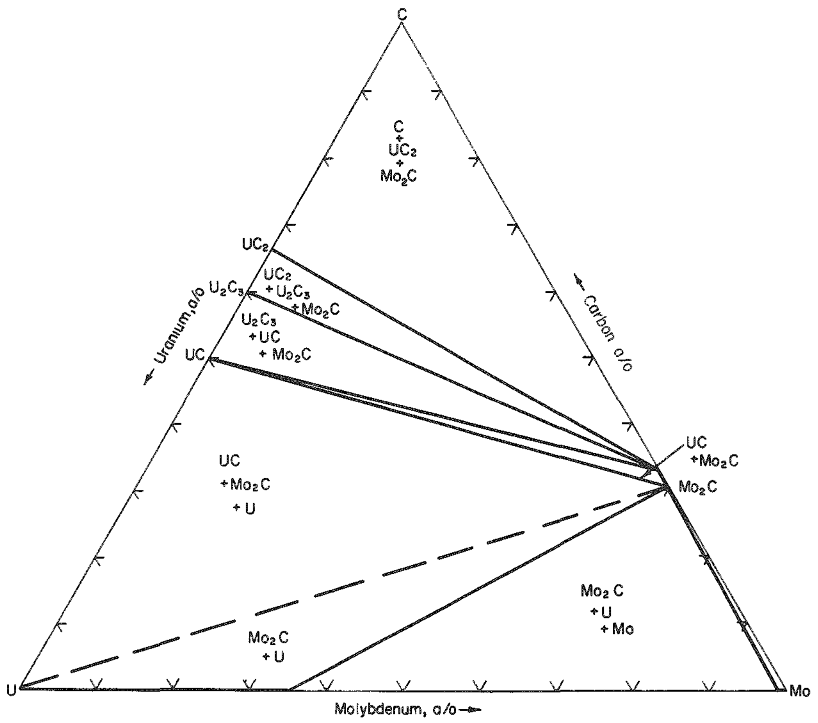

FIGURE 10. URANIUM-CARBON-MOLYBDENUM TERNARY SECTION AT 1000 C

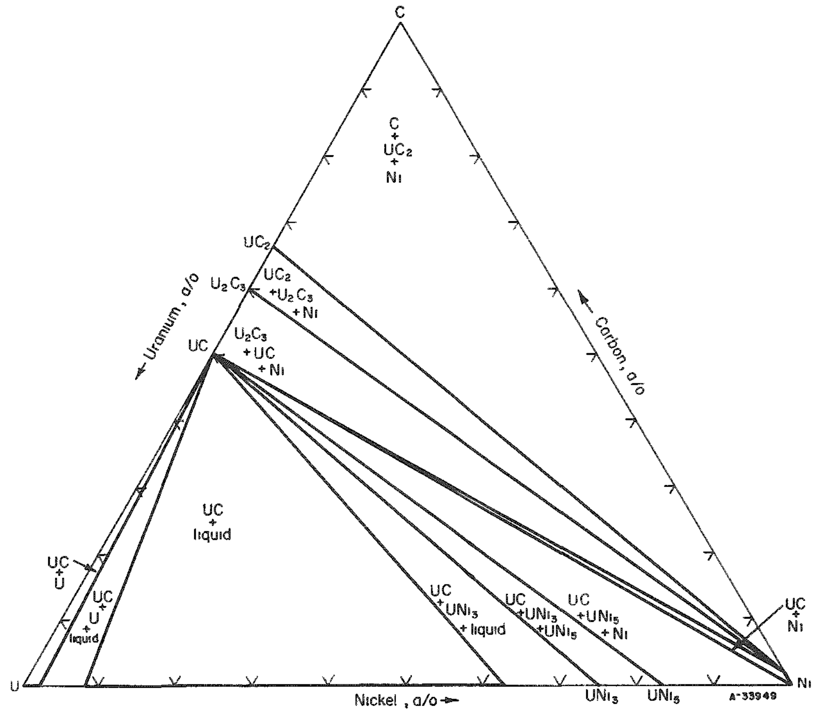

FIGURE 11. URANIUM-CARBON-NICKEL TERNARY SECTION AT 1000 C

## Niobium

### Constitution

The uranium-carbon-niobium diagram at 1000 C is shown in Figure 12. The existence of complete solubility between NbC and UC has been established.(1,2,3) Brownlee(1) reports that the liquidus of the pseudobinary system, UC-NbC, is a smooth curve between the terminal compositions, and that the melting point of NbC is 3485 C. Appreciable solubility of uranium in $Nb_2C$, analogous to the solubility of uranium in $Ta_2C$ is to be expected.

$Nb_2C$ decomposes peritectically at about 3260 C.(5) The melting point of NbC is about 3500 C.

### Crystallography

$Nb_2C$: hcp, a = 3.117 A, c = 4.951 A, one molecule per unit cell; density = 7.9 g per $cm^3$.

NbC: fcc (NaCl, B1 type), a = 4.459 A, four molecules per unit cell; density = 7.82 g per $cm^3$.

### References

(1) Brownlee, L. D., "The Pseudo-Binary Systems of UC with ZrC, TaC, and NbC", J. Inst. Metals, 87, 58-61 (October, 1958).

(2) Nowotny, H., Kieffer, R., and Benesovsky, F., "Preparation of UC and its Relation to the Carbides of Refractory Transition Metals", Rev. met., 55, 453-58 (May, 1958); see also Reference (4).

(3) Roof, R. B., and Lombardo, J. J., "A Pseudo-Binary in the U-Nb-C System", Trans. AIME, 212, 50 (February, 1958).

(4) Nowotny, H., Kieffer, R., Benesovsky, F., and Laube, E., "Contribution to the Knowledge of the Partial Systems: UC with TiC, ZrC, VC, NbC, TaC, $Cr_3C_2$, $Mo_2C$, and WC", Monatsh. Chem., 88, 336-43 (June, 1957).

(5) Pochon, M. L., McKinsey, C. R., Perkins, R. A., and Foreng, W. D., "Solubility of Carbon and Structure of Carbide Phases in Ta and Nb", AIME Reactive Metals Conference, Buffalo, May 1958, Reactive Metals, Interscience Publishers, New York (1960).

## Nitrogen

### Constitution

The existence of complete solubility between UN and UC has been established.(1,2,3) The existence of extensive solutions between $U_2C_3$ and $U_2N_3$ and between $UC_2$ and $UN_2$ is considered likely. The pressure of nitrogen over UN reaches 1 atm at a temperature between 2300 C and its melting point, 2630 C. It has been found that $U_2N_3$ decomposes peritectoidally at 1300 to 1550 C. The $UN_2$ compound can be prepared only at high pressures. A ternary section is shown in Figure 13.

### Crystallography

UN: fcc (NaCl, B1 type), a = 4.880 A, four molecules per unit cell; density = 14.3 g per $cm^3$

$U_2N_3$: bcc, a = 10.678 A; density = 11.24 g per $cm^3$

$UN_2$: fcc ($CaF_2$, C1 type), a = 5.31 A; density = 11.73 g per $cm^3$.

### References

(1) Rundle, R. E., Baenziger, N. C., Wilson, A. S., and McDonald, R. A., "The Structures of the Carbides, Nitrides, and Oxides of Uranium", J. Am. Chem. Soc., 70, 99-105 (1948).

(2) Austin, A. E., and Gerds, A. F., "The Uranium-Nitrogen-Carbon System", BMI-1272 (June, 1958).

(3) Williams, J., and Sambell, R. A. J., "The Uranium Monocarbide-Uranium Mononitride System", J. Less Common Metals, 1, 217-26 (June, 1959).

## Oxygen

Uranium monocarbide reacts with uranium dioxide to produce uranium metal and carbon monoxide in a vacuum at detectable rates at temperatures above 1300 C. At pressures near atmospheric, uranium monocarbide and uranium dioxide are stable in contact with one another to about 1800 C. Molten uranium monocarbide reacts with uranium dioxide at pressures near atmospheric, rejecting the oxygen as carbon dioxide so that generally less than 200 ppm of oxygen is found in the solidified ingot.

The phase once identified as a solid solution of UC and UO(1) is believed on the basis of recent observations(2) to have been a solid solution of UC and UN.

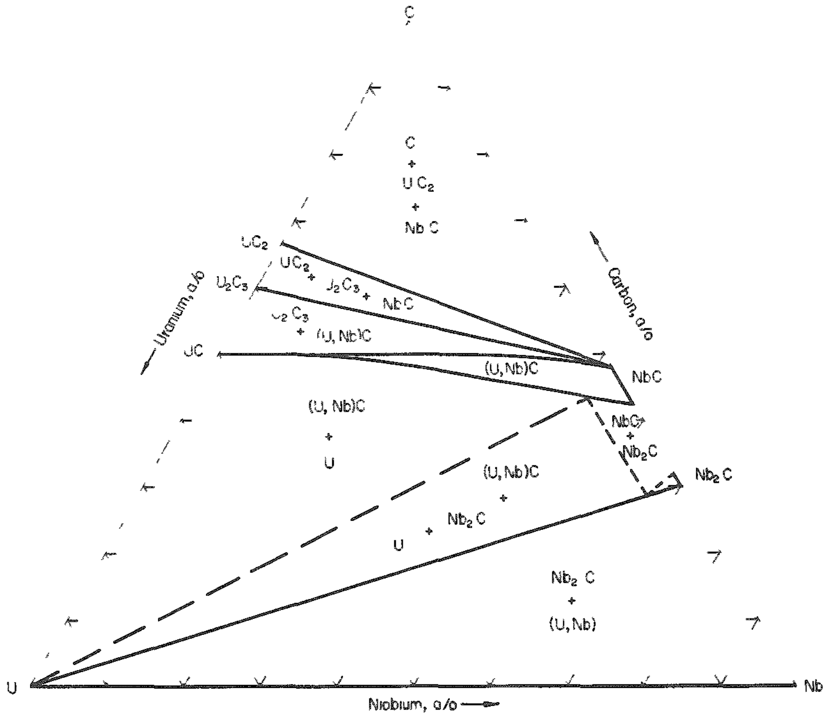

FIGURE 12. URANIUM-CARBON-NIOBIUM TERNARY SECTION AT 1000 C

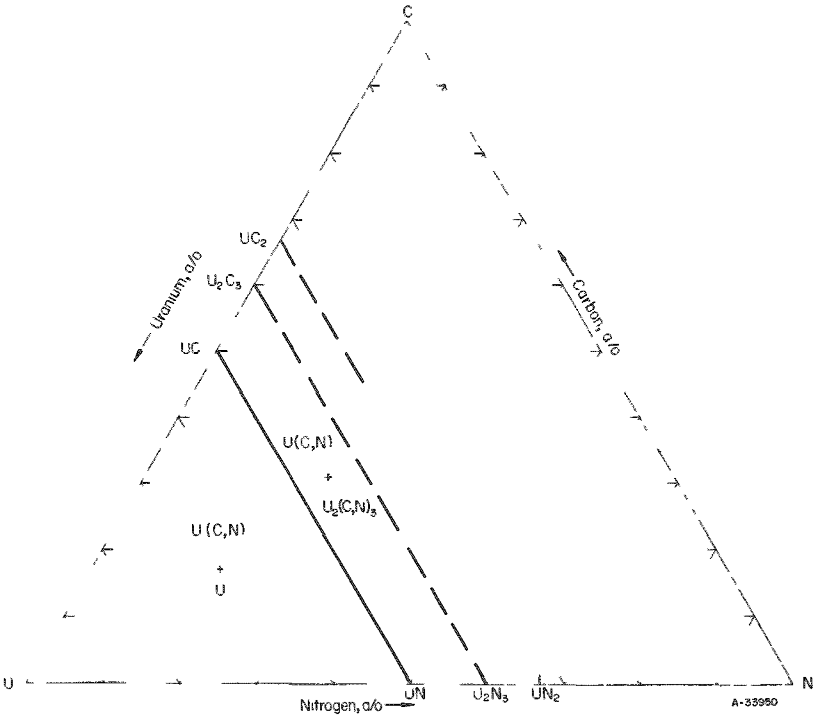

FIGURE 13. URANIUM-CARBON-NITROGEN TERNARY SECTION AT 1000 C

### References

(1) Vaughan, D. A., Melton, C. W., and Gerds, A. F., "Experiments on the Preparation of $UO_{2-x}$ and UO", BMI-1175 (March 6, 1957).

(2) Kehl, G. L., Mendel, E., F. [sic], E. J., Mueller, M. H., "Metallographic Identification of Inclusions in Uranium", Trans. ASM, 51, 717-35 (1959).

## Plutonium

### Constitution

The existence of complete solubility between PuC and UC has been suggested(1); and extensive solid solubility between $Pu_2C_3$ and $U_2C_3$ is to be expected.

PuC decomposes peritectically between 1200 and 1850 C.

$Pu_2C_3$ melts at about 1900 C.

A higher carbide, near 67 a/o carbon, melts at about 2200 C.

The uranium-carbon-plutonium diagram at 1000 C appears in Figure 14.

### Crystallography

PuC: fcc (NaCl, B1 type), a = 4.97 A, four molecules per unit cell; density = 13.6 g per $cm^3$.

$Pu_2C_3$: bcc (space group $I\bar{4}3d$), a = 8.13 A, eight molecules per unit cell; density = 12.7 g per $cm^3$.

### Reference

(1) Nowotny, H., Kieffer, R., and Benesovsky, F., "Preparation of UC and its Relation to the Carbides of Refractory Transition Metals", Rev. met., 55, 453-58 (May, 1958).

## Rhenium

### Constitution

Bowman(1) has reported that UC and rhenium do not dissolve in one another but produce a simple eutectic at 1850 C. This would imply a pseudobinary between UC and rhenium, but no diagram has been constructed.

### Crystallography

Carbides of rhenium, if they exist, are relatively unstable and do not form above 1600 C.

### Reference

(1) Bowman, M. G., LASL, Private Communication (August, 1959).

## Silicon

### Constitution

According to Boettcher and Schneider(1), silicon reacts with UC at 1000 C to form $USi_3$.

Ivanov and Badayeva(2) report no solubility between UC and SiC.

SiC decomposes by a peritectic reaction between 2200 and 2700 C.

A uranium-carbon-silicon ternary section is shown in Figure 15.

### Crystallography

SiC has many polymorphic forms. Beta SiC: fcc, a = 4.359 A; density = 3.2 g per $cm^3$.

### References

(1) Boettcher, A., and Schneider, G., "Some Properties of Uranium Monocarbide", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Vol 6, A/Conf. 15/P/964, pp 561-63.

(2) Ivanov, O. S., and Badayeva, T. A., "Phase Diagrams of Certain Uranium and Thorium Systems", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Vol 6, A/Conf. 15/P/2043, p 139.

## Tantalum

### Constitution

The existence of a continuous solid solution between TaC and UC has been established.(1-4). Brownlee(4) and Bowman(2) report that the liquidus of the pseudobinary system, UC-TaC, is a smooth curve between the terminal compositions. Brownlee gives the melting point of TaC as 3780 C. Bowman(2) found that tantalum displaces

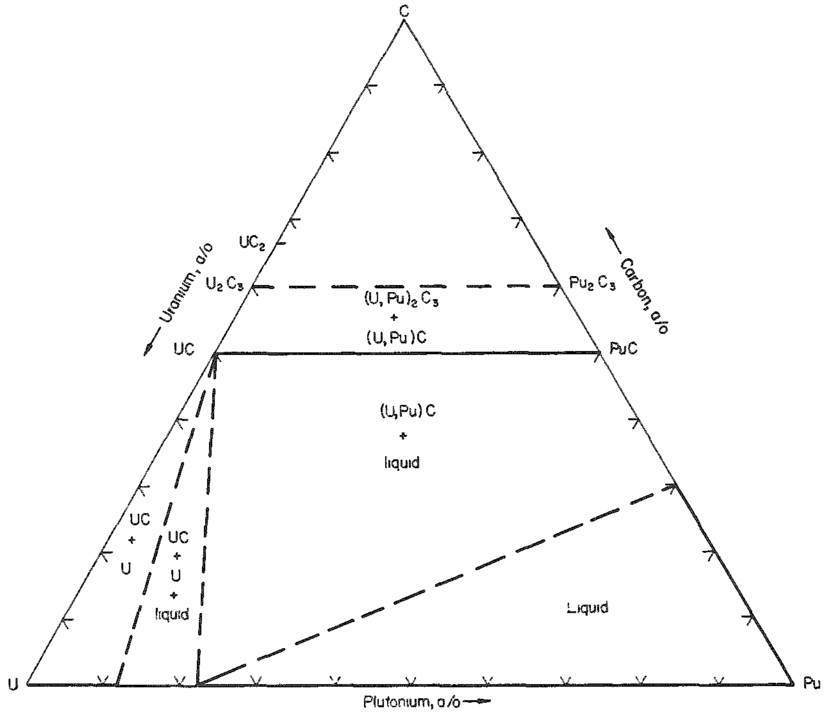

FIGURE 14. URANIUM-CARBON-PLUTONIUM TERNARY SECTION AT 1000 C

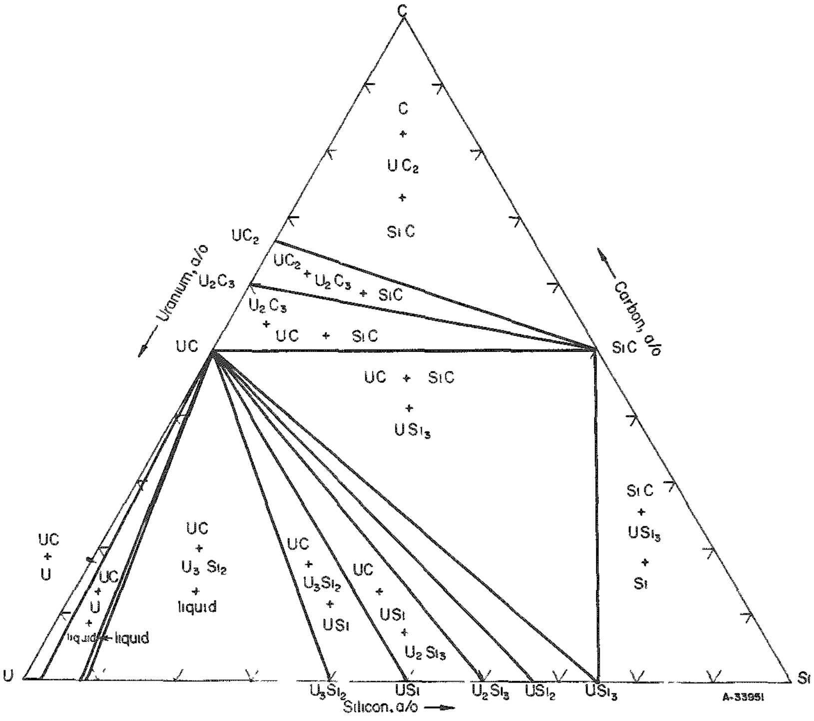

FIGURE 15. URANIUM-CARBON-SILICON TERNARY SECTION AT 1000 C

uranium from uranium carbide at increasingly rapid rates at temperatures above 1800 C. He successfully retarded this reaction (forming liquid uranium) by introducing layers of TaC and $Ta_2C$ between the tantalum and the UC. Parthe and Pemsler(1) state that there are no ternary compounds in the uranium-carbon-tantalum system at less than 50 a/o carbon, and that the only three-phase field in this region involves $Ta_2C$, the face-centered-cubic (Ta,U)C solution, and a body-centered-cubic metal, either uranium or tantalum. Apparently, they regarded tantalum and uranium as a single phase because they are structurally isomorphous. Some solubility of uranium in $Ta_2C$ is indicated, but the extent is unknown.(1)

The ternary sections shown in Figures 16 and 17 are based on the above statements. The section shown at 2000 C is regarded as typical of most uranium-carbon ternary constitution diagrams above the melting point of uranium.

The melting point of TaC is about 3800 C.

$Ta_2C$ decomposes peritectically at about 3400 C.

## Crystallography

TaC: fcc (NaCl, B1 type), a = 4.446 A, four molecules per unit cell; density = 14.48 g per $cm^3$.

$Ta_2C$: hexagonal (C27 type), a = 3.09 A, c = 4.93 A, one molecule per unit cell; density = 15.1 g per $cm^3$.

## References

(1) Parthe, E., and Pemsler, J. P., "Note on the Existence of '$UTa_{10}C_4$'", Trans. AIME, 215, 1070 (December, 1959).

(2) Bowman, M. G., "Bonding Uranium Carbide to Tantalum", AECU-4303 (May, 1959).

(3) Nowotny, H., Kieffer, R., and Benesovsky, F., "Preparation of UC and its Relation to the Carbides of Refractory Transition Metals", Rev. met., 55, 453-58 (May, 1958); see also Reference (5).

(4) Brownlee, L. D., "The Pseudo-Binary Systems of UC with ZrC, TaC, and NbC", J. Inst. Metals, 87, 58-61 (October 1958).

(5) Nowotny, H., Kieffer, R., Benesovsky, F., and Laube, E., "Contribution to the Knowledge of the Partial Systems: UC with TiC, ZrC, VC, NbC, TaC, $Cr_3C_2$, $Mo_2C$, and WC", Monatsh. Chem., 88, 336-43 (June, 1957).

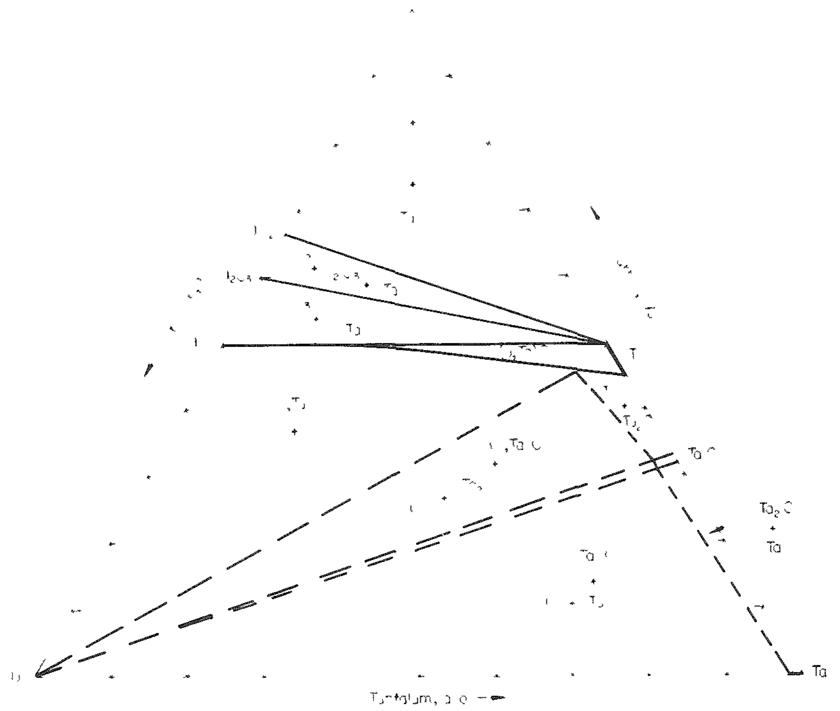

FIGURE 16. URANIUM-CARBON-TANTALUM TERNARY SECTION AT 1000 C

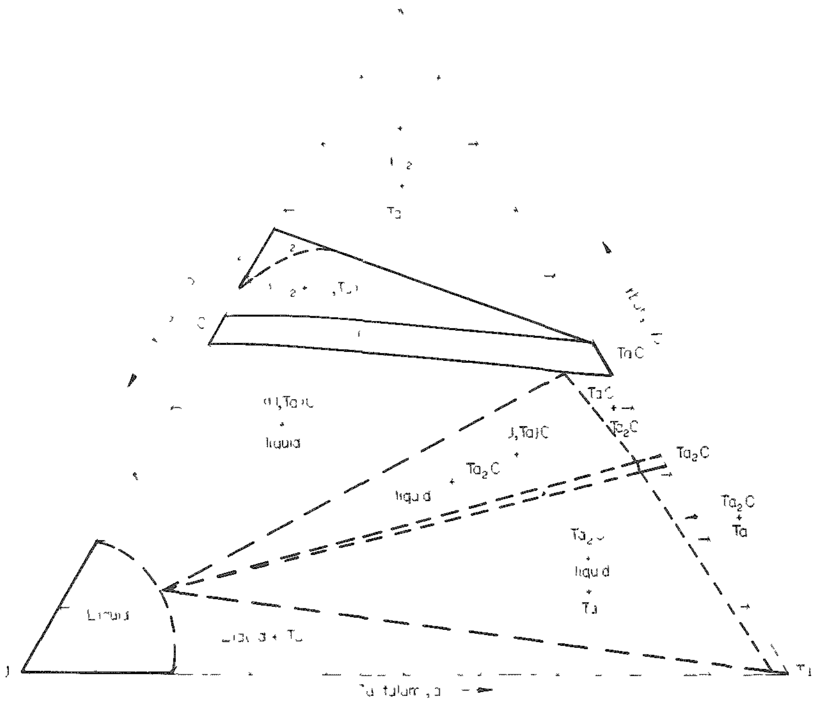

FIGURE 17. URANIUM-CARBON-TANTALUM TERNARY SECTION AT 2000 C

# Thorium

## Constitution

The existence of complete solubility between ThC and UC has been established.(1-4) Ivanov and Badayeva(1) report that there is complete solubility between ThC and UC, that thorium dissolves about 10 a/o carbon, and that thorium reacts with UC to produce uranium plus (Th,U)C. They found that between UC and thorium, the two-phase region, (U,Th)C + uranium, exists up to 40 a/o thorium, the three-phase region, (U,Th)C + uranium + thorium, exists between 40 and 81 a/o thorium, and the two-phase region, uranium + thorium, exists above 81 a/o thorium. The section shown in Figure 18 is based on these data. Brett, Law, and Livey(2) suggest a polymorphic transition in $ThC_2$ (probably similar to that in $UC_2$) which results in complete solubility between $UC_2$ and $ThC_2$ above 1900 C, but which may produce immiscibility below 1900 C.

The melting point of ThC is about 2620 C.

The melting point of $ThC_2$ is about 2660 C.

## Crystallography

ThC: fcc (NaCl, B1 type), a = 5.34 A, four molecules per unit cell; density = 10.67 g per cm$^3$.

$ThC_2$: monoclinic, a = 6.53 A, b = 4.24 A, c = 6.56 A, $\beta$ = 104°, four molecules per unit cell; density = 9.6 g per cm$^3$.

## References

(1) Ivanov, O., and Badayeva, T., "Phase Diagrams of Certain Uranium and Thorium Systems", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Vol 6, A/Conf. 15/P/2043, p 139.

(2) Brett, N., Law, O., and Livey, D. T., "Some Investigations of the U:Th:C System", AERE-M/R-2574 (June, 1958).

(3) Nowotny, H., Kieffer, R., Benesovsky, F., and Laube, E., "Note on the Partial System UC-ThC", Planseeber. Pulvermet., 5, 102-3 (December, 1957).

(4) Cirilli, V., and Brisi, C., "Solid Solutions Between UC and ThC", Ricerca sci., 28, 1431-34 (July, 1958).

## Titanium

### Constitution

Nowotny, Kieffer, and Benesovsky(1) report that UC dissolves less than 10 mole per cent of TiC and that TiC dissolves about 20 mole per cent of UC. Phillips(2) suggests a eutectic between UC and TiC at about 12 mole per cent, and no solubility of titanium metal in UC.

The melting point of TiC is about 3200 C.

The uranium-carbon-titanium diagram at 1000 C is shown in Figure 19.

### Crystallography

TiC: fcc (NaCl, B1 type), a = 4.32 A, four molecules per unit cell; density = 4.25 g per $cm^3$.

### References

(1) Nowotny, H., Kieffer, R., and Benesovsky, F., "Preparation of UC and its Relation to the Carbides of Refractory Transition Metals", Rev. met., 55, 453-58 (May, 1958); see also Reference (3).

(2) Phillips, W. M., BMI, Private Communication (November, 1959).

(3) Nowotny, H., Kieffer, R., Benesovsky, F., and Laube, E., "Contribution to the Knowledge of the Partial Systems: UC with TiC, ZrC, VC, NbC, TaC, $Cr_3C_2$, $Mo_2C$, and WC", Monatsh. Chem., 88, 336-43 (June, 1957).

## Tungsten

### Constitution

Newkirk and Bates(1) observed that UC in contact with tungsten melted at 2280 C.

Nowotny, Kieffer, and Benesovsky(2) report that UC dissolves about 10 mole per cent WC, but that WC dissolves no UC.

$W_2C$ melts at about 2800 C.

WC melts at about 2800 C.

The uranium-carbon-tungsten diagram at 1000 C is shown in Figure 20.

### Crystallography

$W_2C$: hcp, a = 2.99 A, c = 4.72 A, one molecule per unit cell; density = 17.2 g per $cm^3$.

WC: hexagonal, a = 2.90 A, c = 2.83 A, one molecule per unit cell; density = 15.5 g per $cm^3$.

### References

(1) Newkirk, H. W., and Bates, J. L., "The Melting Points of $UO_2$, UC, and UN", HW-59468 (March, 1959).

(2) Nowotny, H., Kieffer, R., and Benesovsky, F., "Preparation of UC and its Relation to the Carbides of Refractory Transition Metals", Rev. met., 55, 453-58 (May, 1958); see also Reference (3).

(3) Nowotny, H., Kieffer, R., Benesovsky, F., and Laube, E., "Contribution to the Knowledge of the Partial Systems: UC with TiC, ZrC, VC, NbC, TaC, $Cr_3C_2$, $Mo_2C$, and WC", Monatsh. Chem., 88, 336-43 (June, 1957).

## Vanadium

### Constitution

Nowotny, Kieffer, and Benesovsky(1) report that UC dissolves about 20 mole per cent of VC and that VC dissolves practically no UC.

$V_2C$ decomposes peritectically at a temperature above 1800 C.

The melting point of VC is about 2800 C.

A uranium-carbon-vanadium section is shown in Figure 21.

### Crystallography

$V_2C$: hcp (L'3 type), a = 2.906 A, c = 4.597 A, one molecule per unit cell; density = 5.6 g per $cm^3$.

VC: fcc (NaCl, B1 type), a = 4.17 A, four molecules per unit cell; density = 5.36 g per $cm^3$.

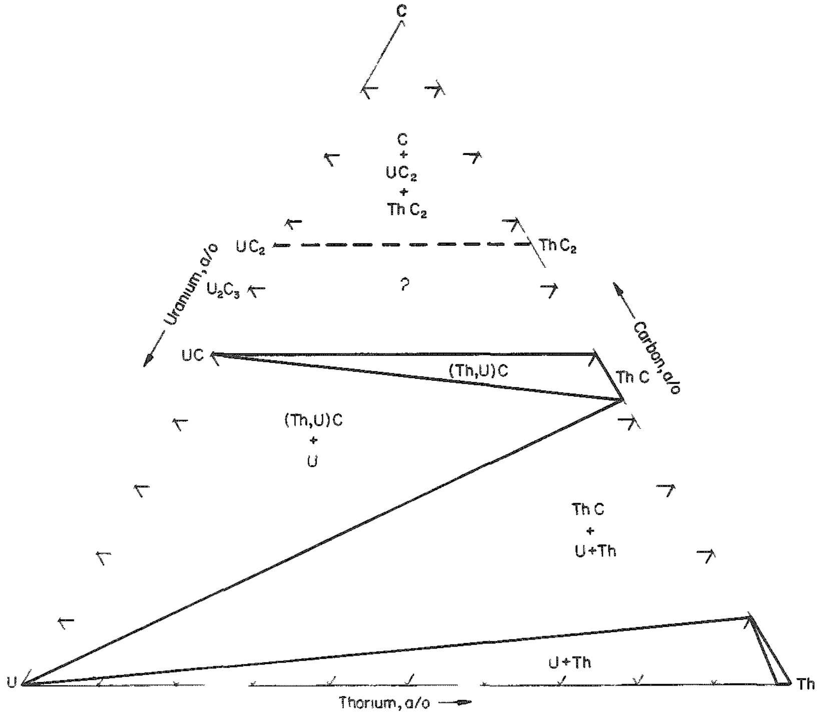

FIGURE 18. URANIUM-CARBON-THORIUM TERNARY SECTION AT 1000 C

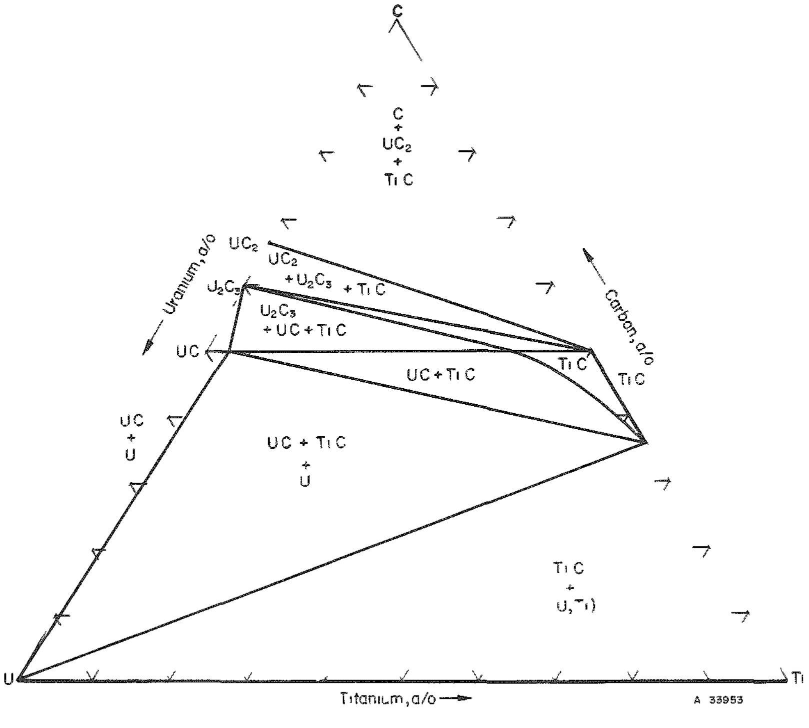

FIGURE 19. URANIUM-CARBON-TITANIUM TERNARY SECTION AT 1000 C

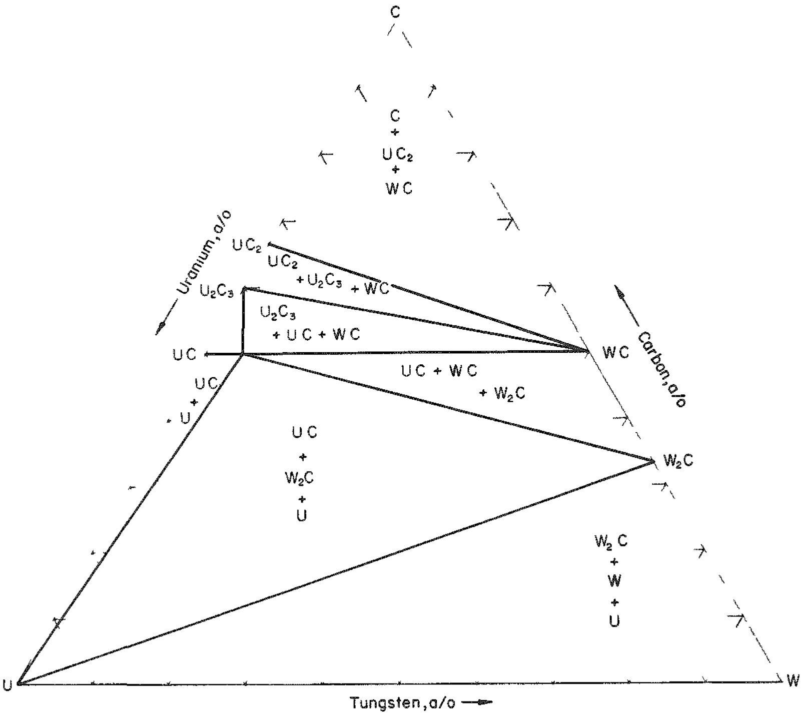

FIGURE 20. URANIUM-CARBON-TUNGSTEN TERNARY SECTION AT 1000 C

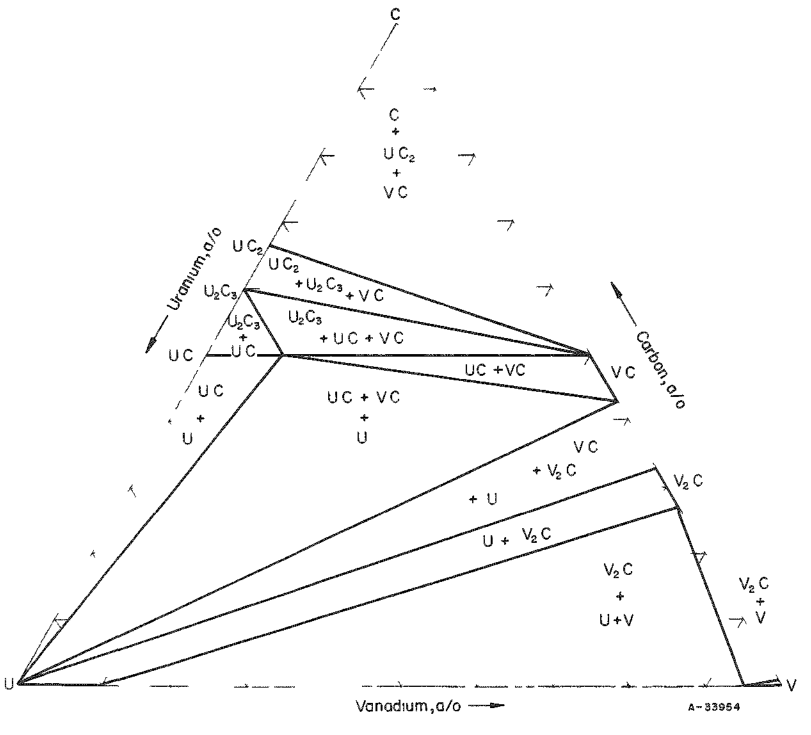

FIGURE 21. URANIUM-CARBON-VANADIUM TERNARY SECTION AT 1000 C

## References

(1) Nowotny, H., Kieffer, R., and Benesovsky, F., "Preparation of UC and its Relation to the Carbides of Refractory Transition Metals", Rev. met., 55, 453-58 (May, 1958); see also Reference (2).

(2) Nowotny, H., Kieffer, R., Benesovsky, F., and Laube, E., "Contribution to the Knowledge of the Partial Systems: UC with TiC, ZrC, VC, NbC, TaC, $Cr_3C_2$, $Mo_2C$, and WC", Monatsh. Chem., 88, 336-43 (June, 1957).

# Zinc

## Constitution

Boettcher and Schneider(1) report that UC is wet by molten zinc.

## Reference

(1) Boettcher, A., and Schneider, G., "Some Properties of Uranium Monocarbide", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Vol 6, A/Conf. 15/P/964, pp 561-63.

# Zirconium

## Constitution

The existence of complete solubility between ZrC and UC has been established.(1-4) Brownlee(1) reports that the liquidus of the pseudobinary system, UC-ZrC, is a smooth curve between the terminal compositions, and that the melting point of ZrC is 3535 C.

The melting point of ZrC is about 3500 C.

A ternary section is presented in Figure 22.

## Crystallography

ZrC: fcc (NaCl, B1 type), a = 4.687 A, four molecules per unit cell; density = 6.9 g per $cm^3$.

## References

(1) Brownlee, L. D., "The Pseudo-Binary Systems of UC with ZrC, TaC, and NbC", J. Inst. Metals, 87, 58-61 (October, 1958).

(2) Ivanov, O., and Badayeva, T., "Phase Diagrams of Certain Uranium and Thorium Systems", Proceedings of Second United Nations International Conference on Peaceful Uses of Atomic Energy", Geneva (1958), Vol 6, A/Conf. 15/P/2043, p 139.

(3) Nowotny, H., Kieffer, R., and Benesovsky, F., "Preparation of UC and its Relation to the Carbides of Refractory Transition Metals", Rev. met., 55, 453-58 (May, 1958); see also Reference (5).

(4) Witteman, W. G., Leitnaker, J. M., and Bowman, M. G., "The Solid Solubility of UC and ZrC", LA-2159 (April, 1958).

(5) Nowotny, H., Kieffer, R., Benesovsky, F., and Laube, E., "Contribution to the Knowledge of the Partial Systems: UC with TiC, ZrC, VC, NbC, TaC, $Cr_3C_2$, $Mo_2C$, and WC", Monatsh. Chem., 88, 336-43 (June, 1957).

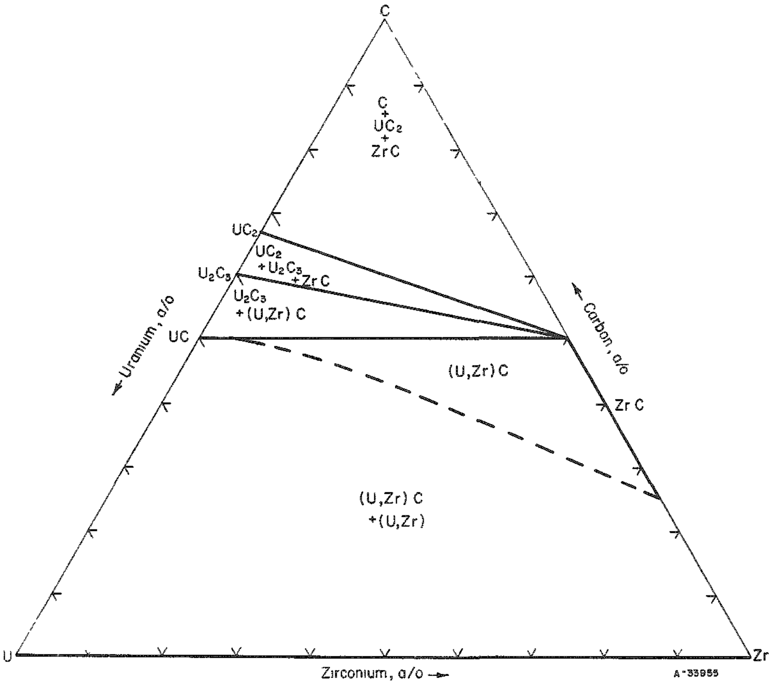

FIGURE 22. URANIUM-CARBON-ZIRCONIUM TERNARY SYSTEM AT 1000 C

# THE THORIUM-CARBON BINARY SYSTEM

## Constitution

The melting points of ThC and $ThC_2$ were found to be 2625 and 2655 C by Wilhelm and Chiotti(1). The banded structure of $ThC_2$ obtained by Wilhelm and Chiotti is identical to that produced in $UC_2$ by transformation from the high-temperature cubic structure to the low-temperature form. Brett, Law, and Livey(2) suggest that $ThC_2$ has a polymorphic transition at about 1900 C. The structure obtained by Wilhelm and Chiotti on cooling a thorium-7.2 w/o carbon alloy from 2400 C suggests that ThC and $ThC_2$ are immiscible at this temperature. The structure obtained by Wilhelm and Chiotti on cooling a thorium-6.1 w/o carbon alloy from 2615 C is clearly a eutectic structure as postulated by their constitution diagram. The structure obtained on cooling a thorium-8 w/o carbon alloy from 2655 C is consistent with an eutectoid near 8 w/o carbon and 1900 C resulting from the polymorphic transition suggested by Brett, Law, and Livey.

The existence of an allotropic transformation in thorium was discovered by Chiotti(3). This discovery of a transition from the low-temperature face-centered-cubic to the high-temperature body-centered-cubic structure has been confirmed, and the temperature of transformation has been established as about 1360 C. Wilhelm and Chiotti(1) found a region of single-phase solid solution at 2.6 w/o carbon and 1900 C and indicated that this meant a region of solid solution between thorium and thorium carbide. While such a construction is not impossible, as Hansen and Anderko(4) point out, continuous solid solubility of carbon from the metallic face-centered-cubic structure of thorium, through the ionic (NaCl) structure of ThC, to the unknown (probably $CaF_2$) high-temperature structure of $ThC_2$ is not conceivable. Wilhelm and Chiotti(1) have apparently ignored a two-phase structure obtained at 4.1 w/o carbon and 2110 C indicating that ThC has low solubility for thorium.

A possible constitution diagram based on the above data and suggestions has been constructed (Figure 23). The existence of a phase, $Th_2C_3$, similar to $U_2C_3$ has not been ruled out by the above investigations.

## Crystallography

ThC: fcc (NaCl, B1 type), a = 5.34 A, four molecules per unit cell; density = 10.6 g per $cm^3$.

$ThC_2$ (below 1900 C): monoclinic, a = 6.53 A, b = 4.24 A, c = 6.56 A, four molecules per unit cell; density = 9.6 per $cm^3$.

$ThC_2$ (above 1900 C): structure unknown, probably face-centered cubic of the $CaF_2$ type since Brett, Law, and Livey(2) suggest complete solubility above 1900 C between $UC_2$ and $ThC_2$.

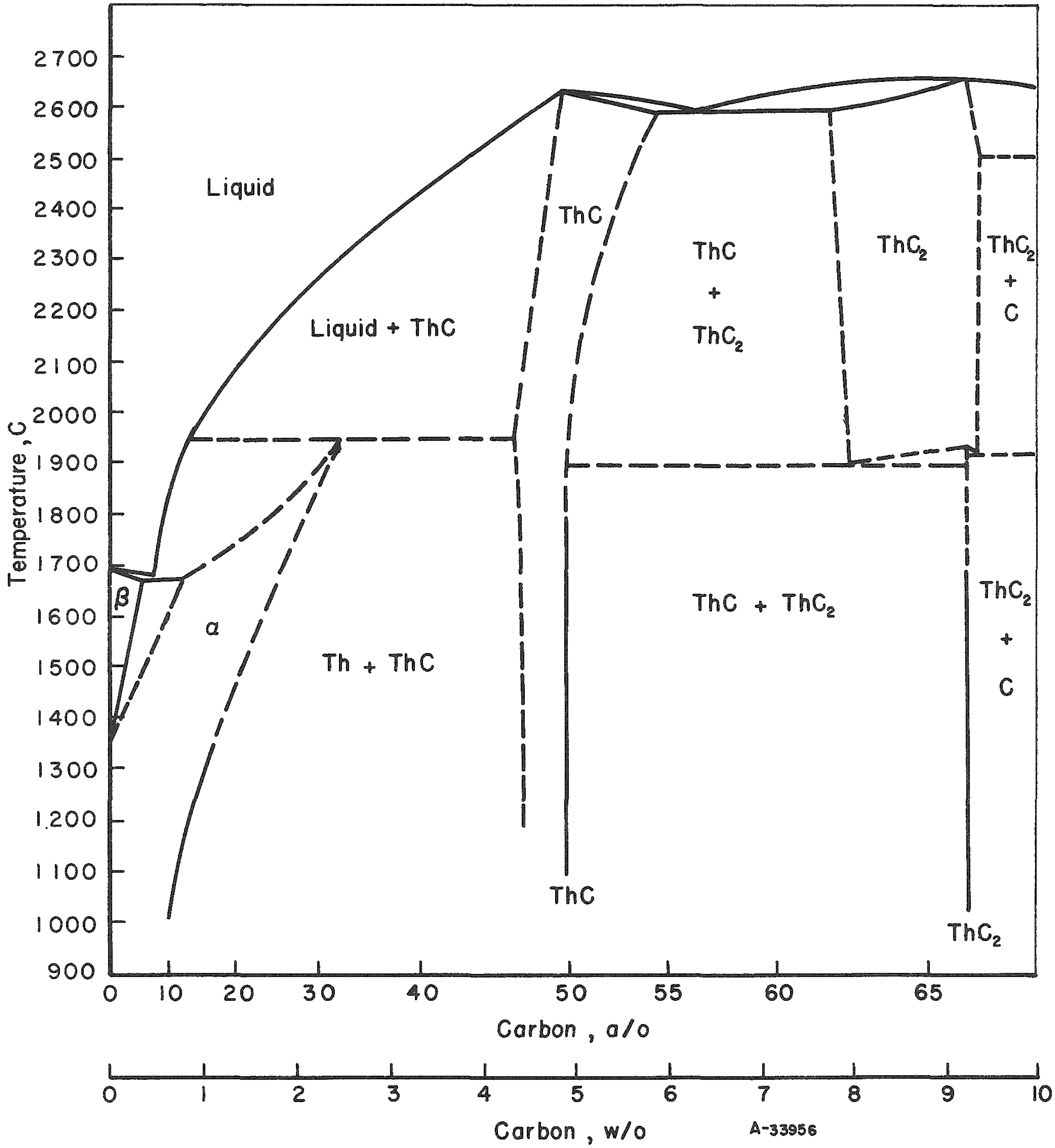

FIGURE 23. THORIUM-CARBON CONSTITUTIONAL DIAGRAM

### References

(1) Wilhelm, H. A., and Chiotti, P., "Thorium-Carbon System", Trans. ASM, 42, 1295-1310 (1950).

(2) Brett, N., Law, D., and Livey, D. T., "Some Investigations of the U:Th:C System", AERE-M/R-2574 (June, 1958).

(3) Chiotti, P., "High-Temperature Crystal Structure of Thorium", J. Electrochem. Soc., 101, 567-570 (1954).

(4) Hansen, M., and Anderko, K., Constitution of Binary Alloys, McGraw-Hill Book Company, Inc., New York (1958), p 382.

## THORIUM-CARBON TERNARY SYSTEMS

### Nitrogen

### Constitution

It has been reported by Scaife and Wylie(1) that one of the thorium nitrides (probably ThN) is more stable than $ThC_2$ below 2100 C.

The melting point of ThN is about 2600 C, and it is apparently stable in a vacuum at temperatures below 2000 C.(2) It is known that $Th_2N_3$ is not stable in a vacuum at 1500 C.

### Crystallography

ThN: fcc (NaCl, B1 type), a = 5.21 A, four molecules per unit cell; density = 11.6 g per $cm^3$.

$Th_2N_3$: hexagonal, a = 3.87 A, c = 6.16 A, one molecule per unit cell; density = 10.5 g per $cm^3$.

### References

(1) Scaife, D. E., and Wylie, A. W., "The Preparation of $ThC_2$ and some Aspects of the High Temperature Decontamination of Irradiated Carbide Fuels", Australian Atomic Energy Symposium (1958), "Section 1, High Temperature and Ceramics", pp 172-81.

(2) Chiotti, P., "Experimental Refractory Bodies of High Melting Nitrides, Carbides, and Uranium Dioxide", J. Am. Ceram. Soc., 35, pp 123-30 (May, 1952).

## Oxygen

Thorium monocarbide hydrolyses rapidly in moist air and tends to oxidize at room temperature. It should be stored in a dry, inert atmosphere.

Thorium metal has practically no solubility for oxygen, and it may be presumed that the same is true of the thorium carbides.

## Uranium

Thorium-carbon-uranium compositions are discussed in the section on uranium-carbon ternary systems.

## Zirconium

### Constitution

Thorium monocarbide is evidently a very poor solvent, for, according to Ivanov and Badayeva(1), it dissolves only 6 mole per cent of ZrC, which is one of the few monocarbides likely to dissolve in ThC. There is no solubility of ThC in ZrC.

Murray(2) reports that zirconium reacts with carbon present in solution in thorium to form zirconium carbide.

The thorium-carbon-zirconium diagram at 1000 C is shown in Figure 24.

### Crystallography

ZrC: fcc (NaCl, B1 type), a = 4.687 A, four molecules per unit cell; density = 6.9 g per $cm^3$.

### References

(1) Ivanov, O. S., and Badayeva, T. A., "Phase Diagrams of Certain Uranium and Thorium Systems", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Vol 6, A/Conf. 15/P/2043, p 139.

(2) Murray, J. R., "The Constitution of Thorium-Zirconium Alloys Containing more than 15 Per Cent Zirconium", AERE-R-3048 (September, 1959).

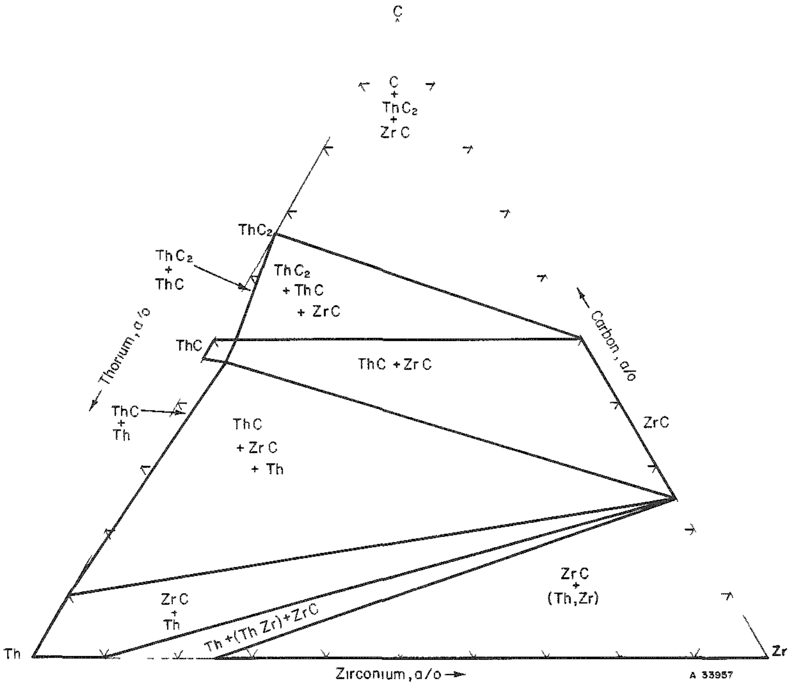

FIGURE 24. THORIUM-CARBON-ZIRCONIUM TERNARY SECTION AT 1000 C

## THE PLUTONIUM-CARBON BINARY SYSTEM

### Constitution

The plutonium-carbon constitutional diagram is shown in Figure 25. The melting points of PuC and $Pu_2C_3$ were found by Drummond, McDonald, Ockenden, and Welch(1) to be about 1850 and 1900 C, respectively. Drummond, et al., found an additional substance containing from 8.5 to 9.5 w/o carbon (corresponding to $PuC_2$) which melts at about 2200 C.

Shonfeld, Cramer, Miner, Ellinger, and Coffinberry(2) report that there is a eutectic between PuC and plutonium at an unknown location and that PuC forms by a peritectic reaction at about 1200 C. In view of the fact that plutonium is a material with a very low melting point, the formation of PuC by a peritectic reaction seems reasonable. The data obtained by Drummond, et al., may represent a material having some contamination by uranium.

### Crystallography

PuC: fcc (NaCl, B1 type), a = 4.97 A, four molecules per unit cell; density = 13.6 g per $cm^3$.

$Pu_2C_3$: bcc (space group $I\bar{4}3d$), a = 8.129 A, eight molecules per unit cell; density = 12.7 g per $cm^3$.

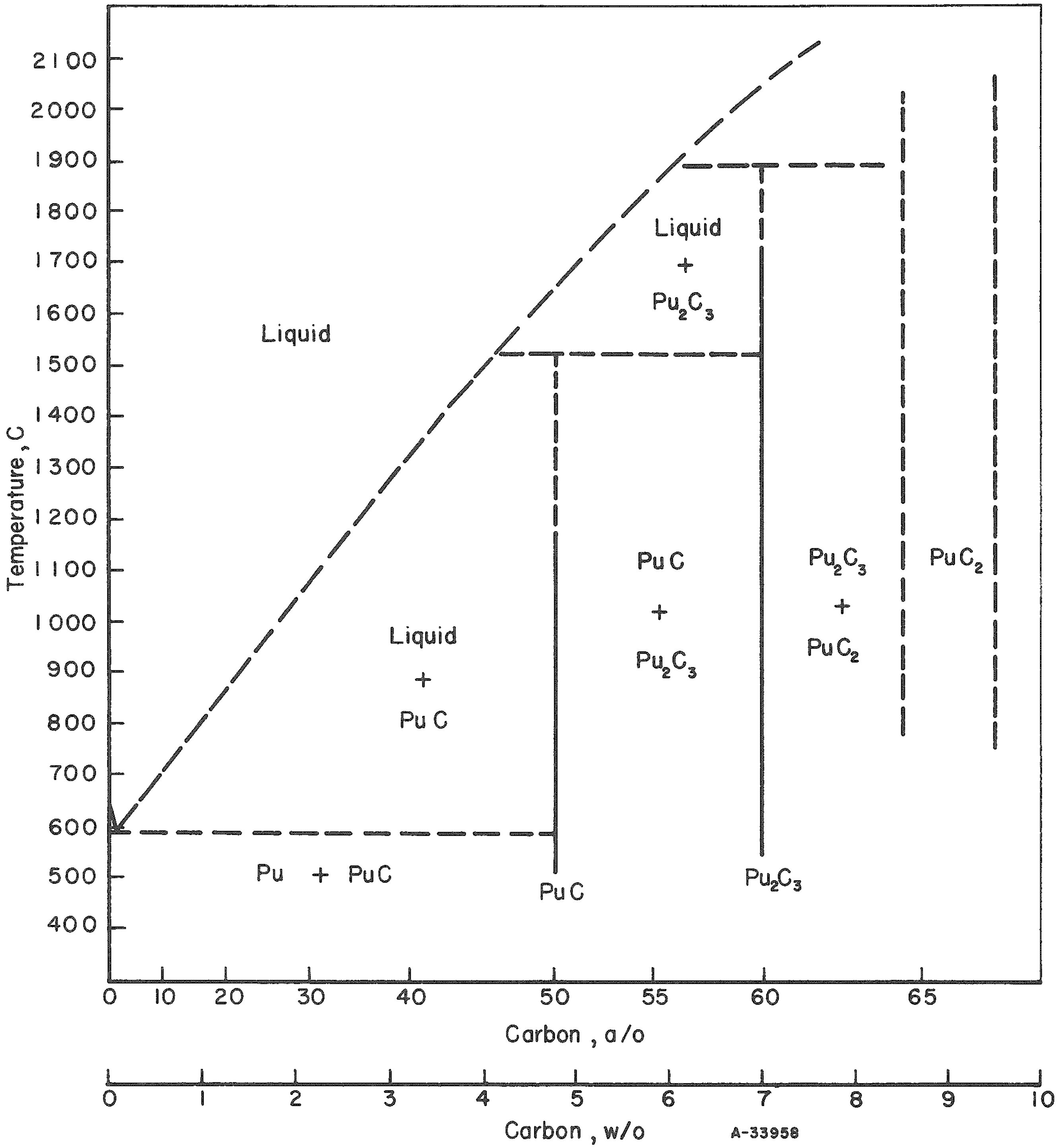

FIGURE 25. PLUTONIUM-CARBON CONSTITUTIONAL DIAGRAM

## References

(1) Drummond, J. L., McDonald, B. J., Ockenden, H. M., Welch, G. A., "The Preparation and Properties of Some Plutonium Compounds, VII, Plutonium Carbide", J. Chem. Soc. (London), p 4785 (1957).

(2) Schonfeld, F. W., Cramer, E. M., Miner, W. N., Ellinger, F. H., and Coffinberry, A. S., "Plutonium Constitutional Diagrams", Progress in Nuclear Energy, Series V, Metallurgy and Fuels, Vol II, Pergamon Press, New York (1959), pp 579-99.

# PLUTONIUM-CARBON TERNARY SYSTEMS

## Nitrogen

### Constitution

Coffinberry and Ellinger(1) state that "PuC, PuN, and PuO have appreciable mutual solid solubility, as well as homogeneity ranges for each binary phase, and differences in content of carbon, nitrogen, and oxygen are difficult to control or to determine". Since PuC and PuN are isomorphous and their unit-cell sizes differ by only 1 per cent, it would be very surprising if PuC and PuN were not completely soluble in one another.

### Crystallography

PuN: fcc (NaCl, B1 type), a = 4.905 A, four molecules per unit cell; density = 14.2 g per $cm^3$.

### Reference

(1) Coffinberry, A. S., and Ellinger, F. H., "The Intermetallic Compounds of Plutonium", No. 826, Proceedings of the [First United Nations] International Conference on the Peaceful Uses of Atomic Energy, New York (1956), Vol 9, A/Conf. 8/P/826, pp 138-46.

## Oxygen

### Constitution

In 1955, Coffinberry and Ellinger(1) reported that PuO and PuC had appreciable mutual solid solubility and that PuO was face-centered cubic with a lattice parameter of 4.96 A. Since this is intermediate to that of PuC (a = 4.97 A) and PuN (a = 4.90 A), which are probably mutually soluble, it seems likely that the PuO observed was really Pu(C,N).

In 1959, Schonfeld, Cramer, Miner, Ellinger, and Coffinberry(2) stated that "PuO has not been observed except as formed under special conditions." They also observed that "The solubility of oxygen in molten plutonium up to 1000 C does not exceed 30 ppm by weight." Since plutonium represents an oxidation state intermediate to that of PuC and plutonium oxide, it may be assumed that the solubility of oxygen in the plutonium carbides is similar to or less than that of oxygen in plutonium.

### References

(1) Coffinberry, A. S., and Ellinger, F. H., "The Intermetallic Compounds of Plutonium", Proceedings of the [ First United Nations] International Conference on the Peaceful Uses of Atomic Energy, New York (1956), Vol 9, A/Conf. 8/P/826, pp 138-46.

(2) Schonfeld, F. W., Cramer, E. M., Miner, W. N., Ellinger, F. H., and Coffinberry, A. S., "Plutonium Constitutional Diagrams", Progress in Nuclear Energy, Series V, Metallurgy and Fuels, Vol II, Pergamon Press, New York (1959), pp 579-599.

### Uranium

Plutonium-carbon-uranium compositions are discussed in the section on uranium-carbon ternary systems.

## QUATERNARY SYSTEMS

### Uranium-Thorium-Carbon-Zirconium

#### Constitution

The pseudoternary system involving the monocarbides of thorium, uranium, and zirconium has been investigated by Ivanov and Badayeva(1). This investigation disclosed the existence of solubility in the pseudoternary system in all alloys containing more than 70 mole per cent UC and in all alloys containing less than 6 mole per cent ZrC. The alloys were examined both in the as-cast condition and as annealed at 2000 C and furnace cooled. No changes in constitution were observed as a result of these changes in heat treatment.

A ThC-UC-ZrC section is shown in Figure 26.

Reference

(1) Ivanov, O. S., and Badayeva, T. A., "Phase Diagrams of Certain Uranium and Thorium Systems", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Vol 6, A/Conf. 15/P/2043, p 139.

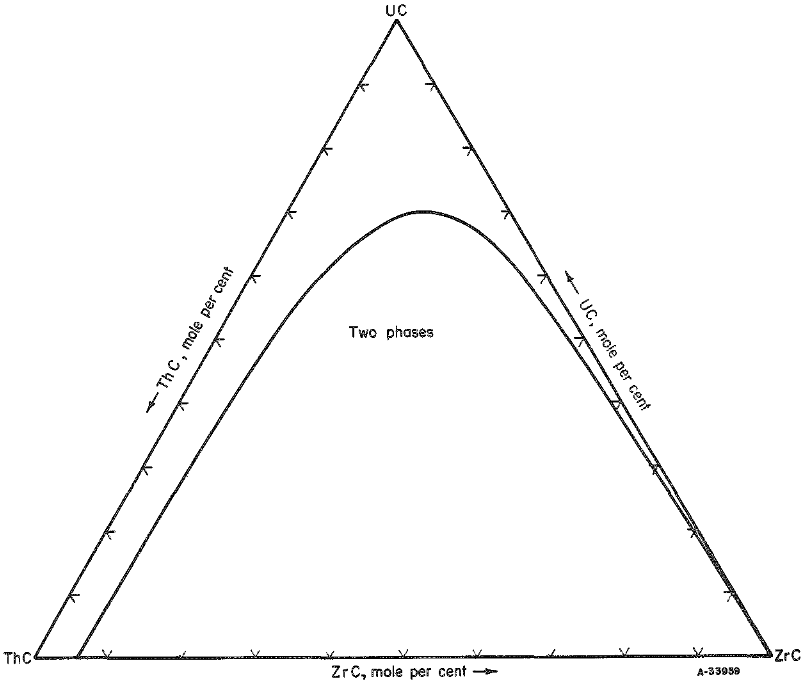

FIGURE 26. ThC-UC-ZrC SECTION AT 2000 TO 2400 C

# COMPATIBILITY AND CORROSION BEHAVIOR OF NUCLEAR CARBIDES

W. M. Phillips and J. J. Ward

## Introduction

This section consists of a brief summary of the presently available data on compatibility and corrosion behavior of uranium carbides. Essentially, no such data are available on thorium and plutonium carbides. The data reviewed include those available on compatibility with metallic cladding or matrix materials, and with liquid and gaseous coolants and chemicals. Also included are thermodynamic data calculated for the reaction of uranium, thorium, and plutonium carbides with various selected coolants. Similar data are included for the reaction of UC with the refractory metals molybdenum, niobium, tantalum, and tungsten. Additional information on the compatibility of these carbides with metallic materials can be obtained in the section on constitution.

At best, compatibility is a difficult thing to define, and usually the observed results are highly dependent on the experimental conditions and the quality of materials used in the test. The data presented are sparse and based on limited experimentation, and offer little opportunity for evaluation. The situation is rather similar for the few data available for the corrosion of carbides in various media. Here also the results will be greatly affected by fabrication history and the quality of materials, since variations in chemical composition and type and amount of porosity and cracking will affect both the chemical reactivity and the rate of attack.

The thermodynamic data presented are believed to be the best available. However, the relatively low free energy of formation of these carbides means that appreciable error may be present in calculations of the free energy of the various chemical reactions considered.

## Thermodynamics of Reactions With Coolants and With Claddings

The thermodynamics of reaction of gaseous coolants such as nitrogen, oxygen, CO, $CO_2$, and $H_2O$ are presented in Table 5. Liquid coolants such as NaK, sodium and terphenyl were also considered. No reaction between these liquids and UC is predicted; but the data are not completely satisfactory, since the solubility of the carbides in the liquids is not known. Thus, the calculated data are not included.

Similarly, thermodynamic data on the reaction of carbides with metals cannot be considered completely satisfactory unless data on the solubility of the carbides in the metals are available. Although the needed solubility data are not available, data are presented in Table 6 for the reaction potentials of UC with molybdenum, niobium, tantalum, and tungsten, neglecting the possibility of solubility of the UC in these metals. The results indicate that molybdenum and tungsten should not react with UC while tantalum and niobium should. One obvious discrepancy arises when these predictions are compared with the data shown below and in the constitution section. It is reported that molybdenum reacts with UC to form $Mo_2C$.

## TABLE 5. STANDARD FREE-ENERGY CHANGE FOR CARBIDE REACTIONS WITH COOLANTS

| Reaction | Standard Free-Energy Change, $\Delta G^{o}_{T}$, cal | | | | |
|---|---|---|---|---|---|
| | 600 K | 800 K | 1000 K | 1200 K | 1400 K |
| $UC(s) + 3H_2O(g) \rightleftharpoons UO_2(c) + 3H_2(g) + CO(g)$ | -100,320 | -105,010 | -- | -- | -- |
| $UC_2(c) + 4H_2O(g) \rightleftharpoons UO_2(c) + 4H_2(g) + 2CO(g)$ | -68,020 | -79,300 | -- | -- | -- |
| $ThC_2(c) + 4H_2O(g) \rightleftharpoons ThO_2(c) + 4H_2(g) + 2CO(g)$ | -95,780 | -105,680 | -- | -- | -- |
| $PuC(c) + 3H_2O(g) \rightleftharpoons PuO_2(c) + 3H_2(g) + CO(g)$ | -82,610 | -86,860 | -- | -- | -- |
| $UC(c) + 3/2O_2(g) \rightleftharpoons UO_2(c) + CO(g)$ | -253,770 | -250,930 | -- | -- | -- |
| $UC_2(c) + 2O_2(g) \rightleftharpoons UO_2(c) + 2CO(g)$ | -272,600 | -273,860 | -- | -- | -- |
| $ThC_2(c) + 2O_2(g) \rightleftharpoons ThO_2(c) + 2CO(g)$ | -300,380 | -300,240 | -- | -- | -- |
| $PuC(c) + 3/2O_2(g) \rightleftharpoons PuO_2(c) + CO(g)$ | -236,060 | -232,780 | -- | -- | -- |
| $UC(c) + 3CO_2(g) \rightleftharpoons UO_2(c) + 4CO(g)$ | -88,650 | -98,350 | -- | -- | -- |
| $UC_2(c) + 4CO_2(g) \rightleftharpoons UO_2(c) + 6CO(g)$ | -52,460 | -70,420 | -- | -- | -- |
| $ThC_2(c) + 4CO_2(g) \rightleftharpoons ThO_2(c) + 6CO(g)$ | -80,220 | -96,800 | -- | -- | -- |
| $PuC(c) + 3CO_2(g) \rightleftharpoons PuO_2(c) + 4CO(g)$ | -79,940 | -80,200 | -- | -- | -- |
| $UC(c) + 2CO(g) \rightleftharpoons UO_2(c) + 3C(graphite)$ | -135,690 | -119,890 | -- | -- | -72,980 |
| $UC_2(c) + 2CO(g) \rightleftharpoons UO_2(c) + 4C(graphite)$ | -115,180 | -99,140 | -- | -- | -51,480 |
| $ThC_2(c) + 2CO(g) \rightleftharpoons ThO_2(c) + 4C(graphite)$ | -142,940 | -125,520 | -- | -- | -74,320 |
| $PuC(c) + 2CO(g) \rightleftharpoons PuO_2(c) + 3C(graphite)$ | -117,980 | -101,740 | -- | -- | -53,180 |
| $UC(c) + 1/2N_2(g) \rightleftharpoons UN(c) + C(graphite)$ | -35,910 | -29,790 | -28,990 | -25,530 | -22,100 |
| $UC_2(c) + 1/2N_2(g) \rightleftharpoons UN(c) + 2C(graphite)$ | -15,400 | -11,700 | -8,000 | -4,300 | -600 |
| $ThC_2(c) + 2/3N_2(g) \rightleftharpoons 1/3\ Th_3N_4(c) + 2C(graphite)$ | -42,000 | -36,550 | -31,090 | -25,640 | -20,190 |
| $PuC(c) + 1/2N_2(g) \rightleftharpoons PuN(c) + C(graphite)$ | -61,000 | -58,000 | -55,000 | -52,000 | -49,000 |

TABLE 6. REACTION POTENTIAL[(a)] OF URANIUM MONOCARBIDE WITH MOLYBDENUM, NIOBIUM, TANTALUM, AND TUNGSTEN METALS AS A FUNCTION OF TEMPERATURE

| | Standard Free Energy of Reaction, $\Delta G^o_T$, cal | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 900 K | 1000 K | 1200 K | 1400 K | 1600 K | 1800 K | 2000 K | 2200 K | 2400 K |
| $UC(c) + 2Mo(c) \rightarrow U + Mo_2C(c)$ | +11,700 | +11,310 | +10,470 | +9,600 | +8,500 | +7,900 | +7,300 | +6,700 | +6,100 |
| $UC(c) + W(c) \rightleftharpoons U + WC(c)$ | +9,660 | +9,310 | +8,550 | +7,760 | +6,740 | +6,220 | +5,700 | +5,180 | +4,660 |
| $UC(c) + Ta(c) \rightleftharpoons U + TaC(c)$ | -19,060 | -19,330 | -19,940 | -20,580 | -21,140 | -21,810 | -22,180 | -22,550 | -22,920 |
| $UC(c) + Nb(c) \rightleftharpoons U + NbC(c)$ | -14,220 | -14,490 | -15,090 | -15,720 | -16,580 | -16,940 | -17,300 | -17,660 | -18,020 |

(a) These data indicate that UC is chemically stable with respect to tungsten and molybdenum over the range of 900 to 2400 K. The stability tends to decrease with increasing temperature. The data indicate that tantalum and niobium tend to react chemically with UC and that the tendency increases with increasing temperature. These data give no information on behavior patterns dependent upon solubilities of carbides in metals.

## Compatibility With Metals

### Aluminum

Work at Oak Ridge(1) has shown the reaction between aluminum and uranium carbide at 620 C to vary as a function of carbon content, as shown in Table 7.

TABLE 7. REACTION BETWEEN ALUMINUM AND UC AT 620 C(1)

| Time at 620 C, hr | Reaction[(a)] Occurring With Alloy Shown | | | | | | |
|---|---|---|---|---|---|---|---|
| | U-9.2 w/o C | U-8.24 w/o C | U-7.98 w/o C | U-6.96 w/o C | U-5.75 w/o C | U-4.86 w/o C | U-4.46 w/o C |
| 4 | NR | NR | NR | NR | NR | NR | $\Delta V = 1.2\%$ |
| 10 | NR | NR | NR | NR | $\Delta V = 71\%$ | $\Delta V = 88\%$ | CD |
| 16 | NR | NR | NR | NR | | | |
| 24 | NR | NR | NR | 5% $UAl_4$,<br>$\Delta V = 4.6\%$ | | | |
| 48 | NR | 5% $UAl_3$ | 1% $UAl_3$,<br>1% $UAl_4$,<br>$V = 0.6\%$ | | | | |
| 74 | NR | 5% $UAl_3$ | | | | | |
| 96 | 4% $UAl_4$ | | | | | | |

(a) Code:
NR = No reaction
$\Delta V$ = Change in volume of specimen
CD = Complete disintegration.

### Beryllium

A. Boettcher, et al.,(2) found beryllium to bond to UC at 650 C in 12 hr under a pressure of 15 kg per $mm^2$.

P. Murray, et al., (3) found reaction between $U_2C_3$ or $UC_2$ and beryllium between 600 and 1000 C.

## Bismuth

No reaction between molten bismuth and UC was observed during heating to 950 C and subsequent cooling. (4) At 1100 C, bismuth does not react with either $UC_2$ or $U_2C_3$(4), both of which are considered to be more reactive than the monocarbide.

## Lead

Molten lead will not wet UC by dipping. (2)

## Molybdenum

Reaction between UC and molybdenum was observed metallographically after sintering at 1200 C. (5)

## Nickel

Nickel has been deposited on UC by both vacuum evaporation and electrolytic deposition. Annealing of these specimens for 10 min at 1000 C produced two layers between the UC and the nickel, one $U_6Ni$, the other of unknown composition. (2)

## Nichrome V

A mixture of 30 volume per cent of UC in Nichrome V showed metallographic evidence of reaction and melting after sintering at 1200 C. (5)

## Niobium

Metallographic evidence of reaction between niobium and UC was observed after sintering at 1200 C. (5)

## Niobium-Titanium

A niobium-40 a/o titanium alloy in contact with UC was found to react, producing a molten phase at 1200 C. (5)

## Silicon

Siliconization was found to take place at 1000 C, producing $USi_3$ on the surface of UC in contact with silicon metal. (2)

## Sodium and NaK

Nichols(6) reports satisfactory compatibility of UC with NaK at 800 C after 1 month's exposure. Price, et al., (7) ran tests involving cast uranium-5 w/o carbon specimens held in molybdenum or Type 304 stainless steel baskets immersed in NaK-filled stainless steel capsules. After 2 to 6 weeks at 1300 F and 12 weeks at 1100 F, the carbide specimens were intact except for minor weight losses.

## Steel

Mild steel was found to react with uranium monocarbide at 1000 C in 24 hr. (8)

## Stainless Steel

Stainless steel could not be bonded to uranium monocarbide at 650 C in 12 hr under a pressure of 15 kg per mm$^2$. (2) Uranium monocarbide was found to react with stainless steel in 24 hr at 1000 C. (8) Type 304 stainless steel, used to contain UC specimens in a NaK environment, was embrittled by an exposure of 12 weeks at 1100 F. (7) Nichols(6) reports that UC and stainless are compatible at 1000 C and that 0.004 in. penetration occurred during 6 days at 1100 C.

## Tantalum

Tantalum will displace uranium from uranium monocarbide. The reaction is slow at 1000 C but becomes rapid near the melting point of uranium monocarbide. (9)

## Tin

Molten tin will not wet uranium carbide by dipping. (2)

## Titanium

Nichols(6) reports that reaction occurs between UC and titanium at 1100 C, the penetration amounting to 0.005 in. in 6 days at temperature. Very marked reaction was observed at 1200 C.

## Zinc

Molten zinc will wet uranium carbide by dipping. (2)

## Zircaloy-2

Zircaloy-2 was found to react with uranium carbide in 1 hr at 1200 C(10) but not at 800 C(11).

### Zirconium

Zirconium was bonded to uranium carbide at 650 C in 12 hr under a pressure of 15 kg per $mm^2$.(2) Considerable reaction was observed between zirconium and uranium carbide at 1000 C and 1200 C in 24 hr.(5, 8)

### Air, Oxygen, and Nitrogen

Uranium monocarbide is attacked very slowly by moist air at room temperature, but it can be handled in bulk form, if exposure to moisture is minimized as by storage in a desiccator. It is reported that $UC_2$ is attacked more rapidly in air than is UC. Thus, the presence of $UC_2$ as a second phase in UC may accentuate this difficulty.(12)

Uranium dicarbide reacts with both oxygen and nitrogen at a rate which is parabolic as a function of temperature. At 300 C, the reaction with oxygen becomes anisothermal. A summary of these data appears in Table 8.

TABLE 8. CORROSION OF URANIUM DICARBIDE IN WATER VAPOR, NITROGEN, AND OXYGEN

| Test Medium | Temperature, C | Corrosion Rate | | Reference |
|---|---|---|---|---|
| | | Linear, $mg/(cm^2)(sec)$ | Parabolic, $(mg/cm^2)^2/sec$ | |
| 29 mm $H_2O$ | 50 | 0.04 | -- | 13 and 14 |
| | 150 | 0.66 | -- | 13 and 14 |
| | 200 | 3.2 | -- | 13 and 14 |
| $H_2O$ vapor | 250 | -- | 6520 | 13 |
| | 300 | -- | 9210 | 13 |
| | 300 | -- | 6840 | 13 |
| Nitrogen | 400 | -- | 16 | 14 |
| | 600 | -- | 860 | 14 |
| | 700 | -- | 3300 | 14 |
| Oxygen | 150 | -- | 6.1 | 14 |
| | 200 | -- | 75 | 14 |
| | 250 | -- | 900 | 14 |
| | 300 | -- | Anisothermal | 14 |

## Compatibility With Liquids and Gases

### Water

It has been generally noted that UC has very poor compatibility with water at any temperature. Nichols(6) reports that rapid decomposition results from exposure to water at temperatures above 80 C. The gaseous reaction products evolved during hydrolysis of UC at 83 to 400 C were analyzed by Litz(15). The liberated gas was composed of hydrogen and methane with a hydrogen concentration varying from 12 per cent at 83 C to 100 per cent at 400 C. At all temperatures, the solid reaction product was

$UO_2$. Appreciable rates of reaction between water and uranium carbide have been noted at temperatures as low as 40 C.(16) Several investigators have determined the corrosion rate of the dicarbide in water vapor as summarized in Table 8. The results indicate that the rate is linear at 200 C and below, but parabolic above this temperature.

## Alkalies and Acids

Concentrated acids will react slowly with UC at room temperature, the reaction rate increasing with temperature.(17) Alkalies will readily decompose $UC_2$.(18)

## Organics

Some organic materials react with the carbides of uranium. When UC was exposed in glycerin at 100 C a weight-loss rate of 50 mg/($cm^2$)(hr) was measured.(2) Terphenyl (Santowax R) corroded UC at the rate of approximately 5 mg/($cm^2$)(hr) at 350 C, probably as a result of traces of contained moisture. A weight loss of 0.4 mg/($cm^2$)(hr) occurred during exposure of UC to ethylene glycol at 150 C.(19)

## Halogens

Uranium dicarbide will react with the halogens, usually to form compounds of the $UX_4$ type. The results are summarized in Table 9.(17)

TABLE 9. REACTION OF $UC_2$ WITH THE HALOGENS(17)

| Reactant | Temperature, C | Product | Comments |
|---|---|---|---|
| Chlorine | 350 | Volatile chloride | -- |
| | 600 | $UCl_4$ | -- |
| Fluorine | 30 | -- | No reaction |
| | 30 | -- | Explosive reaction |
| Bromine | 390 | -- | Ignites in bromine vapor |
| | 800-900 | $UBr_4$ | -- |
| Iodine | 500 | $UI_4$ | -- |

## $CO_2$

Uranium monocarbide oxidizes at 500 C in a $CO_2$ atmosphere at an 8-atm gas pressure.(6)

## $H_2S$

Uranium monocarbide ignited in $H_2S$ at 600 C producing a sulfide.(17)

### $NH_3$

Uranium dicarbide was partially decomposed by $NH_3$ at a red heat.(17)

### Hydrogen

UC is compatible with hydrogen, if no second phases are present.(6)

### Solvents

Acetone, alcohol, benezene, carbon tetrachloride, kerosene, xylene, and Zyglo solutions did not react with UC during a 5-hr exposure at room temperature.(7)

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# PREPARATION AND FABRICATION OF NUCLEAR CARBIDES

## THERMODYNAMICS

J. J. Ward and G. W. Cunningham

### Introduction

The thermodynamic data presented here have been used primarily in studies of the preparation of carbides. Although the basic data were obtained from the literature, as indicated, calculations made by the authors on some of the more interesting reactions also have been included. In the latter instances, it was necessary to extrapolate low-temperature data for use at high temperatures, and, consequently, the calculated data presented for various reactions are estimated values only.

Reactions considered for preparation of the carbides include those involving gaseous reactants, condensed-phase reactants (gas-liquid and gas-solid), and solid-solid reactants. Basic data available for uranium, thorium, and plutonium carbides which apply to all these reactions are listed in Table 10. These data were selected for use because they appear to be the most reliable data available. A more detailed compilation of the thermodynamic data available in the literature has been published by Strasser(1).

TABLE 10. THERMODYNAMIC PROPERTIES(a) OF THE CARBIDES OF URANIUM, THORIUM, AND PLUTONIUM

| | UC(b) | $UC_2$(b) | $ThC_2$ | PuC |
|---|---|---|---|---|
| Heat of Formation at 25 C, $\Delta H_f^\circ$, cal per g mole | -20,000 | -42,000 | -44,800 | -25,000 |
| Free Energy of Formation at 25 C, $\Delta G_f^\circ$, cal per g mole | -18,900 | -41,100 | -44,030 | -24,400 |
| Entropy of Formation at 25 C, $\Delta S_f$, cal/(g mole)(K) | -3.70 | -3.0 | -2.6 | -2.0 |
| Reference | (2,3) | (4) | (5) | (6) |

(a) Thermodynamic data for the metal carbides at higher temperatures were computed by the method given in "Chemistry and Metallurgy of Miscellaneous Materials", TID-5212 (1955).

(b) Heat-Capacity Equations for Uranium Carbides:

| | Reference |
|---|---|
| $UC_2 = 8.92 + 5.95 \times 10^{-3}\ T$ | (7) |
| $UC = 7.6 + 2.85 \times 10^{-3}\ T$ | (2) |

### Preparation of Carbides - Gaseous Reactants

Hydrocarbon gases have been considered for reduction of both gaseous and condensed uranium phases. The relative reduction potential of the various hydrocarbons can be obtained by examination of the data in Table 11. Although the free energy of formation is positive for most of the gases at relatively low temperatures, cracking into hydrogen, carbon, and unsaturated hydrocarbons does not usually occur without benefit of a catalyst up to relatively high temperatures (approximately 1800 F). If cracking does not occur until the reaction takes place, those gases with a higher positive free energy will contribute more driving force for the production of the carbide. Although data have not been reported, the catalytic effect of plutonium, uranium, thorium, or their compounds, on the cracking of the hydrocarbons should be considered in reactions of this type. Also, those materials used in the reaction vessel or purification train should not produce cracking. It is evident that, if cracking occurs before the reaction takes place, the reactants are the fuel compound and carbon in a hydrogen atmosphere. In the case of gases such as acetylene, considerable driving force for the production of the carbide would be lost.

TABLE 11. HYDROCARBON REDUCTION POTENTIAL OF FUEL COMPOUNDS(a) STANDARD FREE ENERGY OF FORMATION OF HYDROCARBONS(8)

| Temperature | | Standard Free Energy of Formation, $\Delta G_f^\circ$, cal per g atom carbon | | | | | |
|---|---|---|---|---|---|---|---|
| F | K | Methane, $CH_4$ | Propane, $1/3C_3H_8$ | n-Butane, $1/4C_4H_{10}$ | n-Octane, $1/8C_8H_{10}$ | Acetylene, $1/2C_2H_2$ | Benzene, $1/6C_6H_6$ |
| 620 | 600 | -5,490 | +5,170 | +6,150 | +7,750 | +22,920 | +7,280 |
| 980 | 800 | -550 | +10,150 | +11,130 | +12,770 | +21,590 | +8,810 |
| 1340 | 1000 | +4,610 | +15,230 | +16,180 | +17,850 | +20,300 | +10,380 |
| 1700 | 1200 | +9,850 | +20,330 | +21,260 | +22,940 | +19,045 | +11,970 |

(a) The higher the positive value of $\Delta G_f^\circ$, the greater is the reducing power of the hydrocarbon. At higher temperatures, the data are unrealistic since thermal cracking may occur.

The reduction of $UF_6$ to UC by hydrocarbons has been considered in detail(9) and some of the results, based on data by Glassner(10), are shown in Table 12. These results indicate that $UF_4$ would form as an intermediate product and that, under equilibrium conditions, the reduction of $UF_6$ to UC would not go to completion. Reactions with other halides were not considered. Bromides, chlorides, and iodides are not generally considered for preparation of the carbides, since other fuel compounds are more readily available. However, since $UF_6$ is used to produce other uranium compounds its use would be desirable if conditions could be found under which UC could be produced from $UF_6$.

## Preparation of Carbides — Condensed Phase Reactants

The most commonly considered reactions for the production of carbides by use of a hydrocarbon gas involve the reaction of the metal, the oxide, or, in some cases, the hydride with methane. The data for these reactions are given in Table 13. Similar results would be expected with other hydrocarbons, although more favorable results would be indicated for those compounds with a higher positive free energy of formation as listed in Table 11.

The reduction of $UF_6$ to UC by graphite has also been considered(9), and, as indicated in Table 14, the reaction is not favorable. Another reaction which is feasible but which involves the separation of solid products is the reduction of $UF_6$ to UC by calcium carbide and calcium. Data for this reaction are given in Table 15. Since $UF_4$ will also be reduced no difficulty is encountered because of $UF_4$ formation.

TABLE 12. STANDARD FREE-ENERGY CHANGES OF THE REACTION OF $UF_6(g)$ TO UC(c) SHOWING THE FREE-ENERGY CHANGES OF THE INTERMEDIATE $UF_4(c, g, l)$

The over-all reaction(9) is: $UF_6(g) + H_2(g) + CH_4(g) \rightleftharpoons UC(c) + 6HF(g)$.

| | | Standard Free-Energy Change, $\Delta G^\circ_T$, cal | | | |
|---|---|---|---|---|---|
| Reaction | Reaction | 1000 K (1340 F) | 1200 K (1700 F) | 1500 K (2240 F) | 2073 K (3270 F) |
| 1(a) | $UF_6(g) + H_2(g) \rightarrow UF_4(c, l) + 2HF(g)$ | -69,070 | -70,690 | -71,270 | -84,670 |
| 2(b) | $UF_6(g) + H_2(g) \rightarrow UF_4(g) + 2HF(g)$ | -- | -- | -64,870 | -97,440 |
| 3(a, c) | $UF_4(c, l) + CH_4(g) \rightarrow UC(c) + 4HF(g)$ | +83,430 | +64,850 | +39,090 | -8,090 |
| 4(b, c) | $UF_4(g) + CH_4(g) \rightarrow UC(c) + 4HF(g)$ | -- | -- | +32,690 | +4,680 |
| 5(c) | $UF_6(g) + H_2(g) + CH_4(g) \rightarrow UC(c) + 6HF(g)$ | +14,360 | -5,840 | -32,180 | -92,760 |

(a) In Reactions 1 and 3, $UF_4$ is shown as a liquid at 2073 K, which is above the boiling point of $UF_4$. Therefore, this reaction would have to be compressed.

(b) In Reactions 2 and 4, $UF_4$ is shown as a gas at 1500 K. $UF_4$ boils at 1690 K, and therefore, this reaction would have to be carried out at diminished pressures.

(c) Methane would crack to carbon and hydrogen above 1700 F.

TABLE 13. STANDARD FREE-ENERGY CHANGE OF THE REACTION OF FUEL METALS, OXIDES, AND HYDRIDES WITH METHANE GAS

| | Standard Free-Energy Change, $\Delta G^\circ_T$, cal | |
|---|---|---|
| Reaction | 1000 K | 1200 K |
| $UO_2(c) + 4CH_4(g) \rightleftharpoons UC_2(c) + 2CO(g) + 8H_2(g)$ | | |
| $UO_2(c) + 3CH_4(g) \rightleftharpoons UC(c) + 2CO(g) + 6H_2(g)$ | +90,380 | +66,560 |
| $ThO_2(c) + 4CH_4(g) \rightleftharpoons ThC_2(c) + 2CO(g) + 8H_2(g)$ | +93,910 | +53,870 |
| $PuO_2(c) + 3CH_4(g) \rightleftharpoons PuC(c) + 2CO(g) + 6H_2(g)$ | +71,850 | +39,550 |
| $U(c) + 2CH_4(g) \rightleftharpoons UC_2(c) + 4H_2(g)$ | -48,220 | -58,100 |
| $U(c) + CH_4(g) \rightleftharpoons UC(c) + 2H_2(g)$ | -22,620 | -27,020 |
| $Th(c) + 2CH_4(g) \rightleftharpoons ThC_2(c) + 4H_2(g)$ | -51,620 | -61,580 |
| $Pu(c) + CH_4(g) \rightleftharpoons PuC(c) + 2H_2(g)$ | -27,610 | -32,450 |
| $2UH_3(c) + 2CH_4(g) \rightleftharpoons 2UC(c) + 7H_2(g)$ | $UH_3$ is dissociated to $U(c) + 3/2$ $H_2(g)$ at these temperatures | |
| $2UH_3(c) + 4CH_4(g) \rightleftharpoons 2UC_2(c) + 11H_2(g)$ | | |

TABLE 14. THE STANDARD FREE-ENERGY CHANGE FOR THE REDUCTION OF $UF_6(g)$ BY CARBON TO UC(c)

$$UF_6(g) + C(c) \rightleftharpoons UC(c) + 3/2CF_4(g).$$

| Temperature<br>F | <br>K | Standard Free-Energy Change, $G^\circ_T$, cal | $\log_{10}$ Equilibrium Constant, $\log_{10} K$ | Equilibrium Conversion of $UF_6(g)$ to UC(c) at 1 Atm Pressure, per cent |
|---|---|---|---|---|
| 3140 | 2000 | +217,050 | -23,716 | -- |
| 4040 | 2500 | +209,650 | -18,326 | $6.1 \times 10^{-11}$ |

TABLE 15. STANDARD FREE-ENERGY CHANGE FOR REDUCTION OF URANIUM FLUORIDES TO UC WITH $CaC_2$ AND CALCIUM

| Reaction | Free-Energy Change, $G^\circ_T$, cal | Temperature, C |
|---|---|---|
| $2UF_6(g) + 5Ca(c,l,g) + CaC_2(c) \rightleftharpoons 2UC(c) + 6CaF_2(c,l)$ | -655,740 | 727 |
| | -550,900 | 1800 |
| | -477,820 | 2227 |
| $2UF_4(g) + 3Ca(c,l,g) + CaC_2(c) \rightleftharpoons 2UC(c) + 4CaF_2(c,l)$ | -283,740 | 727 |
| | -274,900 | 1800 |
| | -233,820 | 2227 |

TABLE 16. STANDARD FREE-ENERGY CHANGE OF REACTIONS FOR THE PREPARATION OF NUCLEAR CARBIDES FROM THEIR CORRESPONDING OXIDES BY THE ACTION OF CARBON

| Reaction | Standard Free-Energy Change, $\Delta G^\circ_T$, cal | | | | | | | | Equilibrium Partial Pressure of CO at 2200 K, mm of mercury |
|---|---|---|---|---|---|---|---|---|---|
| | 900 K | 1000 K | 1200 K | 1400 K | 1600 K | 1800 K | 2000 K | 2200 K | |
| $UO_2(c) + 3C(c) \rightleftharpoons UC(c) + 2CO(g)$ | +112, 060 | +104, 210 | +88, 530 | +72, 980 | +57, 520 | +41, 940 | +26, 350 | +10, 760 | 221.7 |
| $ThO_2(c) + 4C(c) \rightleftharpoons ThC_2(c) + 2CO(g)$ | +116, 900 | +108, 370 | +91, 270 | +74, 320 | +57, 450 | +40, 720 | +24, 080 | +11, 990 | 192.7 |
| $PuO_2(c) + 3C(c) \rightleftharpoons PuC(c) + 2CO(g)$ | +92, 040 | +85, 680 | +69, 100 | +53, 160 | +37, 250 | +21, 360 | +5, 520 | -10, 320 | 2471.5 |

TABLE 17. STANDARD FREE-ENERGY CHANGE FOR THE FORMATION OF CARBIDES BY REACTION OF FUEL METALS WITH CARBON[(a)]

| Reaction | Standard Free-Energy Change, $\Delta G^\circ_T$, cal | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 900 K | 1000 K | 1200 K | 1400 K | 1600 K | 1800 K | 2000 K | 2200 K |
| $U(c) + C(graphite) \rightleftharpoons UC(c)$ | -18, 400 | -18, 010 | -17, 170 | -16, 300 | -15, 200 | -14, 600 | -14, 000 | -13, 400 |
| $U(c) + 2C(graphite) \rightleftharpoons UC_2(c)$ | -39, 300 | -39, 000 | -38, 400 | -37, 800 | -37, 200 | -36, 600 | -36, 000 | -35, 400 |
| $Th(c) + 2C(graphite) \rightleftharpoons ThC_2(c)$ | -42, 660 | -42, 400 | -41, 880 | -41, 360 | -40, 840 | -40, 320 | -39, 800 | -39, 280 |
| $Pu(c) + C(graphite) \rightleftharpoons PuC(c)$ | -24, 820 | -23, 000 | -22, 600 | -22, 220 | -21, 800 | -21, 400 | -21, 000 | -20, 600 |

(a) At all temperatures $UH_3$ will decompose to uranium and hydrogen.

## Preparation of Carbides — Solid-Solid Reactions

The solid-state reactions generally involve the formation of the carbide by reacting the metal, the oxide, the hydride or another carbide with carbon. If extended to a sufficiently high temperature, reactions with the liquid metal may also be considered.

Reactions of carbon with the oxide are listed in Table 16. Because of the relatively low equilibrium pressure of CO, these reactions are usually carried out *in vacuo*.

Reactions of the metal, either as metal or starting with $UH_3$, with carbon are shown in Table 17.

The reaction of carbon with UC to form $UC_2$ is considered in Table 18.

TABLE 18. STANDARD FREE-ENERGY CHANGE(a) OF THE REACTION:

$UC(c) + C(c) \rightleftharpoons UC_2(c)$

| Temperature, K | Free-Energy Change $\Delta G^\circ_T$, cal |
|---|---|
| 900 | -20,900 |
| 1000 | -20,990 |
| 1200 | -21,230 |
| 1400 | -21,500 |
| 1600 | -22,000 |
| 1800 | -22,000 |
| 2000 | -22,000 |
| 2200 | -22,000 |

Other reactions which have been considered, but which do not appear favorable below about 1800 C include: (1) $UF_4 + SiC \rightleftharpoons UC + SiF_4$ and (2) $US + C \rightleftharpoons UC + 1/2S_2$. The first of these reactions probably would be complicated by the formation of a uranium silicide.

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## PREPARATION BY CHEMICAL REACTIONS

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### Introduction

Various methods other than arc melting have been investigated experimentally for the preparation of uranium carbides. These include reaction of uranium with hydrocarbons and the reaction of uranium and uranium oxides with carbon. The thermodynamics of the reactions to be discussed can be found in the previous section.

### Reaction of Uranium With Hydrocarbons

The cracking of alkane hydrocarbons to hydrogen, carbon, and alkenes must be considered in any high-temperature reactions involving these compounds. Thermodynamic calculations predict that the cracking of alkanes should occur at relatively low temperatures, some at room temperature. However, it is known that many of the hydrocarbons are stable at temperatures on the order of 2000 F, and in many cases catalysts are required to crack the compounds at temperatures well above their predicted decomposition temperature.

In the reactions involving the production of UC, it is not known whether uranium acts to any degree as a catalyst. If no catalytic effect is obtained, the reactions are carried out at a temperature at which the hydrocarbon gas is stable. The importance of whether or not the hydrocarbon cracks may be illustrated by comparing the reactions: (1) $U + CH_4 \rightarrow UC + 2H_2$ and (2) $U + C \rightarrow UC$. At 900 K the free-energy change for the first reaction is -23,130 cal, and for the second reaction it is -20,550 cal. Thus, in the second reaction the additional driving force provided by the decomposition of the methane is lost, and, except as a matter of convenience in adding reactants, the same results could be obtained by reacting carbon and uranium in a hydrogen atmosphere.

## Uranium-Methane Reaction

The reaction of uranium with methane, $U + CH_4 \rightarrow UC + 2H_2$, has been successfully used to produce UC of near stoichiometric composition.(1) Nibbled uranium or uranium turnings and powder have been used as the starting material. The uranium should be pickled in a 50:50 nitric acid-water solution to remove oxide, rinsed thoroughly in water and dried in alcohol or acetone. The cleaned uranium should then be quickly transferred to a vacuum chamber to limit oxidation. After thorough outgassing at 250 to 300 C the metal is hydrided at 200 to 250 C to produce a fine uranium powder. This powder is then reacted with methane gas at a pressure of less than 1/2 atm at a temperature of 650 to 700 C. After several charges of methane have been added it is beneficial to drop the temperature and hydride the unreacted metal. This is done to maintain a loose mass so that the reaction with methane will occur freely when the temperature is again raised. The completion of the reaction is indicated when no decrease in pressure occurs as the reaction tube is allowed to cool to room temperature after it has been evacuated and filled with hydrogen at 650 C. If a decrease in pressure is noted, hydriding, breaking down of the hydride, and reaction with methane are repeated until the reaction with methane is complete.

Uranium carbide prepared at Battelle, by the method described above, has a typical chemical analysis of 4.88 w/o total carbon and 0.31 w/o free carbon. An X-ray diffraction pattern of this material shows a very strong UC pattern, a faint $UC_2$ pattern, and a diffuse medium-strong pattern of an unknown.

Litz(2) reports that X-ray diffraction patterns of UC prepared by the above method indicate that metallic uranium and crystalline graphite are absent from the product. He reports a typical analysis as being 94.8 w/o uranium.

Kalish, Bowman, and Crane(3) also report studies of the uranium-methane reaction. Their technique involves passing methane at a rate of 5 $ft^3$ per hr over uranium metal powder and uranium hydride starting material at a temperature of 700 C. After 2 hr at temperature with a starting material of fine uranium powder, X-ray diffraction patterns indicated UC and uranium were present in the product. A duplicate experiment using uranium hydride as a starting material instead of fine uranium powder yielded only UC, as indicated by an X-ray diffraction pattern.

A patent has been issued to R. W. Fisher(4) describing the production of uranium monocarbide by heating uranium metal in the range of 400 to 1125 C in contact with methane, or an aliphatic hydrocarbon. The amount of hydrocarbon employed is adjusted so that its carbon content corresponds to about 4.8 w/o of the uranium metal.

## Uranium-Propane Reaction

Kizer(1) has employed the $U + CH_8 \rightarrow UC + 4H_2$ reaction. Fine uranium powder prepared by the thermal decomposition of uranium hydride was reacted with propane at 538 C to produce UC having a total-carbon analysis of 4.68 w/o and a free-carbon analysis of 0.32 w/o. An X-ray diffraction pattern of the product indicated a very strong but diffuse pattern of UC and a very faint pattern of unknown. No free-uranium or graphitic-carbon lines appeared in the pattern. The procedure for the propane reaction was the same as previously described for the methane reaction except that the chamber was filled with propane at a pressure of 1/4 atm or less, and the reaction was carried out at a temperature of 538 C. Increasing the temperature of the reaction above 538 C to 650 C had no noticeable effect on the reaction rate. The completion of the reaction was indicated when no decrease in pressure occurred as the reaction tube was allowed to cool to room temperature after it was evacuated and filled with hydrogen at 538 C. If a decrease in pressure was noted, hydriding, breaking down of the hydride under vacuum, and reaction with propane was repeated until the reaction with propane was complete.

### Uranium-Acetylene Reaction

The reaction of uranium with acetylene to form UC, $2U + C_2H_2 \rightarrow 2UC + H_2$, has been reported by Litz(2) to have an appreciable rate at 500 C. The product is reported to contain relatively large quantities of carbon, making it impractical for producing pure stoichiometric UC.

## Reaction of Uranium Oxides With Carbon

The standard free-energy change for the reaction $UO_2(c) + 3C(c) \rightleftharpoons UC(c) + 2CO(g)$ is +16,000 cal at 1800 C. Experimental results indicate that the reaction of $UO_2$ with carbon can take place at low temperatures if the CO partial pressure is maintained low enough. If $U_3O_8$ is used instead of $UO_2$ for the formation of UC by combining with carbon, the above reaction would still control as the $U_3O_8$ probably goes to $UO_2$ at a temperature lower than that required for the beginning of the $UO_2$-carbon reaction. This assumption is further verified by experimental data reported by Litz(2). It was observed that after the initial evolution of absorbed gases during vacuum heating of $U_3O_8$-carbon mixtures, at relatively low temperature, no further gas evolution of sufficient magnitude to increase the pressure in the system occurred until the temperature reached 1000 C. A second stage of gas generation occurred at 1400 C. When $UO_2$ was used instead of $U_3O_8$ the lower temperature stage was not observed.

Mixes of the stoichiometric composition of UC have been prepared from $UO_2$ and carbon and from $U_3O_8$ and carbon by ball milling or grinding and then reacting the mixture in vacuum at temperatures as high as 2100 C. Considerable outgassing has been reported at temperatures as low as 1300 C.(5) When the reaction temperature was increased to 1500 C and held until a vacuum of 1 μ was obtained, the X-ray diffraction pattern of the product indicated phases of $UO_2$, UC, and a very faint pattern of unknown. Similar results have been reported for reactions run 10 hr at 1300 C.(3) A mixture of $UO_2$-carbon and UC has been reported after vacuum reacting similar mixes at temperatures as high as 2100 C.(6,7) It has been reported that a temperature of 2500 C is necessary to obtain dense, homogeneous uranium carbides by vacuum reaction of uranium oxide-carbon mixtures.(8)

A patent describing the formation of uranium carbides of low carbon content (less than 10 w/o) from the oxides $UO_2$ or $U_3O_8$ and carbon has been issued to Wilhelm and Daane.(9) In one of the examples cited, a mixture of finely powdered $UO_2$ and graphite was first pressed at 26 tsi to the form of a bar, 1/2 by 1/2 by 2 in., and heated to 2300 C for 20 min in a graphite crucible. The product had a composition of $UC_{1.27}$.

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# AN EVALUATION OF DATA ON NUCLEAR CARBIDES

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May 31, 1960

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Several variants of the method, which concern the mode of mixing, heating, etc., are covered by this patent.

The reaction $UO_2 + 4C \rightarrow UC_2 + 2CO$ has also been studied for the formation of $UC_2$. Similar $UO_2$ and carbon contamination in the product was reported as for the uranium oxide reaction reported above. The reaction was accomplished by heating 20 g of lampblack and 80 g of $UO_2$ in a graphite crucible after pressing at 80 tsi. The reaction time was 1-1/2 hr at 2100 C.(10) The product was a mixture of excess lampblack and small $UC_2$ nodules not clearly separable. Daane, et al., report similar results.(8)

## Reaction of Uranium Metal With Carbon

Several techniques have been investigated for the direct combination of uranium with carbon to form $UC_2$ or UC. Brett, Law, and Livey have prepared $UC_2$ by sintering uranium-graphite powder cores at 1500 C(11) according to the $U + 2C \rightarrow UC_2$ reaction. A minimum sintering temperature of 1500 C is reported necessary to eliminate the presence of UC in the product. Rubenstein and Kopelman(10) describe the preparation of $UC_2$ ingots by melting uranium in a thick-walled graphite crucible. Free carbon was found to be minimized by keeping the temperature of the melt from rising above 2375 C. Carbon analyses of 8.38 to 8.78 w/o were reported for the ingot. Free graphite varied from 1.23 to 3.08 w/o.

The formation of UC by the direct combination of uranium plus carbon, $U + C \rightarrow UC$, has been investigated by several workers. Various methods yield a product varying from fine powder to dense UC pellets.

Uranium monocarbide powder has been prepared by Daane, Spedding, and Wilhelm(8) and Chiotti(12) by mixing graphite and uranium hydride powder. The uranium hydride and graphite were thoroughly mixed, heated slowly to 900 C, and sintered at 1600 to 1700 C. No analysis of the product was reported.

A patent has been issued to Newton and Johnson(13) for the preparation of compounds of uranium and nonmetals. A process is described for preparing a compound of a nonmetal and uranium by reacting uranium hydride with the vapors of a compound of hydrogen and a nonmetal, such as arsenic, boron, carbon, nitrogen, phosphorus, selenium, sulfur, and tellurium.

Litz(2) investigated the feasibility of preparing UC by heating uranium-carbon mixes in beryllium oxide crucibles to 1800 C. The product was a sintered mass containing free metal admixed with graphite. Higher temperatures resulted in excessive crucible attack. When a graphite crucible was used instead of a beryllium oxide crucible, the formation of some $UC_2$ resulted.

Methods of preparing dense UC compacts by extruding or hot compacting uranium-carbon mixes followed by reacting to form UC by sintering at high temperatures are also discussed in a later section of this report.

## Thorium and Plutonium Carbides

Information is not available in the literature on the preparation of thorium or plutonium carbides by chemical reactions; however, the thermodynamics of possible reactions leading to the formation of thorium and plutonium carbides were discussed in the previous section.

## Discussion

There are many variables to consider in the evaluation of the economics of various methods of producing uranium carbide for fuel fabrication. At the present time, it is possible only to point out some of the advantages and disadvantages of different processes. Basically, there are two needs to be met in the production of UC for fuel-element fabrication: (1) production of powders of UC suitable for powder fabrication processes and (2) production of UC in the form of chunk or sinter cake suitable for feed material in the casting process. A process which would produce carbide directly from uranium hexafluoride would be highly desirable from the point of view of costs.

The reaction of hydrocarbons with $UH_3$ or fine uranium metal powder to produce UC powder has been investigated only on a laboratory scale, but the powders produced have been evaluated to some extent. The technique of producing UC powder by reacting fine uranium powder with methane yields a powder with a particle size in the neighborhood of 10 $\mu$ or less. This powder is not extremely pyrophoric; it can be handled for short periods of time in air, although it is advisable to maintain a protective atmosphere wherever possible. There is some indication that the UC powder produced by reacting fine uranium metal powder with methane or propane is more desirable for sintering to high densities than powders produced by other techniques.

In the reaction of uranium oxides with carbon to produce UC, large vacuum-pumping capacities appear necessary to evacuate the large quantity of CO liberated during the reaction. Temperature from 1300 to 2100 C are reported to be necessary to drive the reaction. This process is being considered commercially; however, difficulty may be encountered in separating the products if the reaction does not go to completion. There appears to have been little evaluation conducted on the carbide produced by the reaction. Its suitability as feed material for casting has not been evaluated. Similarly, it has not been seriously evaluated as a source of powder for powder-metallurgy processes.

Several other processes have been considered by the authors, based upon the available thermodynamic data, as indicated in the section on thermodynamics. The reaction which appears most attractive thermodynamically is one involving reduction of $UF_6$ with calcium and calcium carbide to produce UC. Some of the disadvantages of such a process would be the need for separation of the UC from the other reaction products and the unavailability of production quantities of pure calcium carbide. However, if economic production is to be achieved, direct reduction from the fluoride is obviously desirable, and potential processes of this type should be studied.

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## MELTING AND CASTING

B. C. Boesser and E. Foster

### Introduction

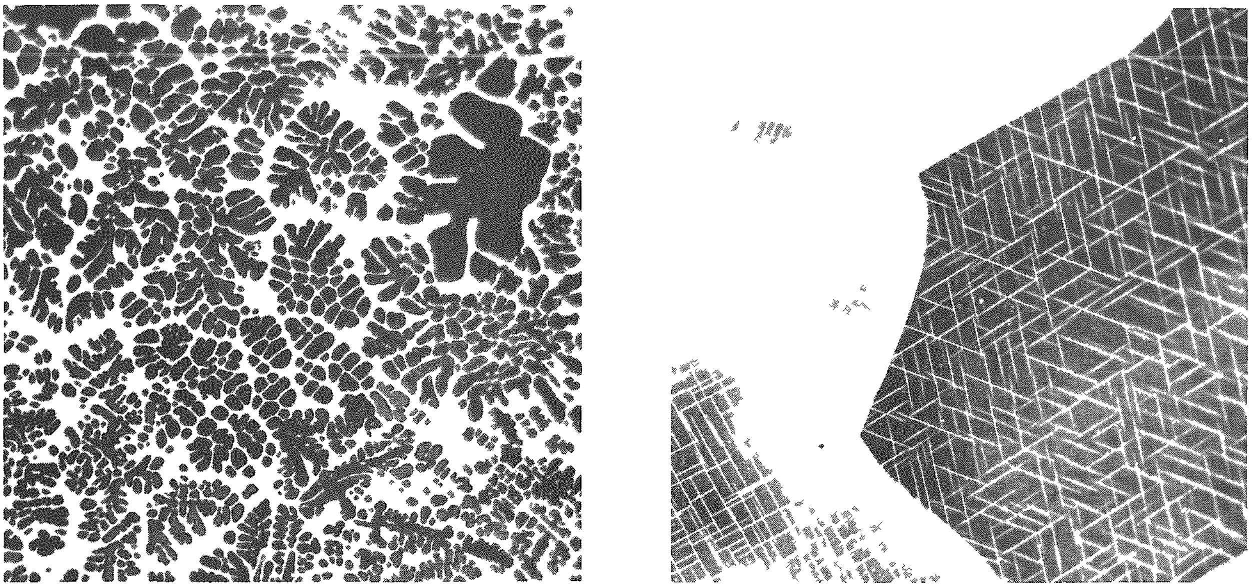
The first castings of uranium carbide were made by the reaction of $UO_2$ and graphite to form $UC_2$.(1) Mallinckrodt $UO_2$ and high-purity graphite in a ratio of 5.62 to 1 were packed into a graphite crucible and induction heated to 2100 to 2300 C, where reaction between the $UO_2$ and graphite occurred. After the evolution of $CO_2$ gas was essentially complete, the temperature was raised to 2500 C, and a plunger in the bottom of the crucible was pulled, allowing the molten carbide to pour into a graphite mold directly under the crucible. The melting was done in a covered crucible without a protective atmosphere. The $UC_2$ casting produced was sound, homogeneous, and possessed a density of 10.8 g per $cm^3$. Alloys containing 7 to 9.2 w/o carbon were made in a similar crucible without a mold. A 5.7 to 1 ratio of $UO_2$ to carbon gave a $UC_2$ ingot which contained 9.15 w/o carbon; a 7.9 to 1 ratio resulted in an ingot containing 7.21 w/o carbon. It is not practical to produce uranium monocarbide by induction melting in a graphite crucible, since UC reacts very rapidly with the crucible, forming $UC_2$.

### Melting Techniques

All three of the stable carbides of uranium have been produced and cast by nonconsumable arc melting under a helium or argon atmosphere.(2-9) Metallic uranium and graphite are charged into an inert-electrode arc furnace equipped with a water-cooled copper hearth. The electrode tips may be either graphite or tungsten. Graphite tips have a tendency to raise the carbon content of the melt; however, tungsten tips have a tendency to erode, resulting in contamination of the charge. Charges are usually melted six or seven times. The buttons are turned over between melts to insure good homogeneity. Castings containing from 2.2 to 10 w/o carbon have been produced by this method. Alloys containing less than 4.8 w/o carbon show free uranium in their microstructures. The microstructures of alloys containing 4.8 w/o carbon show 100 per cent UC, and those containing more than 4.8 w/o carbon and less than 9.1 w/o carbon show either UC with acicular $UC_2$ or $UC_2$ with acicular UC, according to the composition. Castings of 9.16 w/o carbon are 100 per cent $UC_2$. Only by heat treating is $U_2C_3$ produced. Typical microstructures of as-cast and heat-treated alloys are shown in Figure 27.

### Casting Techniques

Small cylindrical UC castings, up to 3/4 in. in diameter by 1-3/4 in. long, have been made by "drop casting" in a helium atmosphere.(2) A thin-walled graphite thimble mold is suspended in a copper support block by an integral graphite collar inside an arc-melting furnace. A photograph of the mold is shown in Figure 28. A 100-g arc-melted button is placed on the mouth of the mold, and most of the button is melted by a low-current arc. By increasing the current and holding the arc directly over the mouth of the mold, the button is melted through and dropped into the mold. The castings produced

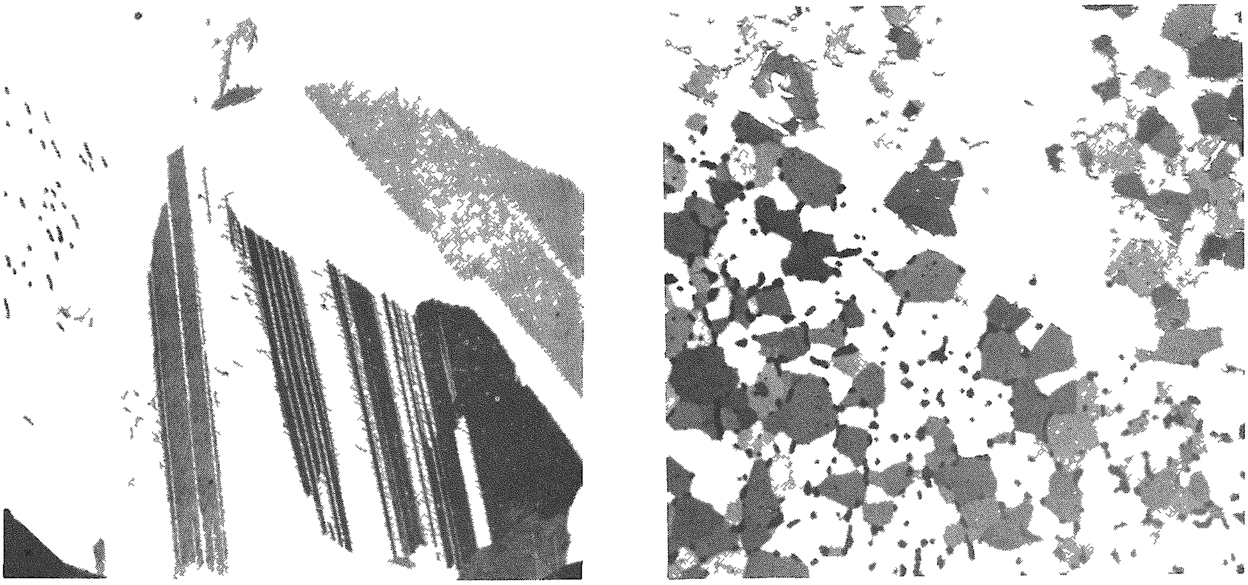


250X RM13806

Uranium-2.2 w/o Carbon As Cast

250X RM13811

Uranium-5.0 w/o Carbon As Cast



250X RM13821

Uranium-8.5 w/o Carbon As Cast

250X RM14461

Uranium-7.0 w/o Carbon Annealed 1 Hr at 1550 C

FIGURE 27. TYPICAL MICROSTRUCTURES OF URANIUM CARBON ALLOYS

N51385

N51387

FIGURE 28. PHOTOGRAPH OF TYPICAL DROP-CASTING MOLD SETUP, CHARGE, AND CASTING

by this method, as shown in Figure 29, are well formed and free of cracks. The reproducibility of this technique is very good, and the castings show good uniformity from top to bottom. Analyses of four typical small castings produced by the drop-casting technique are given in Table 19.(3)

TABLE 19. ANALYSES OF SMALL CAST UC SHAPES PREPARED BY DROP-CASTING TECHNIQUES

| Casting Identification[a] | Location of Sample[b] | Carbon Content, w/o |
|---|---|---|
| 1 | Skull | 5.00 |
| | Top | 5.00 |
| | Bottom | 4.96 |
| 2 | Skull | 4.90 |
| | Top | 4.92 |
| | Bottom | 4.87 |
| 3 | Skull | 4.88 |
| | Top | 4.90 |
| | Bottom | 4.94 |
| 4 | Skull | 5.02 |
| | Top | 4.95 |
| | Bottom | 4.92 |

(a) All castings were 5/8 in. in diameter by 2-1/2 in. long.

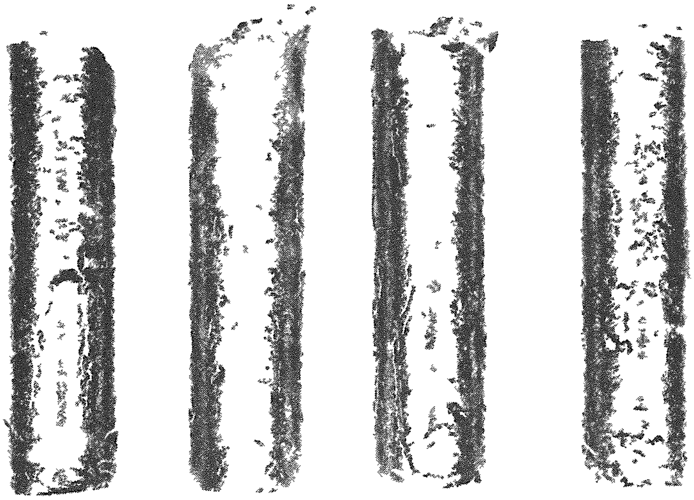
(b) The sample location referred to as "skull" is in the topmost portion of the tack-shaped drop casting.

The sample location referred to as "top" is in the top of the cylindrical section of the drop casting.

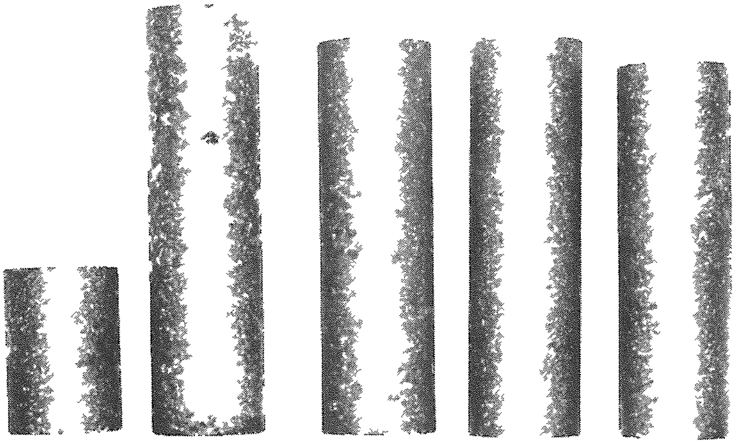
The sample location referred to as "bottom" is in the bottom of the cylindrical section of the drop casting.

Drop-casting techniques have been used to prepare castings up to 0.8 in. in diameter and 6 in. long.(4) The process used is similar to that described above except that a solid graphite hearth is employed. Difficulties have been encountered in controlling the composition of castings made from this hearth, but it is believed that this problem can be solved.

Large cylindrical UC castings up to 2 in. in diameter by 8 in. long have been made by a skull-type arc-melting procedure using an inert atmosphere.(10,11) A large UC skull is prepared in a water-cooled copper crucible from uranium and commercial graphite electrode stock by melting small charges. Metallic uranium and graphite are placed on top of the completed skull and melted at 3600 amp and 20 v, using a graphite electrode tip. When a large molten pool has formed, it is poured quickly into an induction-heated graphite mold. Large, sound castings of several shapes have been produced using this method. A photograph of several of these shapes is shown in Figure 30. Surface quality and homogeneity are very good. Compositional variations from melt to melt exceed those found in drop-cast material (±0.1 w/o carbon for the drop castings as compared with ±0.3 w/o carbon for material made by the skull-casting technique). It has been established that a major portion of this latter variation is caused by inhomogeneities that exist

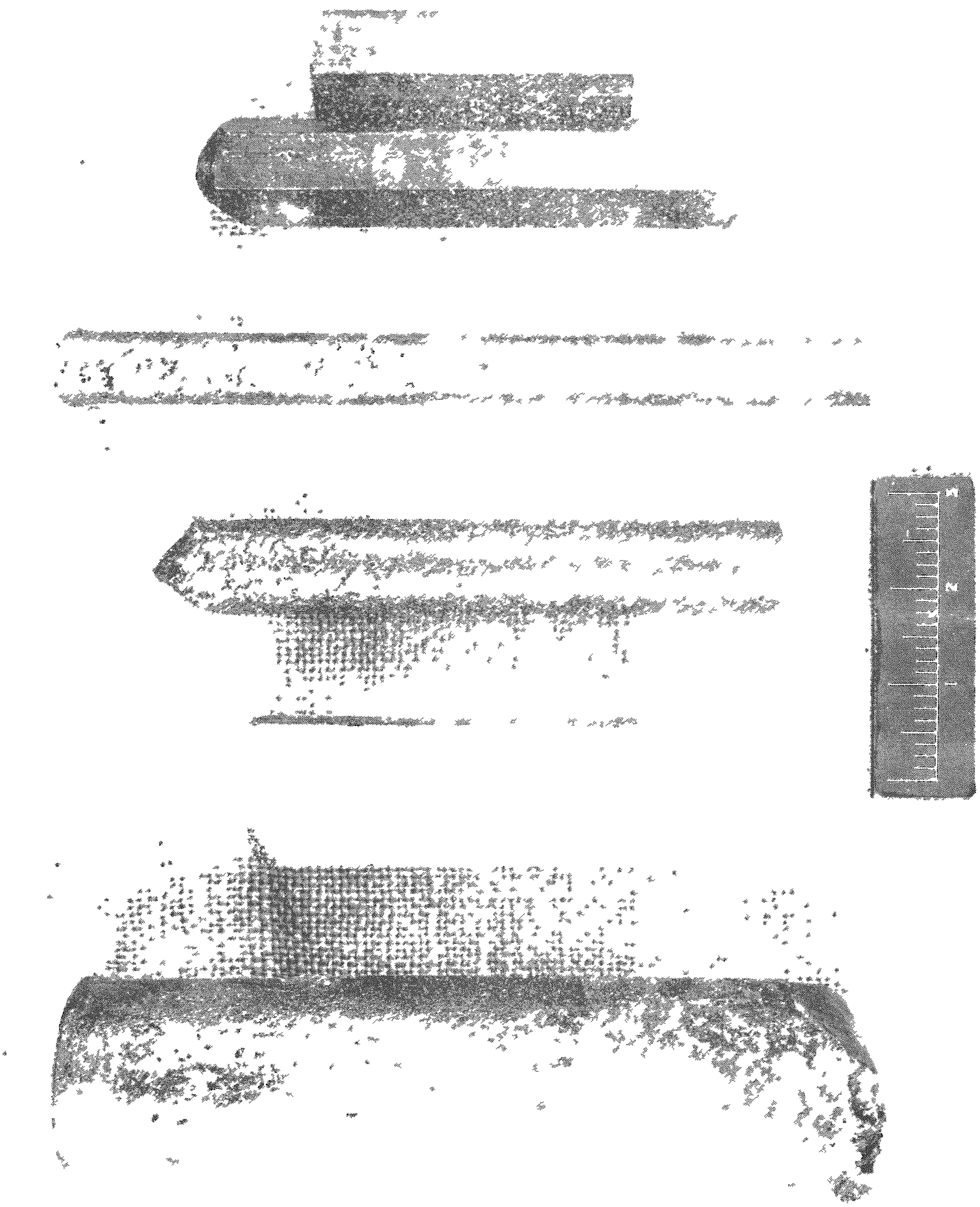


a. As Cast



b. Machined

FIGURE 29. PHOTOGRAPH OF UC SHAPES PRODUCED BY DROP-CASTING TECHNIQUES



N66418

FIGURE 36. PHOTOGRAPH OF A VARIETY OF LARGE CAST SHAPES OF URANIUM CARBIDE PRODUCED BY SKULL-TYPE ARC-MELTING TECHNIQUES

in the carbide skull. It is believed that these inhomogeneities are related to the character of the charge materials from which the skull is formed. It is expected that control of the character of the charge materials will eliminate the inhomogeneity in the skull.

The skull-type arc-melting and -casting technique is believed to have considerable potential for preparing production quantities of cast UC shapes. Quantity production can be attained by mechanization of the melting operation so as to permit the casting of several fuel slugs simultaneously, and by installing ports to allow recharging of the skull without opening the furnace.

Very little literature on the melting or casting of thorium and plutonium carbides is available. However, it appears that the same techniques that are used for uranium carbides can be used in the preparation of thorium and plutonium carbides.

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# SOLID-PHASE FABRICATION

J. M. Fackelmann and D. L. Keller

## Introduction

Dense forms of uranium carbides may be obtained by several powder-metallurgy techniques. Fabrication methods that have been used are: (1) conventional cold pressing and sintering of uranium carbide powder, (2) hot pressing of uranium carbide powder, (3) hot pressing elemental mixtures of uranium and carbon powders and subsequent reaction at high temperature, and (4) hot extruding elemental powders followed by reaction at high temperature.

Because of its higher density and other desirable characteristics, most of the work to date has been concerned with UC rather than $UC_2$. Similar techniques could probably be applied to thorium and plutonium carbides; however, very little data on these materials were found in the literature.

## Cold Pressing and Sintering

Uranium carbide powder may be obtained by several methods, as discussed in another section of this report. Since arc melting provides better compositional control of the powder at the present time, most studies have been performed using powder obtained by crushing arc-melted ingots in ball mills or by mortar and pestles. While no economical use is foreseen for fuel elements prepared from arc-melted, crushed, and sintered UC, data obtained on these powders contribute to the understanding of the basic problems involved. Other types of powders for which data have been obtained are those produced by reaction of uranium with methane or propane.

Finely divided uranium-carbon powders are generally pyrophoric and must be protected from rapid reaction with oxygen or moisture, if handled in air. Thus, the material must be crushed either in a dry box under an inert gas or while it is submerged in a fluid such as kerosene or trichloroethylene. Where the hydrocarbons are reacted with uranium to form UC, the product is already in the powder form, and crushing is carried out only if control of particle size is needed.

Binders needed during the cold pressing of brittle powders have also been used to provide protection against atmospheric attack. For example, successful processing in air can be accomplished by soaking fine uranium carbide powders in a 15 w/o camphor-methyl alcohol solution. After thorough mixing, excess alcohol is siphoned off, and the balance is removed by evaporation in air, leaving a uniform wax coating on each powder particle. This same coating can serve effectively as a binder during cold pressing and greatly enhances the green strength of the pressed compacts.

In Table 20 the measured density of arc-melted uranium-carbon alloys is compared with the maximum density of mixed uranium and carbon powders having the same carbon content. These data are useful in following the various densification and solid-state reaction processes.

TABLE 20. RELATIONSHIP BETWEEN CARBON CONTENT AND DENSITIES OF URANIUM-CARBON COMPOSITIONS

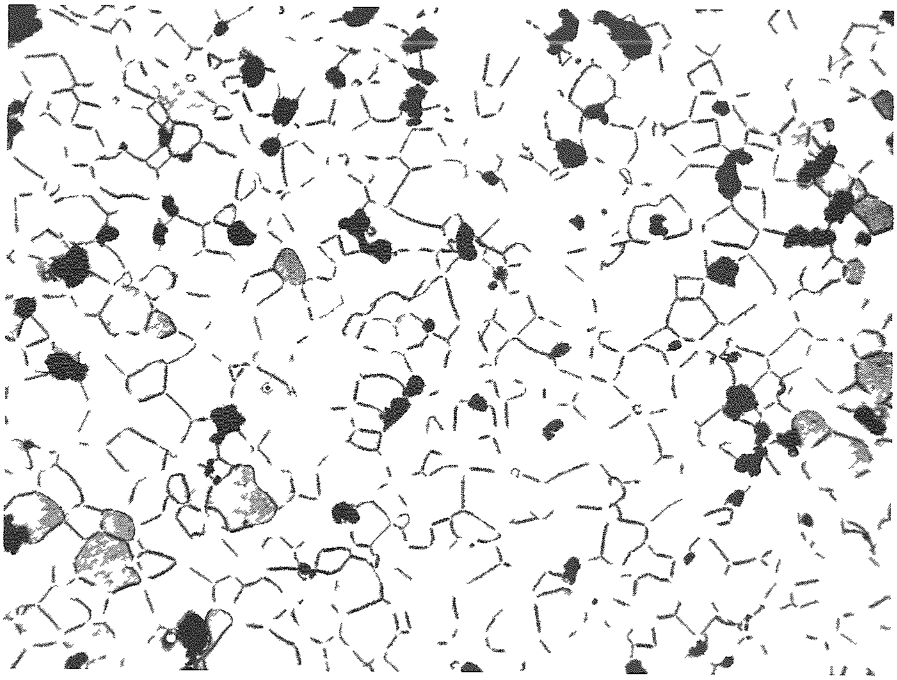
| Carbon Content, w/o | Measured Density of Arc Melted Material, g per $cm^3$ | Maximum Density of Mixed Components, g per $cm^3$ |
|---|---|---|
| 0 | 19.13 | 19.13 |
| 1 | 17.57 | 17.69 |
| 2 | 16.34 | 16.55 |
| 3 | 15.27 | 15.55 |
| 4 | 14.33 | 14.46 |
| 4.8(UC) | 13.63 | 14.01 |
| 5 | 13.42 | 13.86 |
| 9.2($UC_2$) | 11.68 | 12.23 |

Before examining data on sintered carbides it should be pointed out that the carbon content both before and during sintering as well as the impurity level has a profound effect on the sintering characteristics of these particular materials. For example, since the reaction $UC + 1/2\ O_2 \rightarrow U + CO$ will proceed rapidly at high sintering temperatures, the presence of oxygen, either in the powder or in the sintering atmosphere, may introduce liquid uranium in the sintering process even in initially hyperstoichiometric materials. Figure 31 shows typical structures of a rim and core, respectively, of the same UC specimen. In the rim sintering has progressed to a highly advanced stage with only isolated closed voids remaining in the grain boundaries. Appreciable grain growth and formation of equiaxed grains can be observed in this zone. Alpha uranium, produced during sintering, is the major grain-boundary constituent. However, in the core, the original angular shape of the UC powder particles is still intact with a minimum of neck growth and densification.

A uranium carbide piece that contains a grain-boundary uranium phase may be unacceptable as a fuel element, especially for use at high temperatures; therefore, the above effects become extremely important in sintered carbides. Carbon analyses of the piece after sintering plus thorough metallographic examinations in addition to density measurements are required for a true evaluation of the sintered compact.

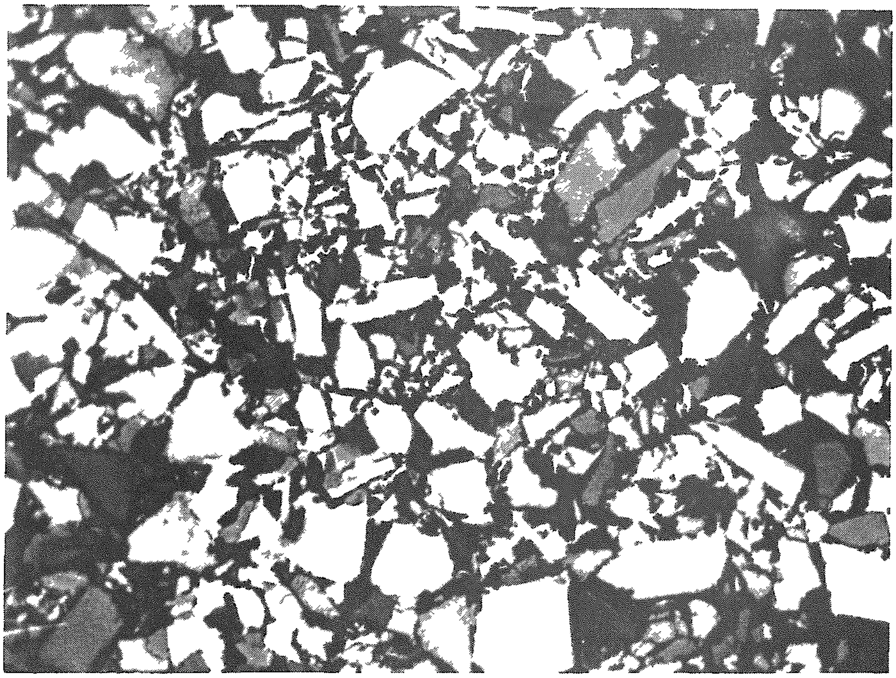
In Figure 32, a relationship is shown between the green density and compacting pressure of three types of uranium-carbon powders: (1) commercial grade, (2) methane product, and (3) crushed arc-melted UC buttons. Naturally, other variables, such as lubricant characteristics, particle size, and geometry, will significantly affect this relationship. The presence of excess uranium in one of the powders (3.23 w/o carbon) sharply increased its compactibility as compared with the other powders which were essentially stoichiometric. These data are included to show the general behavior expected during pressing.

Sintering results for powder obtained by crushing arc-melted uranium carbide are summarized in Table 21. The increase in density resulting from free uranium is shown in the table for the compact sintered 10 min at 1965 C to a density of 11.8 g per $cm^3$. On the other hand, times up to 30 min at temperatures ranging from 1840 to 2120 C yielded densities of 10.8 g per $cm^3$ or lower, this latter series containing considerably less free uranium than the former compact. Examination of Table 21 also shows that use of small particle sizes promotes densification.



100X RM15001

Outer Rim of Compact



250X RM15273

Center of Compact

FIGURE 31. TYPICAL MICROSTRUCTURES OF VACUUM-SINTERED COMPACT MADE FROM STOICHIOMETRIC UC POWDER

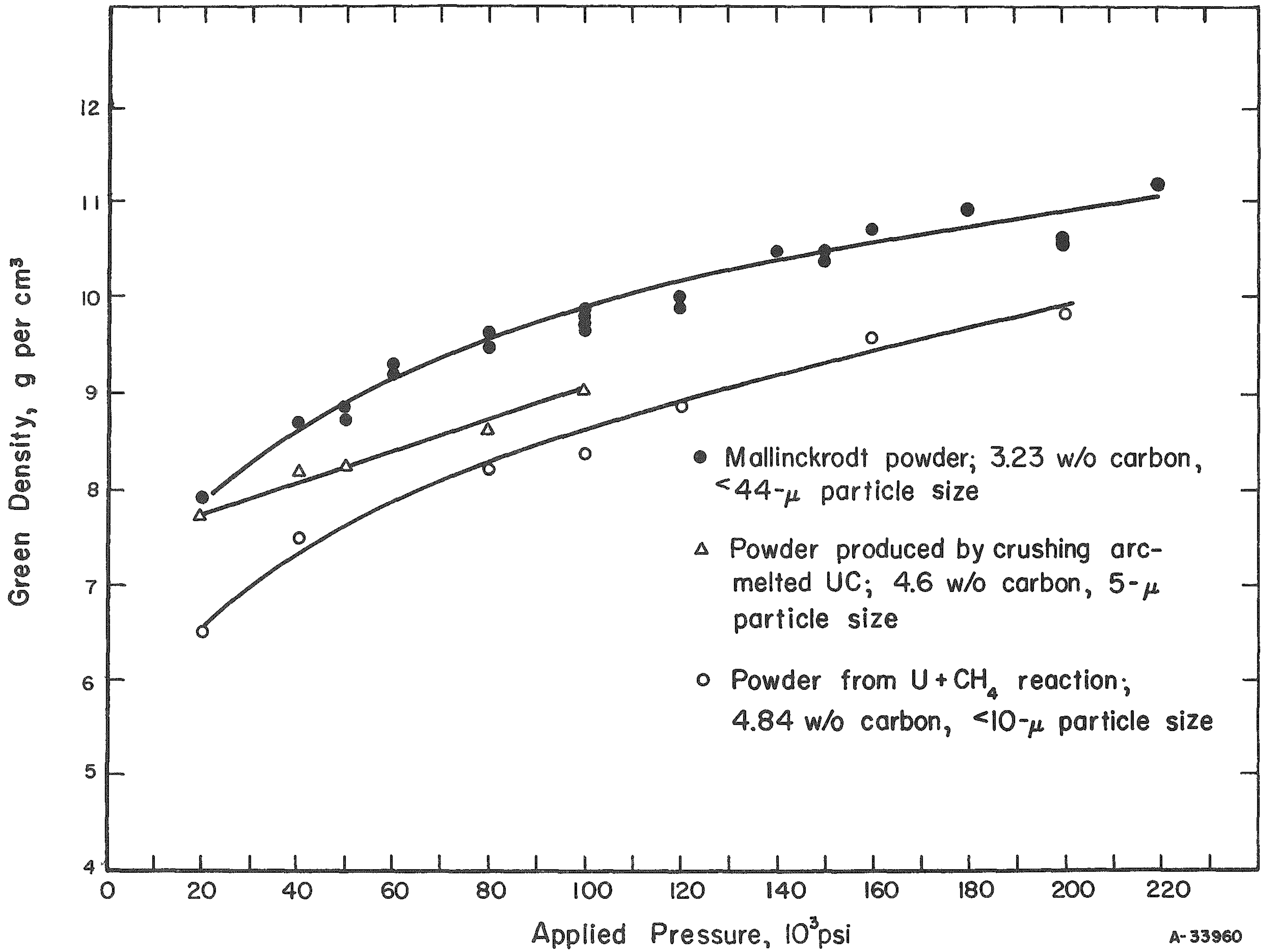


FIGURE 32. RELATIONSHIP BETWEEN GREEN DENSITY AND COMPACTING PRESSURE FOR THREE TYPES OF URANIUM-CARBON POWDERS

TABLE 21. RESULTS OF VACUUM SINTERING URANIUM-CARBON POWDERS PREPARED FROM ARC-MELTED URANIUM AND GRAPHITE

| Analysis of Uranium Carbide Powder | | | | | | | Sintering Conditions | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Total Carbon, w/o | Free Carbon, w/o | Oxygen[a], ppm | Nitrogen[b], ppm | Hydrogen[a], ppm | Particle Size, μ | Green Compacting Pressure, psi | Time, min | Temperature, C | Density, g per $cm^3$ | Reference |
| 4.6 | -- | -- | -- | -- | 5 avg | 100,000 | 60 | 1815 | 12.87 | (1) |
| 4.96 | -- | -- | -- | -- | 6.2 avg | 100,000 | 60-180 | 1600-1800 | 9.9-11.8 | (2) |
| 4.85 | -- | -- | -- | -- | 44 | 80,000 | 30 | 2120 | 11.7 | (3) |
| 4.79 | 0.01 | 3040 | -- | 58 | 44 | 80,000 | 10 | 1965 | 11.8 | Battelle |
| 4.83 | 0.03 | 790 | 110 | 15 | 44 | 30,000 | 5-30 | 1840-2120 | 10.8 | Battelle |
| 4.83 | 0.03 | 790 | 110 | 15 | 44 | 80,000 | 60 | 1900 | 10.1 | Battelle |

(a) Vacuum-fusion analysis.
(b) Kjeldahl analysis.

The sintering characteristics of uranium carbide powder produced by the methane-uranium and propane-uranium reactions are shown in Table 22. Densities of 11.0 g per $cm^3$ are readily attainable at sintering temperatures of 1900 C, but 2 hr at 2050 C was required for densities greater than 12.3 g per $cm^3$ (90 per cent of theoretical) for the compacts using powder produced by the methane reaction. For this high-temperature sintering treatment, it was found that green compacting pressures varying from 40,000 to 200,000 psi produced no significant variation in density. Although no analyses were available after sintering, the analyses given in Table 22 show that high contents of gaseous contaminants were present in the starting powders. The high oxygen contamination, 7000 ppm, and the combined carbon content of 4.40 w/o (4.84 minus 0.44 w/o) indicates that free uranium was present initially. The high nitrogen content may also have influenced sinterability. For powder produced by the propane reaction (Table 22) a density of 11.4 g per $cm^3$ was obtained by sintering at 1900 C, somewhat higher than the density of the methane-produced powder sintered at 1900 C. This powder was purer than that produced by the methane reaction, but the combined carbon content of the powder was only 4.36 w/o. No metallographic or chemical analyses of these sintered compacts are available.

Table 23 lists results obtained by sintering uranium carbide powder that was prepared by reacting $UO_2$ and graphite under various conditions. Some of the results(6) include analyses of the sintered compacts. It may be seen that, where contamination was not high, the sintered densities of these near-stoichiometric UC compacts varied from 8.57 to 10.03 g per $cm^3$ at sintering temperatures of 1900 C and lower. By contrast, Harwell reports densities up to 12.9 g per $cm^3$, a value of 12.1 g per $cm^3$ being obtained after sintering 1/2 hr at 1900 C with considerably coarser powder and lower green compacting pressures.(5) The important point in comparing these results is that the carbon content of the powder used in the latter studies ranged from 4.47 to 4.62 w/o, and no analyses of the sintered compacts are reported. Therefore, it is probable that the high densities reported for this powder, as listed in Table 23, were achieved by liquid-phase sintering. Six-inch-long tubes were also produced at Harwell from this same powder. Wall thickness was 0.2 in., with an outside diameter of 1 in. These tubes could be easily machined after a presintering operation at 1500 C. Density measurements along one such tube ranged from 10.9 to 12.0 g per $cm^3$, as shown in Table 23.

Although carbide powder obtained by the $UO_2$-graphite reaction contained UC as the major phase, weak X-ray diffraction patterns of $UO_2$ and $UC_2$ were also detected at Union Carbide.(6) Analysis of the powder and sintered compact (10.01 g per $cm^3$) before and after sintering for 1 hr at 1800 C, are shown below:

| | Analysis, w/o | |
|---|---|---|
| | Before | After |
| Uranium | 94.22 | 95.21 |
| Total carbon | 4.87 | 4.80 |
| Iron | 0.24 | 0.16 |
| Nitrogen(a) | 0.04 | 0.02 |
| Oxygen(a) | 0.63 | 0.04 |

(a) Vacuum-fusion analysis.

Thus, sintering of this compact reduced impurities to the point where a structure estimated to be 99 per cent UC was obtained.(6) Nitrogen contamination appeared to aid sintering considerably. Examples of this effect may be found in Table 23, which shows that a compact containing 18,200 ppm nitrogen sintered to a density of 13.05 g per $cm^3$,

TABLE 22. VACUUM-SINTERING CHARACTERISTICS OF URANIUM-CARBON POWDERS PREPARED BY REACTING URANIUM WITH METHANE OR PROPANE

| Powder Preparation Reaction | Analysis of Uranium Carbide Powder | | | | | Particle Size, μ | Green Compacting Pressure, psi | Sintering Conditions | | Density, g per cm$^3$ | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Total Carbon, w/o | Free Carbon, w/o | Oxygen[(a)], ppm | Nitrogen[(a)], ppm | Hydrogen[(a)], ppm | | | Time, min | Temperature, C | | |
| Propane | 4.68 | 0.32 | 5600 | 1600 | 46 | 8 avg | 80,000 | 60 | 1900 | 11.4 | Battelle |
| Methane | 5.98 | 0.16 | 6900 | 950 | 350 | 12 avg | 80,000 | 60 | 1900 | 11.0 | Battelle |
| Methane | 4.84 | 0.44 | 7000 | 7100 | 93 | 10 | 60,000-180,000 | 90 | 2050 | 10.7-11.8 | (4) |
| Methane | 4.84 | 0.44 | 7000 | 7100 | 93 | 10 | 40,000-200,000 | 120 | 2050 | 12.5 | (4) |

(a) Vacuum-fusion analysis. Although not accurate for nitrogen, numbers useful in that they represent a minimum.

TABLE 23. SINTERING CHARACTERISTICS OF URANIUM-CARBON POWDERS PREPARED BY REACTING $UO_2$ WITH GRAPHITE

| Analysis | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Powder, w/o | | Sintered Compact(a), ppm | | | | Green Compacting Pressure, psi | Sintering Conditions | | | | |
| Total Carbon | Free Carbon | Total Carbon | Oxygen | Nitrogen | Particle Size, μ | | Time, min | Temperature, C | Atmosphere | Density, g per $cm^3$ | Reference |
| 4.47-4.62 | 0.1 | -- | -- | -- | 50-100 | 11,000 | 30 | 1700 | Vacuum | 11.5 | (5) |
| 4.47-4.62 | 0.1 | -- | -- | -- | 50-100 | 11,000 | 30 | 1900 | Vacuum or argon | 12.1 | (5) |
| 4.47-4.62 | 0.1 | -- | -- | -- | 50-100 | 22,000 | Not specified | 1500 | Vacuum | 11.40(b) | (5) |
| 4.47-4.62 | 0.1 | -- | -- | -- | 20-40 | 22,000 | 60 | 2000 | Flowing argon | Up to 12.9 | (5) |
| 4.47-4.62 | 0.1 | -- | -- | -- | 20-40 | 22,000 | 20<br>30 | 1500<br>2100 | Flowing argon | 10.9-12.0 | (5) |
| -- | -- | 3.96 | 900 | 18,200 | 5 avg | 40,000 | 30 | 1800 | Flowing argon | 13.05 | (6) |
| -- | -- | 4.72 | -- | 1,000 | 5 avg | 40,000 | 30 | 1800 | Flowing argon | 8.57 | (6) |
| -- | -- | 4.80 | 400 | 200 | 5 avg | 40,000 | 60 | 1800 | Flowing argon | 10.01 | (6) |
| -- | -- | 5.35 | -- | -- | 5 avg | 40,000 | 30 | 1750 | Vacuum | 8.84 | (6) |
| -- | -- | 4.87 | 6300 | 400 | 5 avg | 40,000 | 30 | 1800 | Vacuum | 9.40 | (6) |
| -- | -- | 4.75 | -- | -- | 5 avg | 40,000 | 60 | 1900 | Vacuum | 10.03 | (6) |

(a) Vacuum-fusion analysis.

(b) 10 w/o iron added to this compact to aid sintering.

and a compact with 1000 ppm nitrogen sintered to a density of 8.57 g per $cm^3$ after 30 min at 1800 C.(6)

Iron has been added to uranium carbide in an attempt to lower fabrication temperatures by inducing liquid-phase sintering action.(5) A density of 11.40 g per $cm^3$ was obtained by sintering a uranium carbide-10 w/o iron compact at 1500 C, as shown in Table 23. Also, Bowman introduced cobalt, copper, iron, and nickel for liquid-phase sintering in his studies of bonding of UC to tantalum.(7) He reports that the liquid phases aided bonding by a wetting action and were removed by vaporization in vacuo at 2000 to 2200 C, but no data on the effects on densification, fabrication temperatures, or analyses for the metals after heat treating were given. Preliminary work at Battelle on the effect of chromium as a liquid phase on sintering showed that free uranium formation was eliminated, neck growth between particles was appreciable, and that the 10 volume per cent chromium (5.6 w/o) that had been added could be completely removed by a three-stage sintering treatment of 30 min at 1030 C, 50 min at 1930 C, and 50 min at 2000 C. However, little densification occurred. Spectrographic analysis of the resulting compact indicated that less than 0.05 w/o chromium was present. The uranium carbide powder used for this compact contained 4.89 w/o total carbon with less than 0.01 w/o free carbon.

The sintering characteristics of $UC_2$ have received some attention.(1) An average density of 10.7 g per $cm^3$ (theoretical density is 11.7 g per $cm^3$) was observed for compacts prepared from 5-$\mu$ powder that had been obtained by ball milling an arc-melted uranium-8.6 w/o total carbon alloy containing 1.2 w/o of impurities. These compacts were sintered 1-1/2 hr at 1840 C after cold pressing at 100,000 psi.

No data were available on the sintering characteristics of thorium or plutonium carbides. The monocarbide of thorium, being quite similar to UC, probably behaves in a fashion similar to UC in sintering, although sintering temperatures may be higher due to its higher melting point. Considering sintering temperatures to be proportional to melting point, the order of increasing sintering temperatures would probably be plutonium carbides, uranium carbides, and thorium carbides.

## Extrusion

Mixtures of uranium and graphite powders, containing up to 5 w/o carbon, have been successfully extruded at 800 C and subsequently reacted at 1100 C to form uranium carbide. Densities of 96.2 and 85.7 per cent of theoretical were obtained for uranium-4 and -5 w/o carbon mixes, respectively.(5) Mixtures of uranium powder, minus 300-mesh graphite, and paraffin were cold pressed at 22,000 to 55,000 psi, and then hot compacted in the extrusion die to about half of the original length, after the extruding temperature of 800 C was reached. The piece was extruded at pressures of 4,000 to 12,000 psi, using a 12:1 reduction in area, to produce a rod 0.318 in. in diameter. An impure argon atmosphere was used with the wax binder, providing protection from oxidation.(5) The densities after extrusion of the above 4 and 5 w/o carbon pieces were 14.04 and 13.50 g per $cm^3$, respectively, the major constituents of the structure being uranium and graphite. The rods were then reacted at 1100 C (no times given) to form uranium, UC, and $UC_2$. Although no analyses were given to show that the elements had completely reacted, it was stated that uranium-graphite compacts that were heat treated in vacuum 21 hr at 1100 C after hot pressing at 750 C contained no free graphite by X-ray and metallographic analyses. After reacting at 1100 C, the rod densities were 12.73 and 11.91 g per $cm^3$, respectively. The reductions in density are undoubtedly caused by carbon monoxide produced by reaction of the carbon and oxygen present in the powder mixtures.

The surface quality of the 5 w/o carbon rod was described as good, although severe die wear was experienced. A mirror finish was obtained on the 4 w/o carbon rod, and no appreciable die wear occurred in extrusion of this rod when graphite inserts were used.

## Hot Pressing

Uranium carbide pieces have been produced by hot pressing both uranium-carbide powders, and mixed uranium-graphite powders followed by a reaction heat treatment.

Using the latter method, densities consistently greater than 90 per cent of theoretical were obtained for products having carbon contents of 4, 4.8 and 5 w/o, when studies were performed on a small scale; however, lower densities were obtained in larger scale experiments.(5) Results of these experiments are shown in Table 24. Stellite dies were used in preparing these compacts, and it was found that temperatures up to 750 C at pressures of 33,000 psi could be used without excessive die attack. Although the mixing techniques used in obtaining the results in Table 24 were not given, colloidal graphite was mixed with uranium powder. The uranium powder was added to a very fine colloidal graphite in an alcohol suspension. The amount of carbon added to the uranium was varied by adjusting the volume of the suspension, the carbon content of which was estimated by both density measurements and drying. The dried mixture was then pressed. Thorough drying was found to be essential, since some powders that were not dried completely exploded during hot pressing. No metallographic or chemical analyses were reported to give an indication of the completeness of carbide formation.

Dubisson, et al.,(8) hot pressed graphite-uranium mixtures to densities that were consistently 98 per cent of theoretical. The results for various carbon contents up to about 4.6 w/o are plotted in Figure 33. Pressures of 2800 psi were applied for 3 hr at 900 C in a double-action graphite die. Special mixing and powder-preparation techniques were used. A zinc coating applied to the high-purity uranium powder facilitated handling in air without oxidation and activated the surface. No reacting treatment was necessary, since reaction occurred simultaneously with hot pressing at the pressure temperature of 900 C. Analyses for free carbon confirmed metallographic analyses in determining that practically all the carbon had reacted. A free carbon content of 0.045 w/o was typical, and no $UC_2$ was detected by X-ray analyses. Structures contained only UC and uranium. No data were reported for specimens having carbon contents of 4.8 w/o or greater.

Hot pressing of uranium carbide powders has also been studied by Union Carbide.(4) Powder produced commercially by Mallinckrodt which contained 3.23 w/o total carbon was mixed with 1.65 w/o graphite and was compacted for 30 min at 1600 C in a tungsten die in a partial vacuum. A density of 12.50 g per $cm^3$ (91.8 per cent of theoretical) was measured on this compact. The microstructure of this specimen consisted of UC grains with a small amount of $UC_2$ in the grain boundaries.

TABLE 24. EFFECT OF VARIOUS FABRICATION VARIABLES ON THE DENSITY OF URANIUM-CARBONS MIXES(5)

| Type of Carbon | Carbon Content, w/o | Hot-Pressing Conditions Temperature, C | Pressure, psi | Reacting Temperature, C | Density, g per cm$^3$ | Comments |
|---|---|---|---|---|---|---|
| Coarse BDH graphite | 4 | 750 | 33,000 | -- | 14.14 | Small scale |
| Coarse BDH graphite | 5 | 750 | 33,000 | -- | 13.77 | Small scale |
| Coarse BDH graphite | 4 | 750 | 33,000 | 1100 | 13.00 | Small scale |
| Coarse BDH graphite | 5 | 750 | 33,000 | 1100 | 12.20 | Small scale |
| Carbon black | 4 | 670 | 33,000 | -- | 12.20 | Larger scale |
| Carbon black | 4.8 | 670 | 33,000 | -- | 11.20 | Larger scale |
| Carbon black | 4 | 670 | 33,000 | 1000 | 12.27 | Larger scale |
| Carbon black | 4.8 | 670 | 33,000 | 1000 | 11.32 | Larger scale |
| Superfine graphite | 4 | 670 | 33,000 | -- | 13.7 | Larger scale |
| Superfine graphite | 4.8 | 670 | 33,000 | -- | 12.8 | Larger scale |
| Superfine graphite | 5.0 | 670 | 33,000 | -- | 12.0 | Larger scale |

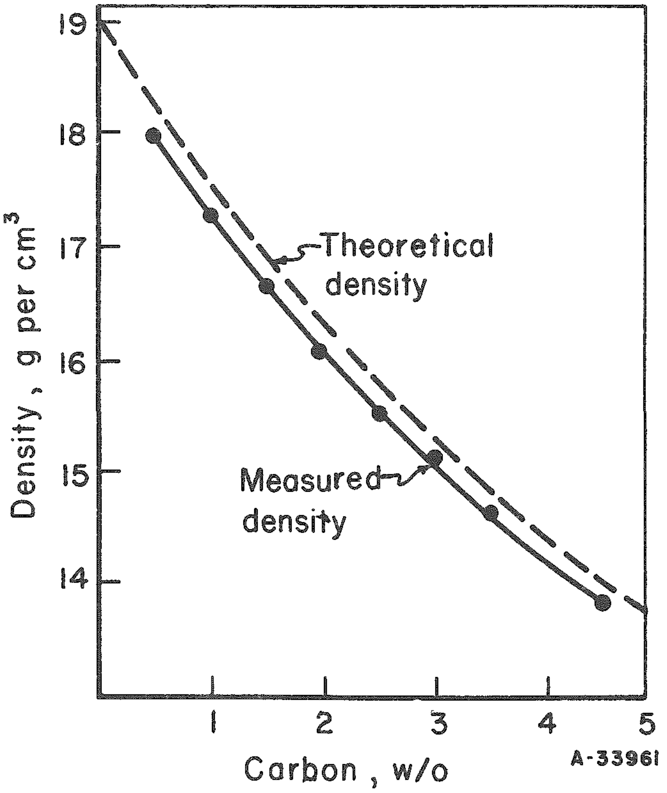


FIGURE 33. DENSITY OF URANIUM-GRAPHITE MIXTURES HOT PRESSED AT 900 C(8)

Nowotny, et al.,(9) has reported densities of 12.8 g per $cm^3$ for hot-pressed UC. Although pressing conditions were not specified, the powder used was prepared by the $UO_2$-graphite reaction and contained 4.84 w/o total carbon and 0.16 w/o free carbon. X-ray analyses of the starting powder indicated that UC was the major phase with a small amount of $UC_2$ present.

## Summary

Preliminary studies indicate that temperatures in excess of 1900 C will be required to fabricate high-density stoichiometric UC pieces from powder by cold pressing and sintering techniques. However, the fabrication temperature may be significantly lowered by resorting to a liquid-phase sintering process. Preliminary indications are that the elements used to provide liquid-phase sintering can be removed by vaporization during sintering. While the use of liquid-phase uranium substantially lowers fabrication temperatures, consideration must be given to its effect upon irradiation resistance and cladding compatibility. Fine particle sizes, in the 5-$\mu$ range, enhance sintering. Compacting pressures in excess of 50,000 psi appear to have little effect on densification of the sintered product.

Extruding or hot pressing mixtures of uranium and graphite powder, and simultaneously or subsequently reacting them to form the carbide appears very attractive. In these processes, high densities can be achieved with maximum temperatures of only about 1100 C. The major problems encountered in extrusion appear to be die wear and control of surface quality because of the formation of small amounts of the abrasive UC or $UC_2$ during billet heating. Although the atmosphere in hot pressing may be more closely controlled than in extrusion, the capacity to produce large pieces is reduced.

While considerable work has been done on solid-phase reactions to form uranium carbide fuel pellets, much additional research is needed to establish a commercial process. Two processes appear to have considerable merit for preparation of high-density bodies of UC, if free uranium is to be eliminated. These are hot pressing or extrusion of mixed powders of uranium and carbon followed by reaction at elevated temperature, and liquid-phase sintering of uranium carbide powders containing additives such as chromium, iron, or nickel. The latter process may become more attractive, if an economical process should be developed for preparation of UC powders.

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## STORAGE AND HANDLING

W. M. Phillips

### Bulk Uranium Carbides

Of the three corrosion media encountered in normal storage and processing (nitrogen, oxygen, and water), water is the most corrosive and damaging to carbide fuels. Saturated water vapor at 40 C will cause complete disintegration of a 10-g (3/8-in.-diameter by 1/2-in.-long cylinder) sample of UC in 24 hr.(1) Because of this type of attack by water vapor, specimens to be kept for long periods of time must be stored in desiccators. Although the weight change observed during a 2-month storage period in a desiccator is insignificant(2), transverse rupture strengths of machined specimens have been observed to decrease slightly as storage time is increased over a period of 2 to 3 months. This would indicate that sufficient moisture was adsorbed on the specimens during handling or machining to produce a surface attack or microcracking of the specimens during storage, although the amount of attack is not measurable in terms of a weight change.

As indicated in the section on compatibility and corrosion, it is believed that $UC_2$ is more readily attacked by moist air than is UC, and that the presence of $UC_2$ as a second phase in UC may thus be undesirable.

Machine grinding of cast uranium carbide has been found to be satisfactory. Specimens ground on a silicon carbide wheel produced some loading of the wheel, accompanied by spalling of the specimen. This spalling was eliminated by the use of a resin-bonded diamond wheel. During the grinding operation, the specimen is held between pressure pads. Specimens have been ground to diameters as small as 3/16 in. with no difficulty.(3)

Three cutting fluids have been used in conjunction with the resin-bonded diamond wheel: kerosene, water-soluble oil, and cutting oil. Kerosene is satisfactory for use with a small cutoff wheel, since no reaction has been observed between UC and kerosene. However, if a heavy cut is taken overheating occurs, and kerosene vapor is produced, resulting in a fire hazard. The water-soluble oil is satisfactory for use with sound specimens, provided the cutting fluid is completely removed prior to storage. This fluid was used to grind a 2-in.-diameter specimen which contained fine radial cracks. After grinding, the specimen began to disintegrate. This continued for a period of more than a week, until the specimen was reduced to small pieces. This is the result of the water-base cutting fluid entering the cracks. Thus, at the present time, all grinding is done using undiluted cutting oil with no resultant decreases in surface quality or in diameter tolerances of the order of ±0.001 in.(1)

Holes 1/8 in. in diameter have been drilled through the center line of 3/8-in.-diameter cast specimens 1 in. long. Ultrasonic drilling techniques involving a steel tool and a silicon carbide abrasive have been found satisfactory.

As indicated in the section on compatibility, there are numerous materials which will wet UC and which might therefore be used as a protective coating. For example, nickel has been vapor deposited on UC for this purpose. Water-corrosion tests of the coated specimen indicated that the corrosion rate was reduced by the coating.(4)

## Uranium Carbide Powders

Extreme care is required in storing and handling fine uranium carbide powders because of the possibility of fires or explosions. Powders, of course, can be protected during handling by coatings or by binders and lubricants, as discussed briefly in the section on solid-state fabrication processes.

## Thorium and Plutonium Carbides

Thorium carbide, even in bulk form, is attacked by dry air at room temperature. It must be stored in an inert atmosphere.

No information is available on the handling characteristics of the plutonium carbides.

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# EFFECTS OF IRRADIATION UPON URANIUM CARBIDE

F. A. Rough

## Introduction

Relatively few data are available on the effects of irradiation upon bulk uranium carbides or upon uranium carbides in any form. The objective of this review is to present and evaluate the results of irradiation upon bulk uranium carbides. Because of possible effects of impurities and the possible effects of reactions between the dispersed phase and the matrix, the results of irradiations of dispersions and cermets containing uranium carbide contribute little to the understanding of the effects of irradiation upon bulk carbides and thus are not included in the present review.

The principal source of information on the effects of irradiation upon uranium carbides is an irradiation program being conducted at Battelle in cooperation with Atomics International. This program involves the irradiation of uranium carbide specimens having carbon compositions in the vicinity of stoichiometric uranium monocarbide, but ranging from 4.6 to 5.3 w/o carbon. The specimens were prepared by inert-electrode arc melting of biscuit uranium and spectrographically pure carbon and then casting the carbide into graphite molds by the technique described in the section on melting and casting. The procedures of preparation, the properties of the carbide, and the irradiation procedures and results obtained in this program have been described in a series of reports and papers.(1-6) The program is largely completed, but one capsule intended to achieve a burnup of 2.2 a/o uranium (20,000 MWD/T of uranium) remains to be examined. A description of the irradiation parameters of the capsules which have been examined appears as Table 25.

## Observed Effects of Irradiation on Uranium Carbide

### Cast Uranium Carbide

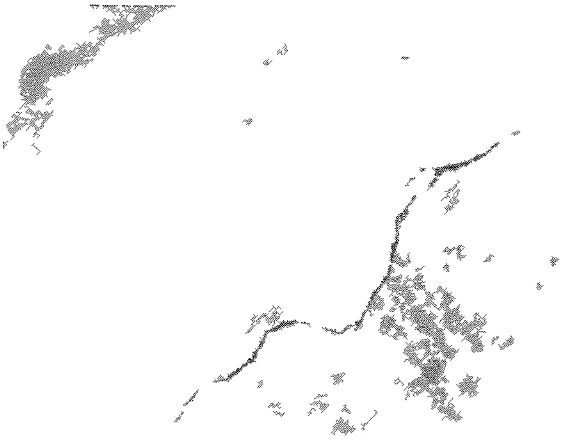
Specimens of as-cast uranium monocarbide, machined to 3/8-in.-diameter cylinders about 2 in. in length, have been irradiated in NaK as shown in Table 25 to burnups of about 1.7 a/o of the uranium. The temperatures during irradiation, as determined by thermocouples, varied; average surface temperatures ranged from 540 to 915 F, while average center-line temperatures ranged from 880 to 1450 F. The maximum surface and center-line temperatures were generally about 200 F higher. The density changes observed were modest, being in the range of -0.6 to -2.5 per cent, regardless of burnup. Cracking occurred probably as a result of thermal stresses, but disintegration attributable to accumulation of fission products was absent, as illustrated by Figure 34. The amount of cracking increased somewhat with increased irradiation. The surfaces were damaged somewhat, apparently by oxygen pickup from the NaK. The quantity of fission gases released into the capsule, as determined by collecting and measuring the krypton-85 contained in the capsule after irradiation, was small. Postirradiation heating for 1 week at 1800 F and 8 hr at 2000 F released very small amounts of the contained fission gases.(2-7)

## TABLE 25. IRRADIATION DATA ON UC SPECIMENS

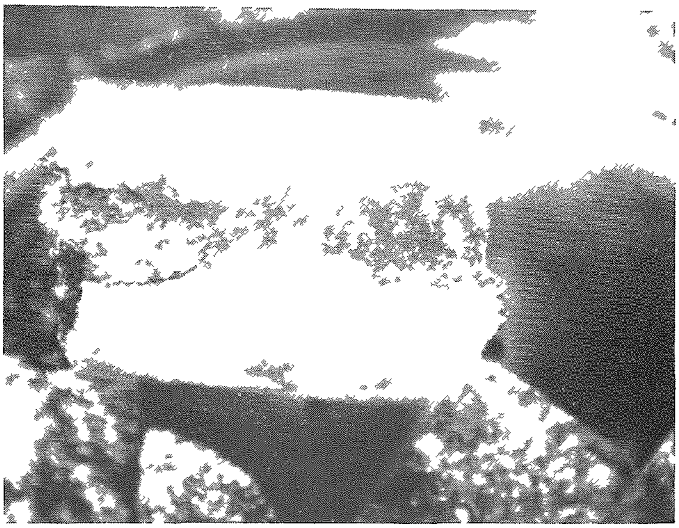
| | Capsule A | | Capsule B | | Capsule C | | Capsule D | | Capsule E | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Top Specimen | Bottom Specimen | Top Specimen | Bottom Specimen | Top Specimen | Bottom Specimen | Top Specimen | Bottom Specimen | Top Specimen | Bottom Specimen |
| Carbon Content, w/o | 5.2 | 5.2 | 5.3 | 5.1 | 5.0 | 5.0 | 4.6 | 4.7 | 4.8 | 4.6 |
| Diameter Change, per cent | 0.4 | 0.3 | 0.9 | 0.9 | -- | 0.8 | 0.8 | 1.2 | 0.5 | 0.5 |
| Density(a) Change, per cent | 0.7-0.9 | 2.5 | 0.6-2.0 | 2.5 | 1.8 | 1.8 | 2.4 | 1.6 | 1.2 | 1.6 |
| Average Temperature, F | | | | | | | | | | |
| Surface | 770 | 540 | 915 | 700 | 765 | 623 | 882 | 772 | 815 | 600 |
| Core | 1,300 | 880 | 1,375 | 1,060 | 1,178 | 1,086 | 1,326 | 1,248 | 1,450 | 950 |
| Surface Heat Flux, Btu/(ft$^2$)(hr) | 680,000 | 850,000 | 880,000 | 940,000 | 750,000 | 700,000 | 900,000 | 710,000 | 600,000 | -- |
| Fission-Gas Release, cm$^3$ of krypton-85 | | | | | | | | | | |
| Estimated Total Produced | $5.9 \times 10^{-2}$ | | $20.9 \times 10^{-2}$ | | -- | | $20.4 \times 10^{-2}$ | | $21.9 \times 10^{-2}$ | |
| Estimated Released by Recoil | $2.5 \times 10^{-5}$ | | $8.8 \times 10^{-5}$ | | -- | | $8.7 \times 10^{-5}$ | | $9.4 \times 10^{-5}$ | |
| Measured Release | $2.4 \times 10^{-5}$ | | $9.7 \times 10^{-5}$ | | (b) | | $8.2 \times 10^{-5}$ | | $8.4 \times 10^{-5}$ | |
| Burnup, a/o of the uranium | 0.16 | 0.20 | 0.6 | 0.8 | 1.7 | 1.7 | 0.9 | 0.9 | -- | -- |
| Burnup, MWD/T of uranium | 1,000 | | 5,000 | | 10,000 | | 5,000 | | 5,000 | |

(a) In every case, density measurements were made on the largest fractions of the original specimens.

(b) Fission-gas sample was lost, apparently by leakage from capsule.



6X HC2292



4X HC3897

FIGURE 34. APPEARANCE OF UC SPECIMENS AFTER IRRADIATIONS TO BURNUPS OF 0.6 a/o OF THE URANIUM AT 1375 F (TOP) AND TO 1.7 a/o OF THE URANIUM AT 1086 F (BOTTOM)

Based upon room-temperature rupture strengths, which vary considerably for UC, one might expect thermal gradients of 50 to 200 F to cause cracking.(7) Although the mechanical-property data needed to evaluate cracking at high temperatures are not available, there is good reason to believe that both the radial and transverse cracking which has been observed in uranium monocarbide is the result of thermal stresses. In some cases, microcracks have been observed in areas at or near the center of specimens as shown in Figure 35. The cause of this type of cracking is uncertain. One might imagine that stress relief due to irradiation annealing could occur at temperature. If so, upon cooling, the center areas of the specimens would be placed in tension, perhaps causing cracking at room temperature.(7)

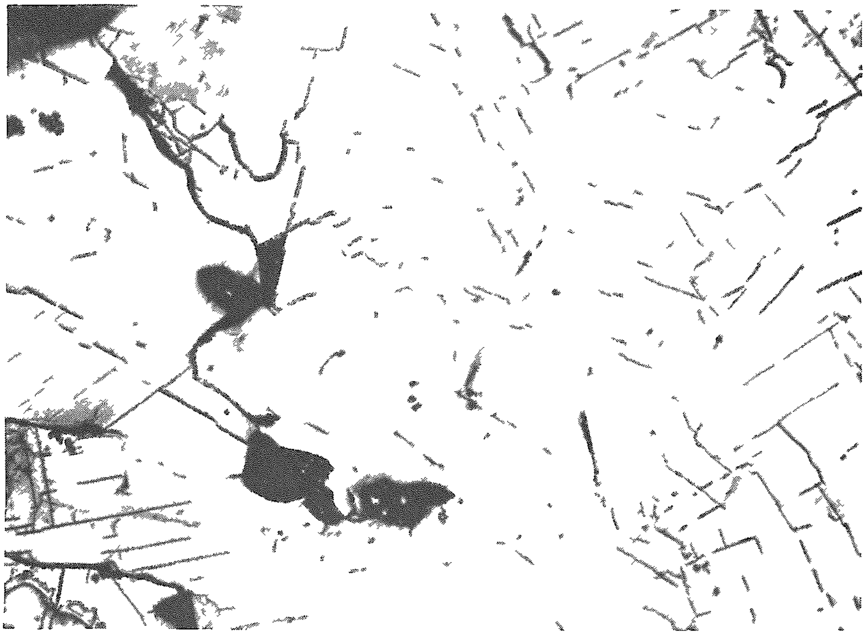
It is believed that the surface damage shown in Figure 36 was caused by reaction of small amounts of oxygen in the NaK-filled capsule with the UC during irradiation. The damage shown is similar in many respects to that produced by exposures of UC to moist air.

Another type of damage manifested by a porous appearance was observed near a thermocouple located in the center of a UC specimen. This location experienced a transient temperature of 1830 F.(3) It is possible that this effect was caused by the action of NaK or by local overheating caused by the formation of NaK vapor. Although the capsule was designed to avoid vaporization of the NaK, local vaporization or boiling may have occurred in the confined space around the thermocouple.

The density decreases shown in Table 25 are about the same regardless of burnup. Thus, the density changes produced in the lattice of UC by accumulation of fission products tend to be obscured by the effects of internal cracks, surface damage, and experimental difficulties. The true density change is probably less than the approximately 1 per cent per a/o uranium burnup observed for the specimens in Capsule C (Table 25) which received burnups of 1.7 a/o of the uranium.

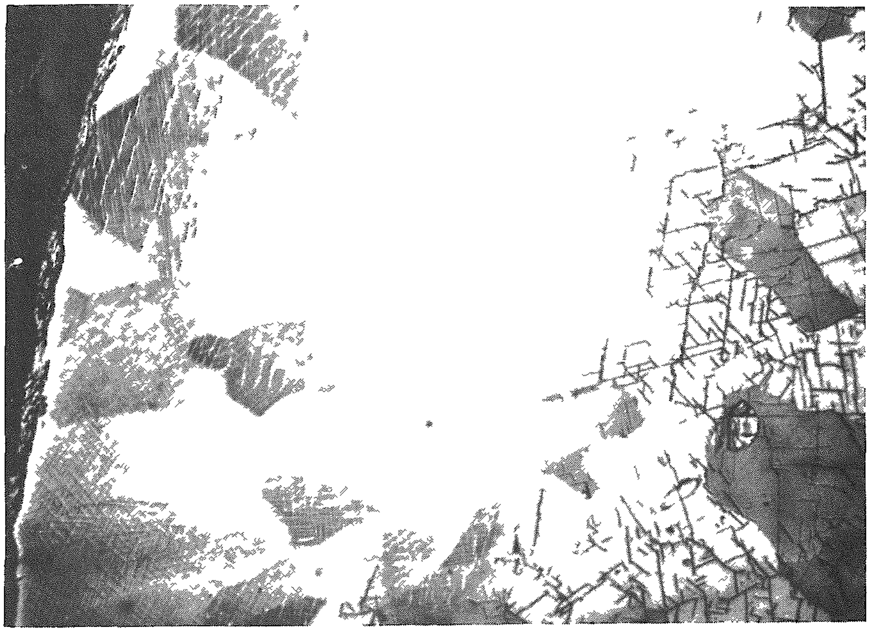
Calculations have been made of the density changes one might expect as a result of the accumulation of fission products in the lattice of UC using various assumptions somewhat similar to calculations that have been made for other alloys.(8) The volume changes calculated for 1 a/o uranium burnup range from +1.0 to +1.6 per cent. The former value refers to high-temperature irradiations, where the fission products are assumed to diffuse to substitutional positions vacated by fissioning uranium atoms. In the latter case, the calculations were made for low temperatures where the fission products were assumed to be immobile, falling equally in substitutional or interstitial positions depending upon the frequency of occurrence of these positions in the lattice.

The principal microstructural change that has been observed in irradiated uranium monocarbide is the disappearance of the $UC_2$ platelets, as shown in Figure 35. In the top specimen in Capsule C (Table 25), the $UC_2$ platelets disappeared from the entire cross section. In the bottom specimen in Capsule C the platelets were completely gone at the center and showed signs of beginning to disappear at the specimen surface. These effects observed at burnups of 0.8 and 1.7 a/o of the uranium are illustrated in Figures 35 and 37. However, this change in microstructure produced no other manifestations of damage. The appearance and over-all effects of irradiation on specimens containing 4.6 w/o to 5.2 w/o carbon at burnups of about 0.2 to 1.7 a/o of the uranium were the same, as can be seen in photomicrographs and in Table 25. It is possible that the $UC_2$ platelets



112X HC2619

Center Section



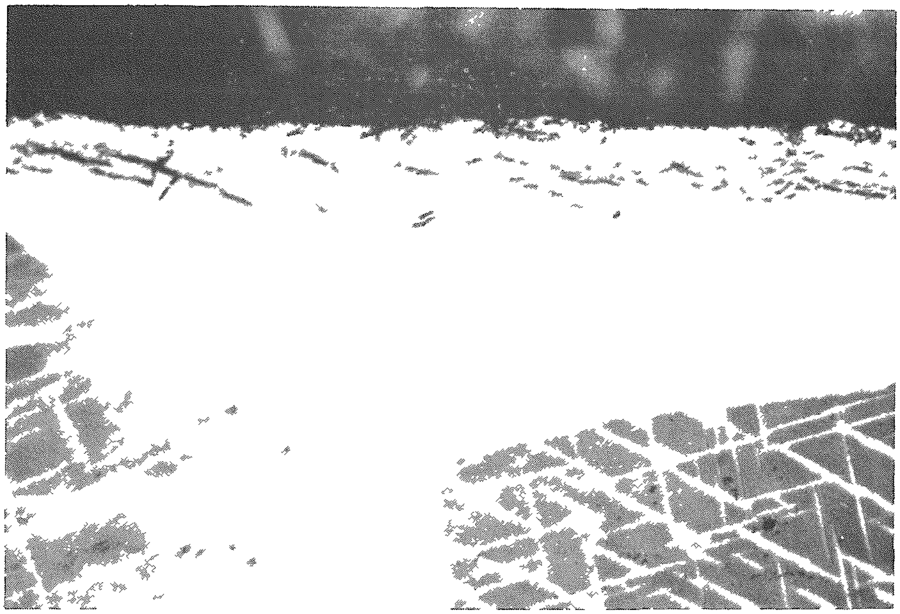
56X HC2618

Center to Edge

FIGURE 35. SECTIONS OF URANIUM-5.1 w/o CARBON SPECIMEN IRRADIATED AT 1060 F TO A BURNUP OF ABOUT 0.8 a/o OF THE URANIUM

270X HC2613

As Polished



270X HC2615

As Etched

FIGURE 36. SURFACE DAMAGE TO A URANIUM-5.1 w/o CARBON SPECIMEN IRRADIATED AT A SURFACE TEMPERATURE OF 700 F IN NaK CONTAINING TRACES OF OXYGEN

100X HC4190

100X HC4189

FIGURE 37. SECTIONS OF URANIUM-5 w/o CARBON SPECIMEN, SHOWING ABSENCE OF $UC_2$ AT CENTER (TOP) AND BEGINNING OF $UC_2$ DISAPPEARANCE NEAR SURFACE (BOTTOM) AFTER IRRADIATION TO A BURNUP OF 1.7 a/o OF THE URANIUM AT ABOUT 1090 F

are caused to disappear by carbon migration during irradiation. Carbon migration might be induced by the presence of the temperature gradient in the specimens during irradiation or by the presence of carbon sinks such as stainless steel in the system. Still another possibility is that the fission fragments can produce enough disturbance of the structure by means of displacement spikes(9,10) to, in effect, homogenize the structure in terms of carbon content. This supersaturated solution of carbon in uranium monocarbide apparently can be produced only as a result of irradiation. Its existence is supported by the apparent fuzziness of the $UC_2$ platelets before they disappear entirely.

Although appreciable cracking and surface damage of UC during irradiation has been observed, fission-gas retention has been excellent. As shown in Table 25, the fission gas detected by sampling is approximately that expected to result from surface recoil. In general, cesium also was retained in the carbide, as evidenced by an analysis of the NaK in each of the capsules. In all cases, the cesium-137 detected in the NaK represented no more than 0.01 a/o burnup of the uranium.

The effective thermal conductivity of uranium carbide samples during irradiation has been estimated using the center and surface temperatures and heat-generation rates listed in Table 25. These estimates are possible because thermocouples were present in a drilled hole at the center of the top specimen and in the NaK near the surface of the same specimen. In each case, the effective conductivity remained about constant throughout the irradiation (or for the life of the thermocouples, if failure occurred), showing that no serious effects of irradiation were produced. In general, the effective conductivities were somewhat lower than the out-of-pile conductivities, but the probable error in such a crude measurement of conductivity is quite large. Thus, it is believed, as a result of the constancy of the effective conductivity in these tests, that no significant effect of irradiation upon the thermal conductivity has been encountered.

### Sintered Uranium Carbide

Murray and Williams(11) report that 2-mm-diameter pins of UC released 10 per cent of their contained fission gases during an irradiation to 3000 MWD/T at 630 C. It is indicated that the pins were of lower density than is normally achieved in sintering of $UO_2$ and that cracking occurred during the irradiation. It is suggested that the low density "... may be in part responsible for the above gas release." Typical specimens of sintered UC such as those used in this study are stated to exhibit 15 per cent porosity.

## Evaluation and Discussion

Cast uranium carbides of 4.6 to 5.2 w/o carbon have demonstrated excellent behavior at burnups of up to 1.7 a/o of the uranium at mean center temperatures of 880 to 1450 F. These results were obtained at volume heat-generation rates comparable with those expected in sodium-cooled reactors. The principal problem encountered is cracking, although this has not been serious. Other more academic problems are surface damage due to oxygen in NaK and the disappearance of the $UC_2$ second phase. The surface damage could be eliminated in practical sodium-bonded fuel elements, since only a small quantity of sodium would be in contact with the carbide. The disappearance of the $UC_2$ has produced no practical problem, but further studies of the effects of composition and specimen environment upon the irradiation behavior of uranium carbides are desirable to define the reasons for this disappearance.

Because of its brittle and nonmetallic nature, it seems likely that burnups of 5 to 10 a/o of the uranium in UC will result in serious damage to bulk uranium carbides. However, the allowable limits of burnup and temperature for uranium carbides remain to be determined.

Sufficient data are not available to select the optimum composition of carbide for any given application, even in the range of 4.6 to 5.2 w/o carbon where results are now available. While there are no irradiation data on $U_2C_3$ and $UC_2$, as such, their lower densities suggest that there is little to recommend consideration of either as a fuel in bulk form for high-temperature use. Thus, compositions ranging near UC should continue to receive primary attention.

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