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PREPARATION AND PROPERTIES OF URANIUM MONOCARBIDE CASTINGS

by

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Using a special arc-melting technique, sound, homogeneous 100-g cylindrical castings of UC of near stoichiometric composition were consistently produced. In the casting process developed, UC buttons previously prepared by arc melting the elements were placed over the opening of a graphite mold in a helium-atmosphere arc furnace. When the UC button became fully molten under the arc, it dropped by gravity into the mold. The densities of the resultant castings were about 98 per cent of theoretical. The castings could be successfully machine ground using a water-base cutting fluid.

In a preliminary determination of some physical properties of cast UC, the thermal conductivity measured at 100, 400, and 700 C was 0.060, 0.053, and 0.060 cal (sec)(cm)(C), respectively. The mean linear thermal expansion coefficient in the temperature range from 20 to 950 C was 11.4×10^{-6} per C. Cast UC encapsuled in stainless steel exhibited good resistance to thermal stress and shock in two series of tests of 100 thermal cycles to 900 C and 100 cycles to 1100 C.

Heat treating a casting specimen for 1 hr at 1000 C produced no significant change in microstructure, but after a subsequent exposure of 1 hr at 1500 C hardening and the appearance of the U_2C_3 phase were evident. In tests of compressive strength on a single specimen rupture occurred at 54, 500 psi.

INTRODUCTION

The continuing search for better fuel materials for nuclear reactors is prompted by the economic advantages to be gained from long-life fuel elements and increased fuel temperatures. Atomics International, acting for the Atomic Energy Commission, shares this interest directly in the evaluation of various types of fuels for use in the Sodium Reactor Experiment (SRE), an experimental nuclear power plant located near Los Angeles, California. The research on uranium carbide discussed in this report was performed at Battelle in support of the SRE program.

A number of material properties must be known before the economic potential of a suggested fuel can be evaluated. Some of the more obvious qualities that are desired in a reactor fuel material are high uranium density, good thermal conductivity, and dimensional and physical stability when subjected to in-pile radiation. In addition, the feasibility of fabricating the material in a form suitable for reactor application must be demonstrated.

Several materials now used in reactors possess acceptable qualities under the conditions imposed by the present state of reactor technology. Unalloyed uranium, uranium alloys, and uranium dioxide are all being employed singularly or in combinations in power reactors with varying degrees of success. However, in all cases an economic advantage would be gained if the material could be operated at a higher power density (high temperature) and/or for longer periods of time between replacement.

A material that offers considerable promise to fulfill these requirements as a reactor fuel is uranium monocarbide. In addition to its high uranium density, it has a thermal conductivity near that of uranium, it is refractory, and it has a structure (face-centered cubic) that is theoretically capable of considerable resistance to radiation damage. Furthermore, in spite of its high melting point, it appears that uranium monocarbide can be fabricated directly to fuel elements by casting techniques. Although uranium monocarbide has received some attention by reactor technologists from time to time, very limited irradiation data are available. Likewise, no information is available in the literature with regard to casting of special shapes, such as would be required for use as reactor fuel elements. However, uranium carbide can be prepared by arc-melting elemental uranium and carbon(1,2,3,4).

Because of its promise as a fuel material, a study with the objectives of developing casting techniques and determining some of the physical properties of cast UC was initiated. The ultimate aim was to produce cast shapes of uranium monocarbide of near stoichiometric composition (4.8 w/o carbon) in a predictable and reproducible manner. Most of the research was done on carbide of about 5.0 w/o carbon.

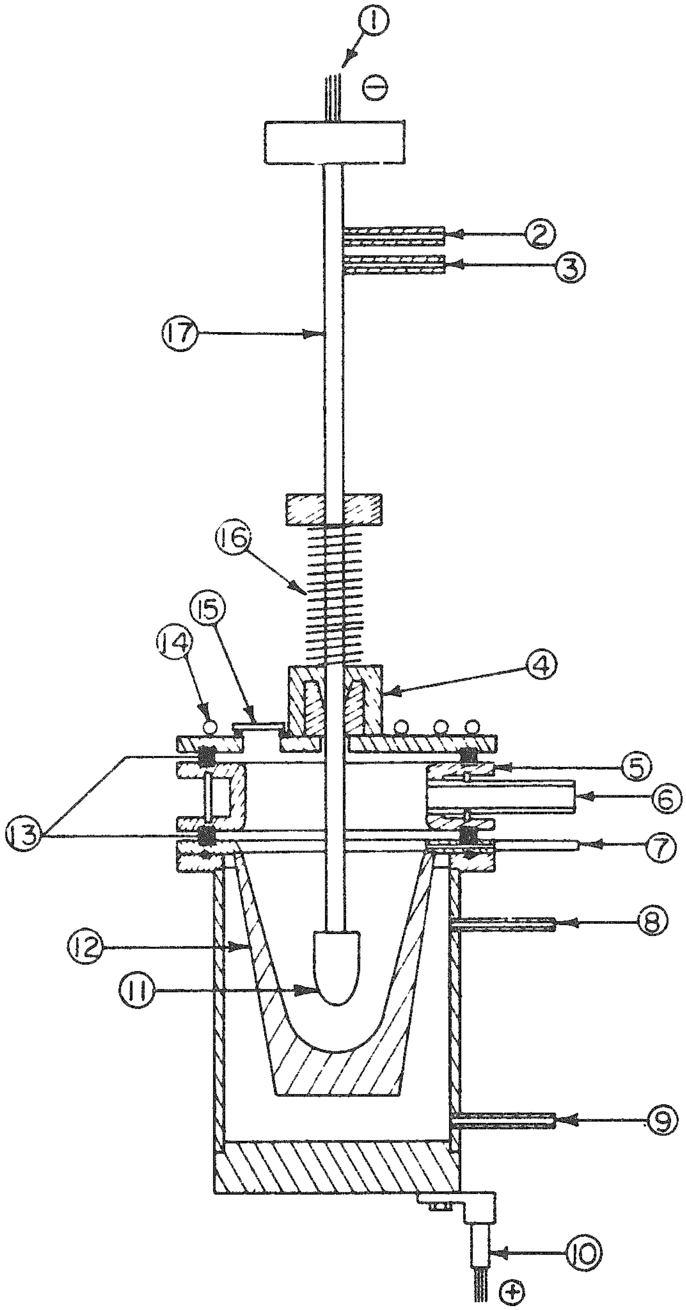
DEVELOPMENT OF MELTING AND CASTING TECHNIQUES FOR UC

Preparation of UC Melting Stock

Based on past experience, a modified arc-melting process was believed to be the best method for preparing high-quality UC. An advantage of the arc-melting technique is that the extremely high temperatures required for melting uranium monocarbide can be reached and maintained with good control. Previous work had shown that a tungsten-tip electrode seriously contaminated UC melts. Therefore, a nonconsumable, carbon-tip electrode was chosen since the only contaminant from such an electrode would be carbon.

Buttons were made by arc melting freshly pickled center-cut biscuit uranium (1/2-in. squares, 50 to 90 mils thick) with crushed spectrographic carbon (1/4 by 5/8-in. pieces) in a water-cooled copper crucible under a helium atmosphere of 10 to 20 in. of mercury. The arc was struck initially on a piece of uranium at 200 amp and 30 to 32 v, then raised to 500 amp to obtain a molten pool. It was found that carbon pickup from the electrode tip was minimized if the melting time was held to 30 sec per melt and if the carbon tip was rounded rather than pointed. A procedure involving a total of six remelts per button for 30-sec intervals produced consistently homogeneous buttons. A specially designed furnace (see Figure 1) was used whereby the button could be flipped over after each melt without opening the furnace.

(1) References at end.



Legend

1. – to rectifiers
2. Water outlet
3. Water inlet
4. Wilson seal
5. Water-cooled spacer
6. Main vacuum line
7. Gas inlet
8. Water outlet
9. Water inlet
10. + to rectifiers
11. Graphite electrode
12. Copper crucible
13. Neoprene gaskets
14. Copper tubing for water cooling
15. Sight glass
16. Compression spring
17. Water-cooled electrode

FIGURE 1. CHARGE-FLIPPING ARC FURNACE

Experimental Casting Procedure

Preliminary investigations showed that casting of UC was a feasible process but that certain refinements and modifications of conventional arc-melting techniques were required in order to obtain sound specimens. For example, it was demonstrated that both in a copper mold and in a solid graphite mold the casting cracked as a result of cooling too rapidly. On the other hand, a graphite thimble mold proved to be quite satisfactory: cooling was slow enough to prevent cracking and no attack of the mold was noted. Usually, the castings slipped out of the thimble easily, thus allowing the mold to be used several times.

Using this type of thin-walled graphite mold, a "drop-casting" technique was adopted for producing cast specimens 3/8 in. in diameter by 1-3/4 in. long. As shown in Figure 2, the mold was suspended in the cavity of a copper supporting block by an integral graphite collar inside an arc-melting furnace. The component parts together with the assembled mold, button, and a finished casting are shown in Figures 3 and 4. In the technique used, a 100-g arc-melted button of UC was placed on the collar of the mold and most of the button was melted by passing a low-amperage arc in concentric circles over the surface of the button. This operation also served to preheat the mold. By increasing the current and power supplied to the arc and by holding the arc directly over the mold opening, all of the UC button was caused to melt and to suddenly drop into the mold as one mass. The steps involved in the casting procedure were as follows:

(1) Evacuate arc-melting furnace

(2) Introduce helium to approximately 20 in. of mercury

(3) Strike off arc on button using 200 amp at 30 to 32 v

(4) Increase to 400 to 600 amp to obtain round molten pool and preheat mold (time: about 60 sec)

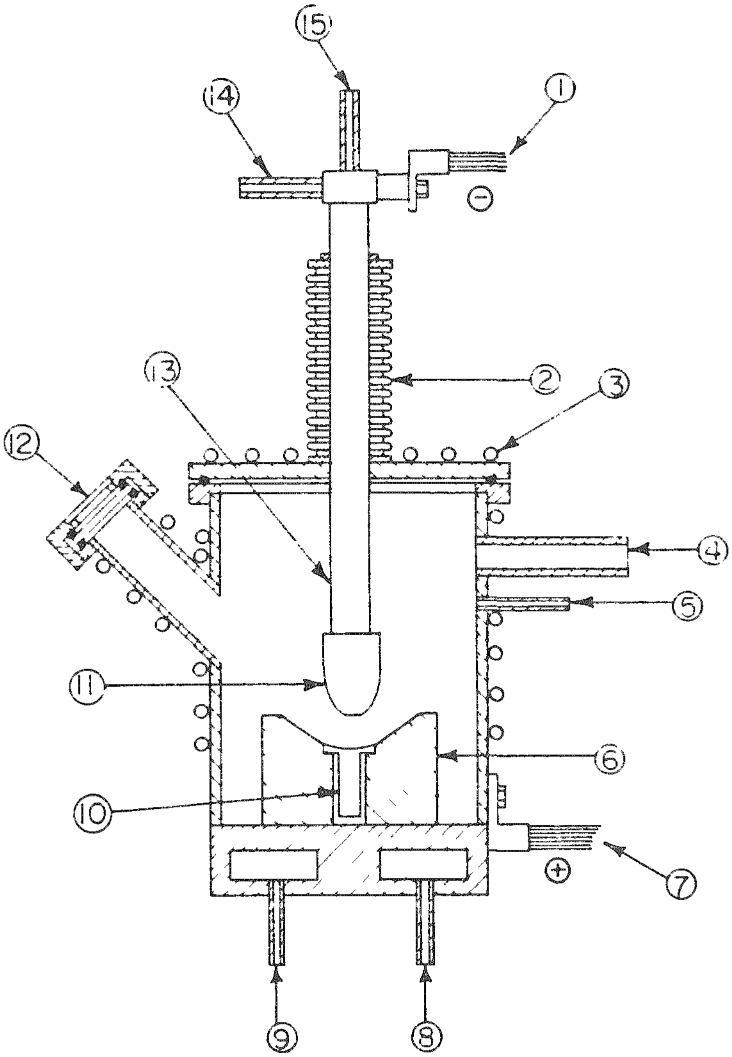
(5) Increase to 800 amp and hold until molten UC drops (time: 15 to 30 sec)

(6) Shut off power to arc and evacuate chamber until red glow has disappeared (time: 1 to 2 min; a significant reduction in the cooling rate was achieved by this evacuation procedure)

(7) Bleed in helium to approximately 20 in. of mercury (to speed cooling by conduction after black heat is obtained)

(8) Remove casting after about 10 min.

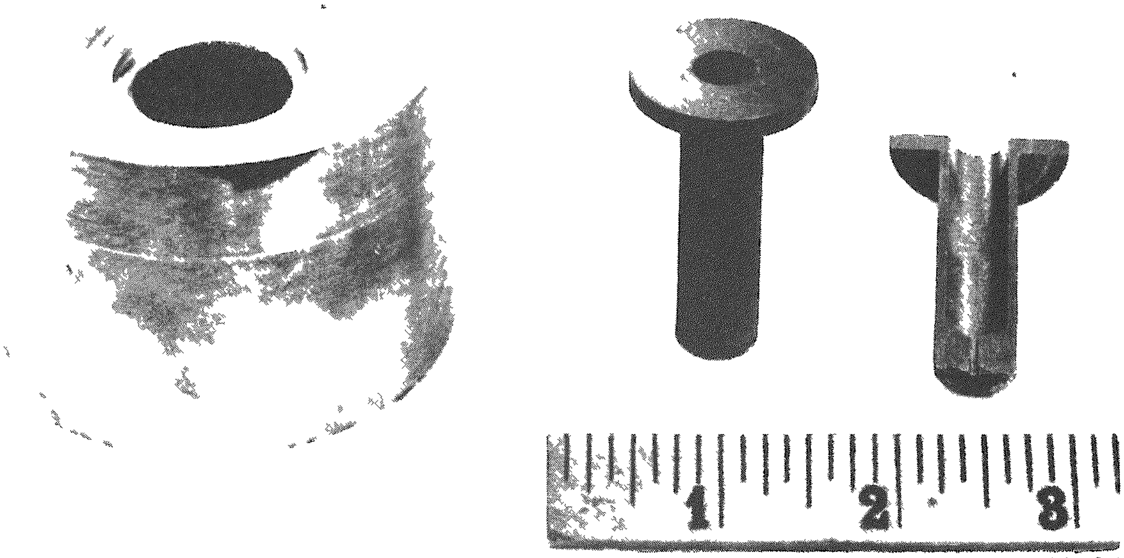
Small castings prepared by the above procedure were extemely well formed and free of cracks. This success was attributed in part to the fact that a 1/32-in. hole was drilled through the bottom of the mold to allow entrapped gases to escape. Surfaces were smooth and in general had a metallic appearance. Density measurements on a typical casting produced an average value of 13.4 g per cm^3, or 98 per cent of the theoretical value of UC. In general, no porosity was observed in the microstructures.



Legend

1. — to rectifiers
2. Brass bellows
3. Copper tubing for water cooling
4. Main vacuum line
5. Gas inlet
6. Copper mold support
7. + to rectifiers
8. Water inlet
9. Water outlet
10. Graphite thimble mold
11. Graphite electrode tip
12. Sight glass
13. Water-cooled electrode
14. Water outlet
15. Water inlet

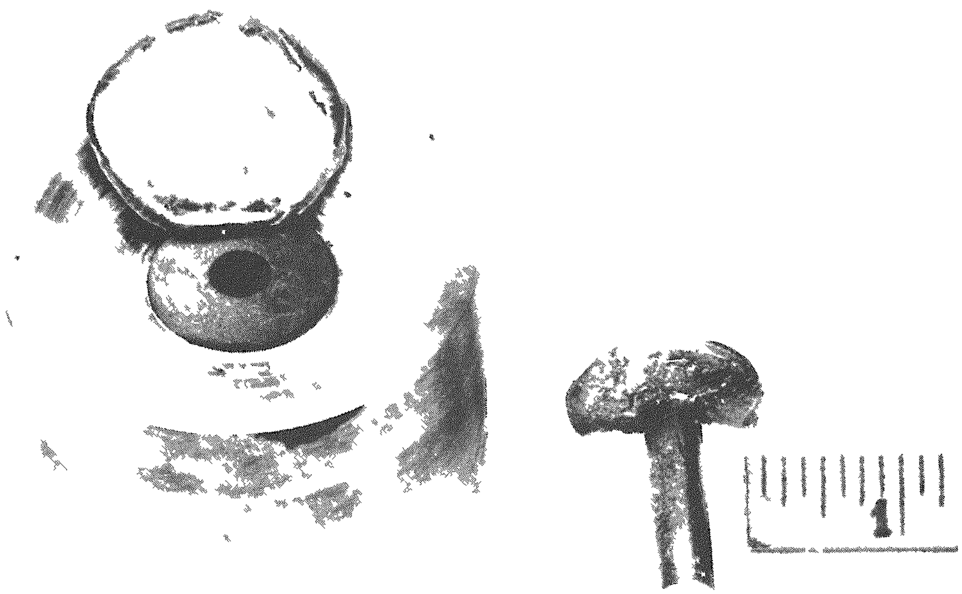
FIGURE 2. LABORATORY-TYPE ARC FURNACE WITH GRAPHITE THIMBLE MOLD AND COPPER MOLD SUPPORT



N51385

FIGURE 3. COPPER SUPPORT AND GRAPHITE THIMBLE MOLD FOR MAKING UC CASTINGS

Notice hole for degassing in bottom of mold sectioned.



N51387

FIGURE 4. ASSEMBLED MOLD WITH ARC-MELTED UC BUTTON CHARGE AND FINISHED CASTING

While sound castings of UC about 3/8 in. in diameter by 1-3/4 in. long could be produced readily by the drop-casting method, the preparation of larger specimens was found to be increasingly more difficult as the size increased. Imperfections such as shrink cavities, cracks, or surface roughness were present in larger castings.

Early in the program it was recognized that a more promising casting procedure for economical production of UC fuel-element shapes would involve skull-type arc-melting techniques. With this type of casting technique, a number of the shapes could potentially be cast at one time, composition control in terms of carbon content would be improved, and the molds could be more readily adapted to give the necessary mold temperatures and casting cooling rates. However, the size, shape, and number of specimens required for the physical tests of this research program did not justify the developmental efforts that would have been required. Attempts to prepare a large skull casting using 200-g UC charges in a bench-scale tilting-hearth arc furnace were unsuccessful only because the cast shapes, while well formed, cracked on cooling. The cracking was attributed to the use of an unheated copper mold and to the inherent rapid cooling of the casting in such a mold. If the copper mold had been replaced by a heated graphite thimble mold the cracking undoubtedly would have been prevented, as demonstrated by the drop-casting procedure.

Reproducibility of Casting Procedure

While the UC button is molten, it is subject to carbon pickup from both the graphite thimble mold and the carbon-tip electrode. The finished casting is, therefore, subject to possible variations in carbon content. In order to determine the reproducibility of composition of specimens prepared by a standard melting and casting procedure, four castings were made from eight 100-g buttons. These buttons, each having been melted six times to achieve homogeneity, varied by only 0.1 w/o from the desired 4.8 w/o carbon content. The castings also showed excellent reproducibility and good uniformity in composition from top to bottom. All sections from the top, middle, and bottom portions had carbon contents of 4.9 w/o ± 0.1 w/o. These analytical results were substantiated by metallographic examination. It has thus been established that the arc-melting procedure can be adequately controlled to yield buttons and castings of consistent composition.

PROPERTIES OF CAST UC

To evaluate the applicability of uranium monocarbide as a reactor fuel material, several properties and characteristics of the material must be known. Properties of the cast monocarbide would, in general, be expected to be similar to those of the carbide prepared by other techniques. However, the cast material may be expected to exhibit some superiority with regard to density, purity, and handling characteristics because there is less opportunity for contamination during its preparation. Some of the physical properties of UC presently available from the literature are listed in Table 1.

TABLE 1. PHYSICAL PROPERTIES OF URANIUM MONOCARBIDE[1,3,4,5]

Surface appearance	Metallic luster
Theoretical density	13.63 g per cm^3
Melting point	2350 C
Crystal structure	Face-centered cubic, a = 4.951 A
Stability	Decomposed by water

To supplement these data, studies were conducted on cast UC to obtain information on thermal conductivity and thermal expansion. Additional information was gained from metallographic, heat-treatment, thermal-cycling, and surface-preparation studies.

Thermal Conductivity

A casting larger than those prepared for the compositional reproducibility study was desired for the thermal-conductivity measurement. A specimen 1/2 in. in diameter by 2 in. long, having a composition of 5.2 w/o carbon, was successfully prepared by the drop-casting technique. Values for steady-state conditions over the temperature range from 100 to 735 C are given in Table 2. While the thermal conductivity of UO_2 decreases with increasing temperature over this range, this sample of UC reached a minimum at about 400 C and at 700 C was equal to the initial value. These values were obtained on a single specimen and additional tests will be required to determine whether the values are generally characteristic of UC.

TABLE 2. THERMAL CONDUCTIVITY OF URANIUM MONOCARBIDE

Temperature, C	Thermal Conductivity, cal/(sec)(cm)(C)
100	0.060
150	0.058
200	0.056
250	0.055
300	0.054
350	0.053
400	0.053
450	0.053
500	0.054
550	0.055
600	0.057
650	0.058
700	0.060
735	0.061

Thermal Expansion

The thermal-expansion coefficients of as-cast machine-ground uranium monocarbide were found to be similar to values reported for UO_2.[5] The mean linear thermal-expansion coefficients determined and calculated for temperature ranges from 20 to 950 C are presented in Table 3, and the experimental dilation data are plotted in Figure 5.

TABLE 3. MEAN LINEAR THERMAL-EXPANSION COEFFICIENTS OF CAST UC

Temperature Range, C	Thermal Expansion on First Thermal Cycle, 10^{-6} per C	
	Heating	Cooling
20-100	9.5	10.3
100-200	10.1	10.6
200-300	10.7	11.1
300-400	11.1	11.7
400-500	11.4	12.2
500-600	11.6	12.4
600-700	12.1	12.8
700-800	12.2	13.1
800-900	12.6	13.4
900-950	13.0	13.6

Metallography, Heat Treatment, and Mechanical Properties

The method for preparing UC specimens for microscopic examination consisted of mounting in Bakelite, grinding through 600-grit SiC papers with kerosene as a lubricant, and polishing first on a wheel covered with Forstmann's cloth impregnated with diamond paste and finally on Microcloth impregnated with Linde "B" alumina abrasive suspended in water. The final polishing time was kept short so that the contact with water was brief. The polished specimens were then etched by immersion in an etchant consisting of equal volumes of nitric acid, acetic acid, and water. An etching time of 5 to 20 sec was usually adequate.

The monocarbide is one of three carbides in the uranium-carbon system; the other two are the sesquicarbide (U_2C_3) and the dicarbide (UC_2).

Figures 6 and 7 show the differences between the microstructures of arc-cast UC containing the 4.8 w/o carbon and alloys containing 4.5 w/o and 5.0 w/o carbon. The alloy containing only 4.5 w/o carbon contains appreciable amounts of alpha uranium as a white phase at the grain boundaries and as isolated small globules. The matrix is the UC phase. The second phase in the higher-than-stoichiometric composition is UC_2, which appears as a light phase at the grain boundaries and also in the Widmanstätten pattern within each grain. Again, the matrix is the UC phase.

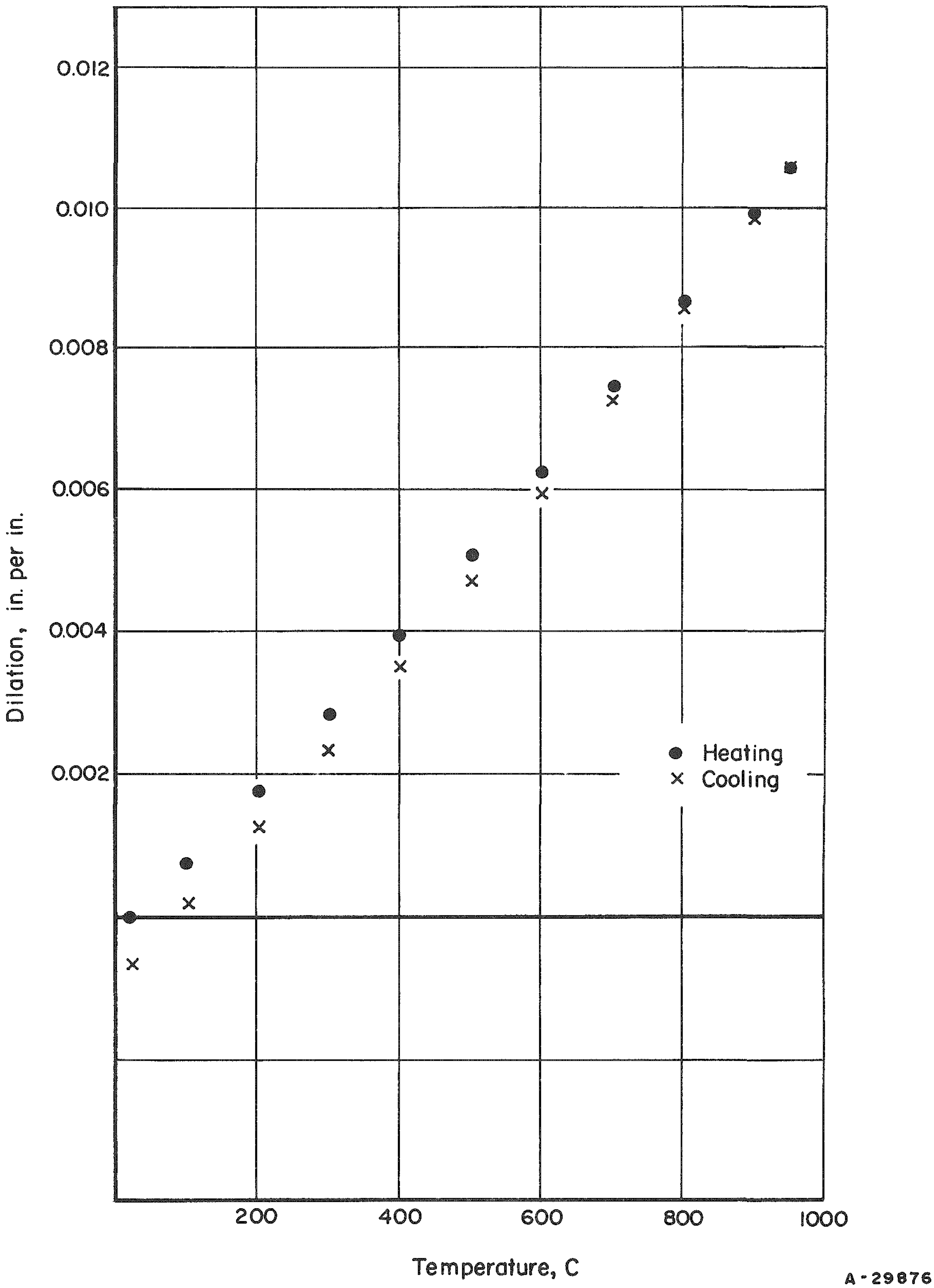


FIGURE 5. DILATION VERSUS TEMPERATURE FOR AS-CAST URANIUM CARBIDE

Heat treating a specimen containing 5.2 w/o carbon at 1000 C for 1 hr produced no significant change in microstructure, whereas further heating to 1500 C for 1 hr was accompanied by a broadening of the precipitated phase as shown in Figure 8. Similar heat treatments and change in microstructure have been associated in the past with the appearance of the sesquicarbide or U_2C_3 phase.[1]

An apparent increase of about 200 Vickers hardness resulted from the 1500 C heat treatment (Figure 8b). However, these hardness measurements should not be regarded as too meaningful because the treated and untreated materials differed in fracture sensitivity to the hardness indenter. This difference in hardness and fracture behavior perhaps indicates that heat treatment of the monocarbide may produce some stress-relieving or other toughening effect.

A single test of the compressive strength of a cast UC specimen was also made. A sample 3/8 in. in diameter by 1-5/8 in. long was subjected to three loading cycles at stresses up to 5,450, 27,250, and 54,500 psi. Rupture occurred at 54,500 psi. The average value of the modulus of elasticity from the three cycles was 31.5×10^6 psi. The strain was elastic over the stress ranges until rupture. Up to this stress, a total strain of 0.17 per cent was observed.

Thermal Cycling

UC specimens in the as-cast and machine-ground condition with carbon contents ranging from 4.5 to 5.0 w/o carbon were subjected to two series of thermal-cycling tests. The first test was 100 thermal cycles to 900 C and the second test was 100 thermal cycles to 1100 C. All specimens were still intact after testing and exhibited no evidence of cracking or growth. Each thermal cycle comprised heating at the specified temperature for 15 min in an evacuated quartz tube, followed by a 15-min cooling period at room temperature. During the tests at 900 C and 1100 C specimens of the three different compositions were in contact with Type 304 stainless steel. No attack on the stainless was noted.

Observations on the Surface Preparation of Cast UC

Due to the tendency of all uranium carbides to react with water, contact of UC specimens with water or water vapor was avoided, whenever possible. Consequently, all buttons and castings were stored in desiccators to provide adequate protection.

For certain physical-property determinations on UC it was necessary to have cylinders of uniform diameter. Machine grinding was found to work satisfactorily. Specimens ground on an Alundum wheel, using a water-base cutting fluid, showed no fracturing, but some loading of the wheel, accompanied by spalling of the specimen, was encountered. Substitution of a resin-bonded diamond wheel for the Alundum wheel completely eliminated the spalling tendency. During the grinding operation, the specimen was held between pressure pads and moved back and forth against the edge of the grinding wheel. Some specimens were ground to as small as 1/4 in. in diameter by 1 in. long. In spite of the tendency of UC to react with water, no detrimental effects were observed on the ground specimens as a result of using a water-base cutting fluid.

250X N49111

a. Uranium-4.8 w/o Carbon

500X N49112

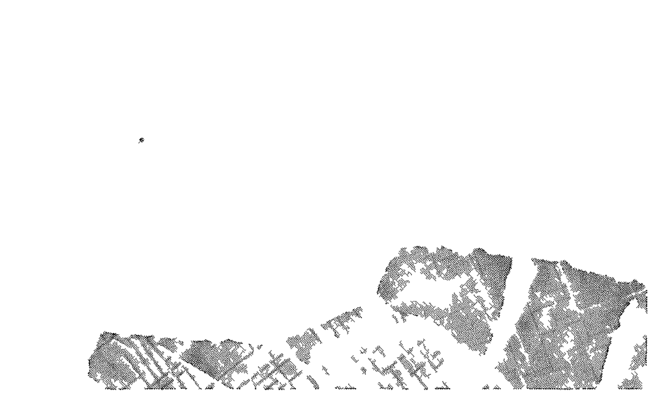
b. Uranium-4.8 w/o Carbon

FIGURE 6. *CAST STRUCTURE OF URANIUM MONOCARBIDE*

A trace of excess metallic uranium appears as white paticles.

250X RM10908

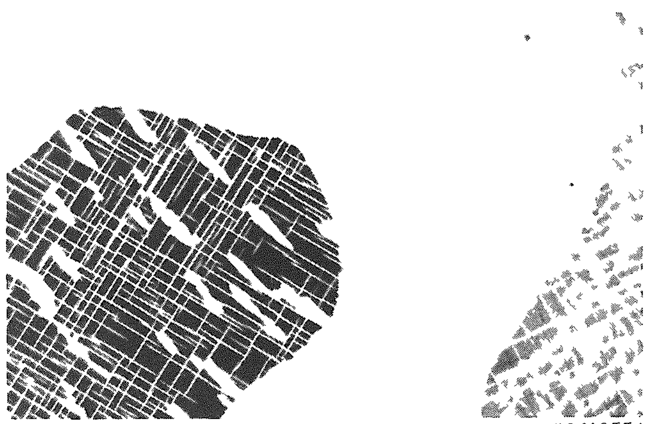
a. Uranium-4.5 w/o Carbon
Uranium (white) plus uranium carbide



250X RM10944

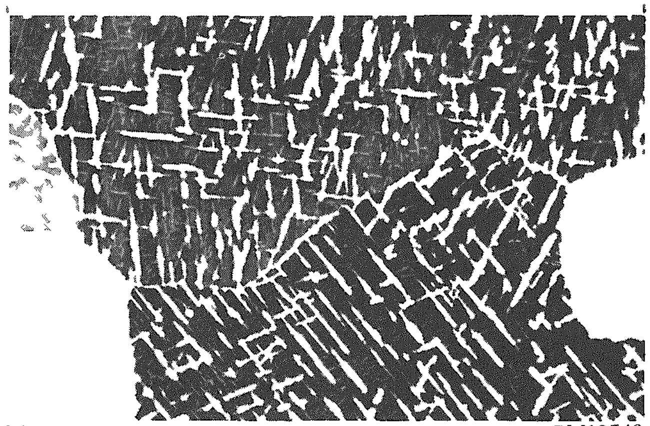
b. Uranium-5.0 w/o Carbon
UC plus acicular UC_2

FIGURE 7. CAST STRUCTURE OF URANIUM-CARBON ALLOYS



250X RM10551

a. After 1 Hr at 1000 C in Vacuum
UC plus UC_2; 560 DPH



250X RM10549

b. After 1 Hr at 1500 C in Vacuum
UC plus U_2C_3; 760 DPH

FIGURE 8. EFFECTS OF HEAT TREATING CAST URANIUM-5.2 w/o CARBON

However, immediately after grinding the specimens were wiped dry and stored in a desiccator.

All machine-ground specimens were radiographed using a cesium-137 source to determine the soundness of specimens. If any defects were present they were revealed in the two exposures taken with the specimens rotated 90 deg. The sensitivity of the examination was sufficient to reveal occasional tiny threadlike defects.

It was observed that machine-ground cast specimens tended to fracture on standing in air more rapidly than did unground castings. On the basis of X-ray and carbon analyses, this difference in stability was attributed to the presence of a thin surface layer of UC_2 on the as-cast unground material. The higher concentration of carbon resulted from contact of the molten monocarbide with the graphite mold. This observation is in agreement with the reported higher stability of UC_2 in air at room temperature.(3,4)

SUMMARY AND CONCLUSIONS

The technique for producing sound, homogeneous castings of uranium monocarbide involving the preparation of arc-melted material by direct alloying of the elements and subsequent arc melting and casting in graphite thimble molds appeared successful. Castings produced by this method were satisfactorily machine ground using a water-base cutting fluid with no evidence of fracturing or other detrimental effects.

Excellent compositional reproducibility and homogeneity were achieved in the preparation of arc-melted UC buttons and castings by adopting a uniform melting and casting procedure. These compositional data were obtained on small buttons and on 3/8-in.-diameter by 1-3/4-in.-long castings containing approximately 4.8 w/o carbon.

In the preliminary study of the physical properties of UC it was found that the thermal conductivity of this material, unlike that of UO_2 which decreases with increases in temperature over the range from 100 to 700 C, decreased only to 400 C and then increased with temperature. The value measured at 700 C, 0.060 cal/(sec)(cm)(C), was identical with that obtained at 100 C.

In thermal-cycling tests made on encapsulated cast uranium monocarbide samples containing 4.5 to 5.0 w/o carbon at both 900 and 1100 C, no evidence of fracturing or growth was observed after 100 thermal cycles (15 min in a furnace at temperature followed by a 15-min cooling period in room-temperature air).

Based on density, thermal-conductivity, and thermal-cycling data, cast uranium monocarbide appears to have all the necessary requirements for use as a reactor fuel material. However, other factors, such as its resistance to irradiation damage and its compatibility with materials used in reactors, need to be studied. On the basis of the preliminary studies reported here, there is every reason to believe that it will be feasible to prepare uranium monocarbide by casting techniques for use as a reactor fuel.

DISCUSSION

In general, cast UC has been shown to exhibit properties that make its use as a fuel exceptionally attractive for certain reactors. However, if it is to find useful application many additional studies should be conducted. These studies should include inquiries into the variation in physical and mechanical properties caused by small changes in impurity or carbon content. Concurrent with these studies of properties two specific fields suggest themselves as areas of profitable inquiry. These relate more directly to the fabrication of cast UC as a fuel element.

The drop-casting technique developed in the course of this work proved satisfactory for the preparation of small experimental castings. However, any large-scale production of cast UC fuel elements will necessitate a more practical and economical casting method. A promising method for production casting was briefly touched upon in this investigation. It involved using a skull-type arc-melting furnace in which the melting and casting operations are carried out consecutively. This method has several potential advantages that cannot be found in any other preparation procedure:

(1) A number of fuel elements could be cast at one time and the molding could be devised to give any desired mold temperature and cooling rate for the casting.

(2) Since arc-melting cycles are very short, high production rates could be achieved with a minimum number of furnaces.

(3) The furnaces, with the exception of the associated handling and molding equipment, also could be used in other metallurgical melting operations.

Developmental studies are needed in order to scale up the current laboratory process for the production of fuel slugs by this skull-arc-melting technique.

The highly reactive chemical nature of UC suggests a field for additional studies on the oxidation resistance and protection of this material. It was observed during the course of this study that a thin coating of UC_2 is beneficial to the room-temperature stability of cast UC fuel elements. Evidently, this film is formed when the molten UC is cast into graphite molds. While very thin, its presence has been confirmed by X-ray diffraction. The protection was evidenced by the ability of unmachined cylindrical surfaces of cast specimens exposed to the atmosphere to remain intact even though some corrosion and cracking was always noted on the cut end. If it is contemplated to use large numbers of cast shapes as fuel elements, the inspection and handling of the elements would be greatly simplified by the presence of a resistant coating, such as UC_2. One of a number of possible methods for applying such a coating might be a gas carburization process to change the surface film from UC to high-integrity UC_2. This film would serve not only to protect the entire specimen from surface deterioration but would also minimize the effect of small irregularities on the surface of the cast specimens. This coating would thereby reduce the tendency of atmospheric corrosion to open cracks.

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