Fifth Quarterly Report

SYNTHESIS AND FABRICATION OF REFRACTORY URANIUM COMPOUNDS

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I. INTRODUCTION

The object of this investigation is to develop refractory uranium materials possessing sufficient advantage over uranium dioxide to warrant their use as reactor fuels. Attention is being centered on UC, UN, and U_3Si_2, all of which have higher uranium densities than UO_2. The work consists of development of economical methods of synthesis and fabrication, and the determination of those properties pertinent to their use as fuels.

II. SUMMARY

Additional quantities of UC, UN and U_3Si_2 were prepared for use in fabrication of test specimens for property determinations. A reduction in oxygen contamination of UN and U_3Si_2 was achieved by improved techniques in synthesis.

A number of specimens for physical tests were fabricated. Improvement in density of the large test specimens was obtained in each of the above three materials.

Preliminary values for thermal expansion, modulus of elasticity, and corrosion in boiling water were obtained for UC, UN and U_3Si_2.

A new glove box facility was installed.

III. SYNTHESIS AND FABRICATION OF URANIUM COMPOUNDS

1. Uranium Monocarbide

Several batches of UC (up to 6 pounds in size) were synthesized by the reaction of carbon with uranium dioxide in vacuum at 1750°C. The analysis shown in Table No. I is typical, and specifically applies to a six-pound batch.

Fabrication experiments have been largely limited to the production of specimens (bars, 3-inch by 1/2-inch by 1/4-inch, cylinders, 1-inch by 1-inch and cylinders, 1/2-inch by 1/2-inch) for property evaluation. Fabrication was by cold pressing and sintering, following a procedure previously worked out and consisting of the following steps. The powder was milled for 48 to 72 hours in a rubber-lined mill with stainless steel balls and pressed at about 10,000 pounds per square inch using 1/2 percent Carbowax as a temporary binder. The shapes were heated slowly to about 1500°C. in flowing helium or argon and then sintered at 1850°C. in vacuum for one hour. Tantalum-lined graphite crucibles were used as containers.

TABLE NO. I

Typical Analysis of Uranium Monocarbide

Chemical Analysis, %			X-Ray Analysis
Total U	=	94.90	Major UC
Total C	=	4.65	Indications of UO_2 and UC_2
Free C	=	0.13	
Fe	=	0.01	
N_2	=	Nil	

Initially, difficulty was experienced in obtaining high density on the larger shapes such as the bars. Currently, however, bars of 93 percent theoretical density are being obtained (small pellets have been made having densities as high as 96 percent of theoretical). Variations in density under the same sintering conditions can result from differences in particle size. Also, recent evidence indicates that freshly milled powder sinters more readily than milled powder kept in storage, even for the relatively short period of a week or so. The latter factor is being investigated more fully.

Metallographic examination of a polished section from one of the test bars showed the composition to be essentially UC with small amounts of UC_2 and another phase, possibly UO_2.

2. Uranium Mononitride

Uranium mononitride was synthesized by hydriding uranium metal shot to produce a fine powder, followed by nitriding at 800°C. to form U_2N_3 and then reducing to UN in a vacuum at 1350°C. X-ray analysis indicated that the resulting powder was single phase UN. Oxygen content, as determined by vacuum fusion, was only 0.01 percent. Results of chemical analysis showed considerable variation in nitrogen content of the same sample and are therefore considered unreliable.

An innovation initiated during the past quarter in preparing uranium nitride from uranium metal shot was to conduct the hydriding and nitriding steps in stainless steel crucibles in a furnace having an Inconel muffle. The U_2N_3 was then transferred to tantalum-lined graphite crucible for vacuum reduction to UN. This has made possible the production of larger batches of UN.

Considerable progress was made in the fabrication of uranium mononitride and test specimens have been produced with densities up to 95 percent theoretical (based on a composition of pure UN). The procedure followed was that described in the last quarterly report and started with milling the UN powders for 48 hours in a rubber-lined ball mill with stainless steel balls. This was followed by cold pressing at 16,000 pounds per square inch with a temporary binder of Carbowax 6000 dissolved in trichlorethylene. The temporary binder was removed by heating at 100° per hour in a flowing atmosphere of argon to 1400°C. Sintering was carried out in vacuum at 1850°C. for one hour. Densities of the test specimens (same size as those described under UC) ranged from 12.5 to 13.6 grams per cubic centimeter.

Metallographic examination of the sintered samples disclosed small amounts of a second phase believed to be uranium metal, possibly resulting from incomplete nitriding, over reduction, or a loss of nitrogen during sintering. This behavior is being given further study.

3. Uranium Silicide (U_3Si_2)

Several one to three pound batches of U_3Si_2 have been made by reacting uranium with silicon, in order to obtain powder for fabricating test specimens. Uranium metal shot was acid-treated to remove surface oxide and rinsed in acetone. The treated metal was next milled with silicon powder for four hours in a rubber-lined ball mill with stainless steel balls. The mixture was then placed in a dense MgO crucible and heated to 1550°C. in a vacuum furnace at a pressure of 100-200 microns. The furnace power was shut off as soon as the temperature reached 1550°C. and allowed to cool. A typical analysis of the resulting material is shown in Table No. II.

TABLE NO. II

Typical Analysis of U_3Si_2 (U, 92.73%; Si, 7.27%)

Chemical Analysis, %			X-Ray Analysis
Total U	=	92.32	Strong U_3Si_2
Total Si	=	6.96	Weak Si
Fe	=	.29	
C	=	.14	
O_2*	=	.073	
N_2*	=	.025	

*Determined by vacuum fusion.

In the Fourth Quarterly Report it was noted that larger batches of reaction product seemed to have lower oxide impurity. The analysis in Table No. II, showing only 0.07 percent oxygen, substantiates this conclusion.

It can be noted that the x-ray analysis of U_3Si_2 produced in the above manner showed an indication of free silicon metal. In an effort to explore this problem a series of experiments were made to determine if more complete equilibrium conditions could be established. Four compositions were reacted which were calculated to the following departures from stoichiometric U_3Si_2: U_3Si_2 + 2% U, U_3Si_2 + 4% U, U_3Si_2 + 2% Si, and U_3Si_2 + 4% Si. After synthesis, the samples were analyzed, using x-ray and metallographic techniques. X-ray analysis was the same for all samples including stoichiometric U_3Si_2, namely, U_3Si_2 with a weak indication of silicon. Metallographic examination of the stoichiometric U_3Si_2 showed essentially single phase material. However, as the composition varied in either direction from U_3Si_2, an increasing amount of a second phase appeared. The interpretation of the x-ray analysis, therefore, seems questionable. Further metallographic examination of the samples will be made in order to resolve this inconsistency.

A number of test specimens (bars and cylinders) were fabricated by cold pressing and sintering during the present report period. The reacted product was crushed, then milled for 48 hours in a rubber-lined ball mill with stainless steel balls. The resulting powder was cold pressed at 16,000 pounds per square inch using Carbowax as a temporary binder. The pressed forms were first heated in flowing argon in tantalum-lined graphite crucibles at the rate of 50°C. per hour to 600°C.; this was followed by rapid heating to 1400°C., which temperature was maintained for two hours. The sintered specimens had a density of approximately 11.8 grams per cubic centimeter, or about 96.8 percent of theoretical, an improvement over similar large-size specimens previously sintered at 1300°C. A polished section of a typical specimen (Figure 1) shows essentially single phase U_3Si_2 of fairly small grains, with perhaps a trace of a second phase.

IV. EVALUATION OF SINTERED UC, UN and U_3Si_2 SPECIMENS

Preliminary physical testing has been started during this quarter. To date, values have been obtained for thermal expansion, modulus of elasticity and corrosion resistance in water. Modulus of rupture determinations are presently in progress and samples are being ground to final size for thermal conductivity tests.

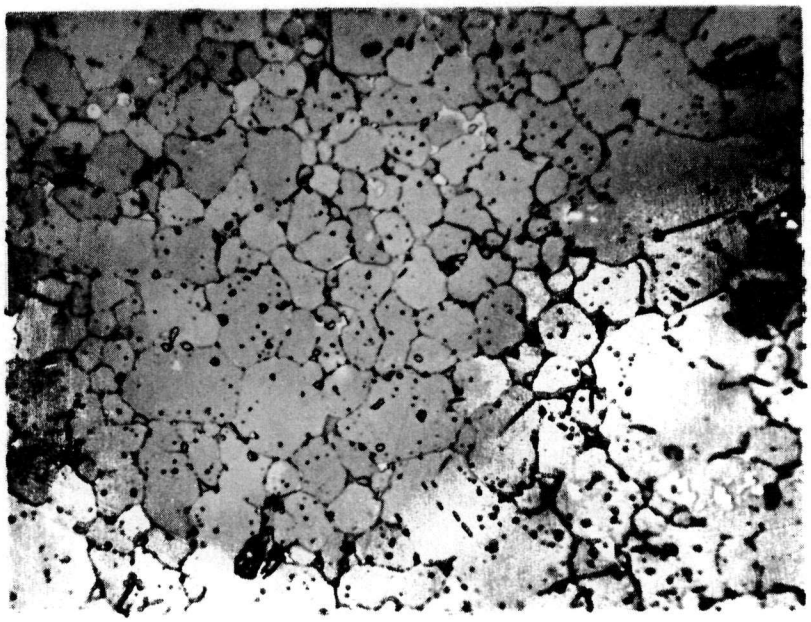

Figure 1 - Sintered U_3Si_2 - 500X.
Fine-grained, essentially single phase.
Density, about 98 percent of theoretical.

Thermal expansion determinations are being conducted in a dilatometer contained in a high density silicon carbide tube. This allows a flowing inert atmosphere to be maintained around the sample, thus protecting it from oxidation during the test. The results of the tests which are reported in Table No. III are to be considered preliminary only. The specimens used to determine thermal expansion and modulus of elasticity are bars having nominal dimensions of 3 inches by 1/2-inch by 1/4-inch.

TABLE NO. III

Properties of Sintered UC, UN and U_3Si_2
(Preliminary Data)

Composition	Density (g/cc.)	Average Thermal Expansion (cm/cm/°C.)	Modulus of Elasticity (psi)	Water Corrosion Resistance
UC	12.3	12.40×10^{-6} (30-1400°C.)	25×10^6	Reacts with water slowly at room temperature and vigorously at 40°C.
UN	12.6	8×10^{-6} (30-600°C.)	24×10^6	Slight discoloration after 48 hours in boiling water - weight loss of 0.11%.
U_3Si_2	12.0	16×10^{-6} (30-1000°C.)	19×10^6	Slight discoloration after 384 hours in boiling water - weight gain of 0.014%.

The modulus of elasticity was determined at room temperature using a sonic method. It should be recalled that modulus of elasticity varies with the density or porosity of the sample. Samples of varying density are being used in an attempt to establish the relationship of density (or porosity) to modulus of elasticity. Preliminary results indicate that the relationship is linear in the low porosity range.

To test the corrosion resistance of UC, UN, and U_3Si_2 to water, samples of each compound were placed in distilled water, heated to the boiling point and held for a number of hours. At periodic intervals the samples were removed and examined visually, weighed and measured. The final results are reported in Table No. III. It should also be noted that there was no measurable volume change in either the UN or U_3Si_2 samples, however the UC pellet completely disintegrated. Further tests of the corrosion resistance of UN and U_3Si_2 will be made.

V. FACILITIES

The additional glove box was received and installed during the last quarter (Figure 2). It is being used in the fabrication of UC, UN and U_3Si_2 test specimens. The box has been equipped with crushing and grinding equipment, ball mills and rolls, balances, molds, a hydraulic press and a ceramic tube furnace.

Plans are being made for a helium purification and recirculation system to be used in conjunction with new glove box. This should improve the quality of the atmosphere in the box and make its use more economical; it is presently being operated with "once-through" helium and nitrogen gas.

VI. FUTURE WORK

Future work will consist of fabrication of additional test specimens as needed and the determination of physical properties of UC, UN, and U_3Si_2. The properties being studied are thermal expansion, thermal conductivity, modulus of rupture, modulus of elasticity and resistance to thermal cycling. Also, if time permits, additional basic work will be done on the synthesis and fabrication of these compounds.

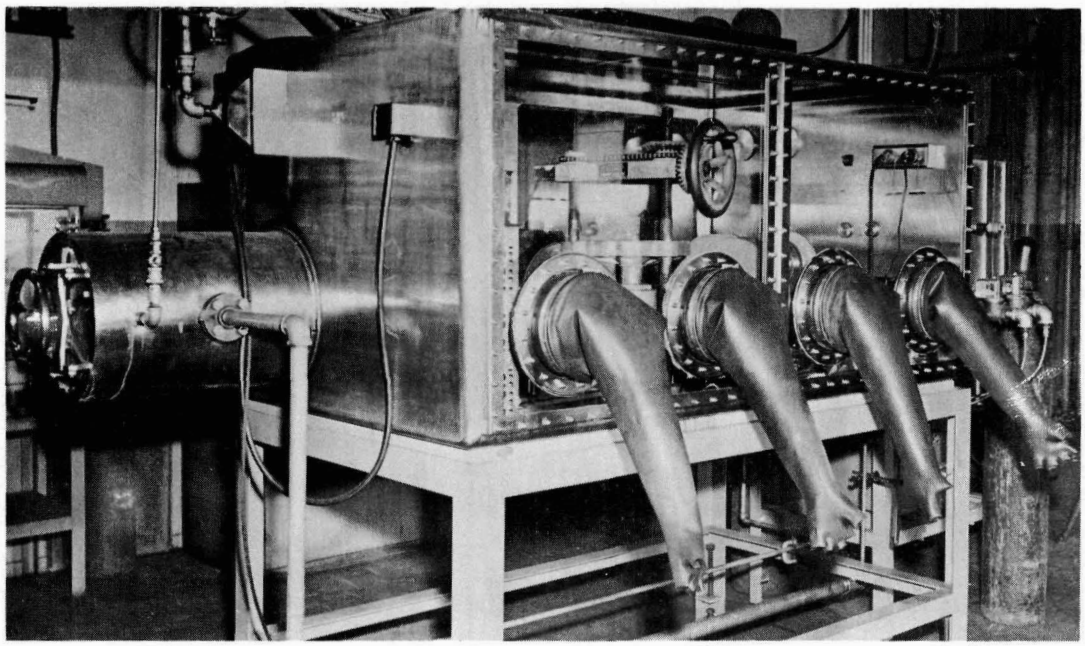

Figure 2 - Glove box for work on refractory uranium compounds.

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