

Monthly Progress Report No. 8  
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**SYNTHESIS AND FABRICATION OF REFRACTORY URANIUM  
COMPOUNDS**

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Uranium Silicide,  $U_3Si_2$

The effort on uranium silicide this month was equally divided between synthesis and fabrication. The goal for the synthesizing effort was to make  $U_3Si_2$  of higher purity than that made in the past, and the goal for the fabrication effort was to make pellets of higher density than the 93 percent of theoretical previously obtained. Both of the above goals were essentially achieved.

1. Synthesis of  $U_3Si_2$

The  $U_3Si_2$  made previous to this time has been characterized to be mainly  $U_3Si_2$ , with small but undetermined amounts of  $UO_2$  and free silicon. In all cases, the final material when removed from the furnace had an oxide coating and even though this was removed, it was thought that not enough of the outer portions were removed to insure complete elimination of  $UO_2$  due to surface oxidation. From a practical standpoint, the above could not be done due to the small sizes of the batches (100 grams and less) with resulting large surface area to volume ratios. An attempt was now made to synthesize a larger batch (one pound) of  $U_3Si_2$ . The procedure was the same as described in previous reports with the exception of using a vacuum induction furnace instead of the usual tube furnace with an argon atmosphere. The resulting material, after removal of the surface portion, was found by x-ray diffraction analysis to be  $U_3Si_2$  with a small amount of free silicon. Metallographic examination showed essentially no porosity with the major  $U_3Si_2$  phase having an occasional small formation of  $UO_2$ . Etching with nitric acid also showed what appeared to be small cracks in the  $U_3Si_2$  grains filled with an unetched phase, presumably free silicon. Densities of various pieces were 100 percent of theoretical for  $U_3Si_2$ . As mentioned in last month's report, the possibility of fusion casting or hot extruding  $U_3Si_2$  is again indicated by these results.

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In all past synthesizing runs, the ratio of the starting materials, uranium and silicon, has always been a stoichiometric one. It was theorized that the surface oxidation during the run was primarily that of uranium which would leave a deficiency of uranium in the central melt, thus causing the unreacted or free silicon in the final material. With the above thought in mind, a second one pound batch of  $U_3Si_2$  was synthesized exactly as above with the exception that uranium was in 2.5 weight percent excess. The resulting material was extremely hard to break up and x-ray diffraction analysis shows it to be  $U_3Si_2$  with still a small amount of free silicon. No other information is available at this time for this material.

In the report for last month, it was mentioned that a batch of  $U_3Si_2$  made with 5 percent excess uranium had a density of 103 percent of theoretical for pure  $U_3Si_2$ . Because the resulting mass was somewhat ductile it was not possible to reduce it for powder x-ray diffraction analysis. However, an x-ray pattern obtained on a polished surface of the material showed a major phase of  $U_3Si_2$  with a minor phase of an unidentifiable silicide presumed to be  $U_3Si_2$ .

During the month a beryllia and a thoria crucible were received and a normal synthesizing run was made in each. The formed  $U_3Si_2$  did not wet the sides or react in any way with either crucible and both crucibles appeared unaffected by their experience, indicating that beryllia and thoria are the best materials evaluated to date for uranium silicide work.

## 2. Fabrication of $U_3Si_2$

The  $U_3Si_2$  material used for fabrication studies this month came from the first one pound batch mentioned in the above section on synthesis of  $U_3Si_2$ . Since this material contained free silicon as the chief impurity, with possible undesirable density effects when sintering, sintering runs were made as described in previous reports with the exception of a 2 weight percent addition of uranium metal during the milling step. After sintering, the pellets had an oxide coating, were cracked, and broke apart easily. After removal of the oxide coating, the pellets had densities in the range of 94 - 95 percent of theoretical. X-ray diffraction analysis showed  $U_3Si_2$  with a small amount of  $UO_2$ . Metallographic examination showed the  $UO_2$  to be at the grain boundaries. Apparently the free silicon in the starting material reacted with some of the excess uranium, and the rest of the free uranium was converted to the oxide.

Simultaneously, another attempt at sintering higher density pellets was made by changing the grinding and sintering procedures. The  $U_3Si_2$  material was milled for 90 hours instead of the usual 20 hours and the resulting densities of the unfired pellets was 70 percent of theoretical as contrasted to the usual 65 percent. A pre-sintering step,  $1000^{\circ}C$ . for 2 hours, was also added. The resulting fired pellets had an oxide coating and were cracked on the surface but otherwise were quite strong. After removal of the oxide coating, the pellets had densities in the range of 97 - 98 percent of theoretical. X-ray diffraction analysis showed no significant change in composition from the starting material except some pick up of  $UO_2$ . Metallographic examination revealed very few definable grain boundaries and minute pores and structures of other phases, presumably  $UO_2$  and free silicon.

It is theorized that the cracking of the pellets is due to the stresses created by the surface oxidation. The next major effort on sintering  $U_3Si_2$  shapes will be aimed at eliminating oxidation with subsequent cracking of the shapes.

#### Simultaneous Synthesis and Fabrication of Uranium Monocarbide

Some additional experiments have been carried out on this process which consists of hot pressing mixtures of uranium metal powder and carbon. In these experiments the uranium metal shot was first hydrided and then the hydride decomposed to obtain fine particle size metal preliminary to mixing it with carbon.

One hundred grams of uranium metal shot was acid treated with dilute nitric acid (1  $HNO_3$ : 8  $H_2O$ ), then washed with water and acetone. The material was placed in a tantalum lined alumina boat and hydrided for one hour at  $250^{\circ}C$ . in a ceramic tube furnace. Then the hydrogen was replaced by purified argon and the product heated for one-half hour at  $350^{\circ}C$ . The temperature was then raised slowly to  $500^{\circ}C$ . and the hydride decomposed further at this temperature for two hours. In this way a fine uranium metal powder was obtained. The powder was mixed with 4.8 percent Acheson graphite No. 38 in a "Spex-Mixer" for one-half hour. In one experiment, a part of above mix was hot-pressed in an argon atmosphere in a graphite die at  $1200^{\circ}C$ . for 2 hours at a pressure of about 1500 pounds per square inch. The hot-pressed pellet had a density of 96 percent of theoretical. Examination of polished sections of this pellet showed a principal phase of UC and agglomerates of uranium metal. It was observed that the amount of free uranium increased from the center to the periphery of the pellet.

In a second experiment, part of the same mix of uranium powder and graphite was hot-pressed for 4 1/2 hours at 1000°C. in an argon atmosphere under a pressure of about 1500 pounds per square inch. The hot-pressed pellet had a density of 97 percent of theoretical. Examination of polished sections of this pellet showed that in the center essentially only one phase, UC, was present. Away from the center free uranium metal was observed, small amounts being located in the grain-boundaries. The amount of uranium increased towards the periphery of the pellet and agglomerates of free uranium were present, although in a smaller amount than in the first experiment.

#### Sintering Experiments With Uranium Mononitride

Previous work on sintering uranium mononitride was done with powder produced by direct nitriding 100 to 250 mesh uranium shot. During the past month sintering experiments have been made with two additional UN powders. The first was produced by acid treating the uranium shot to remove any surface oxide, hydriding the cleaned shot to obtain a fine metal powder and finally nitriding the powder. The second powder was produced by nitriding a stoichiometric mixture of UO<sub>2</sub> and carbon. It was thought that synthesis by these methods might produce finer particle size and therefore more sinterable powders.

The fabrication steps were similar to those previously used for UN and consisted of ball milling the powder in a rubber lined mill with stainless steel balls, cold pressing with carbowax binder and sintering in argon at 1800°C. The resulting densities, however, were no higher than the previously reported 91 to 93 percent of theoretical. Although special precautions were taken to prevent oxidation, x-ray studies on the starting powder and fabricated pellets indicated that appreciable oxidation had taken place. This was further indicated by some tendency of the pellets to crack during sintering. The next experiments will be carried out in improved facilities to reduce oxidation to a minimum; also, liquid phase sintering using small amounts of free uranium metal will be investigated.

#### Facilities and Future Work

No direct work on synthesis or fabrication of uranium materials is planned for May and June, 1960. Instead, this time will be spent

in improving present facilities and in obtaining new equipment. Thermal conductivity equipment for inert atmosphere work is now being assembled. New apparatus for modulus of rupture determinations in inert atmospheres has been obtained and is now being tested. A new and larger glove box and considerable related equipment has been ordered. Work on and expenditures for facilities and capital equipment are not being charged to the present contract.

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