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Fourth Quarterly Report

SYNTHESIS AND FABRICATION OF REFRACTORY URANIUM COMPOUNDS

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DISCLAIMER

TABLE OF CONTENTS

TABLE NO. I

Synthesis of Uranium Mononitride

Experiment No.	Heating Schedule			X-ray Analysis
	Atmosphere	Temperature °C.	Hold Time Hrs.	
1	H_2	0-250	1	Major UN
	N_2	250-400	3	Weak/mod. UO_2
	N_2	400-800	3	
	A	800-1450	8	
2	H_2	0-250	1	Major UN
	N_2	250-400	3	Weak/mod. UO_2
	N_2	400-800	3	
	He	800-1450	8	
3	H_2	0-250	1	Major UN_2 (?)
	N_2	250-400	3	
	N_2	400-800	3	
4	Vacuum reduction of #3			Major UN
		1400	1	
5	H_2	0-250	1	Major UN_2 (?)
	N_2	250-400	6	
	N_2	400-800	6	
6	Vacuum reduction of #5			Major UN
		1350	1	Faint UN_2 type

I. INTRODUCTION

The original contract period was 13 May 1959 through 1 November 1960. Since no work was done during May and June of 1960, to make possible improvements in facilities, contract has been extended through 31 December 1960.

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 the development of economical methods of synthesis and fabrication, and the determination of the physical properties of the fabricated bodies.

II. SUMMARY

Additional work on the synthesis and fabrication of uranium nitride has produced an improved product free of oxide contamination as indicated by x-ray analysis. Further work to increase the density of the sintered pellets is needed.

A stock of several pounds of stoichiometric uranium monocarbide has been prepared by carbon reduction of uranium dioxide. Pellets having bulk densities ranging from 93 to 96 percent of theoretical have been obtained by cold pressing and sintering. Initial experiments on the fabrication of bars, 3 inches by 1/2-inch by 1/4-inch, by cold pressing and sintering, have resulted in sound but somewhat low density bodies.

A few experiments were conducted on the production of uranium monocarbide from ammonium diuranate. The results indicate that considerable additional work may be necessary to consistently produce a stoichiometric product.

The simultaneous synthesis and hot pressing of uranium monocarbide has been further studied and pellets with bulk densities as high as 96.6 percent of theoretical (based on 100 percent UC) have been produced. However, metallographic examination has disclosed the presence of some free uranium metal in all pellets.

The synthesis of one pound batches of U_3Si_2 of improved quality has been successfully carried out by a non-quench method. Using the U_3Si_2 so produced, sound pellets with bulk densities up to 98.5 percent of theoretical have been prepared by cold pressing and sintering. The sintering technique has also been used to produce 3-inch by 1/2-inch by 1/4-inch bars for physical property tests.

III. PREPARATION AND FABRICATION OF URANIUM MONONITRIDE

1. Preparation by Nitriding Uranium Metal Powder

Synthesis experiments were performed primarily to provide freshly prepared uranium mononitride powder for sintering experiments. They also afforded an opportunity to improve the quality of the uranium mononitride over that previously produced in this investigation.

Uranium metal shot was acid-treated to remove surface oxide film, washed with acetone and loaded immediately after drying into a tantalum-lined alumina boat. This was placed in a ceramic tube muffle furnace and hydrided to yield a fine powder. Nitriding was then carried out at a maximum temperature of 800°C. using purified nitrogen. The nitride thus produced was reduced to the mononitride in an atmosphere of argon or helium, or in a vacuum at temperatures of 1350 to 1400°C. The synthesis experiments are summarized in Table No. I.

In the first two experiments where the reduction was carried out in helium and argon, a UO_2 phase appeared in the x-ray analysis. Subsequent experiments were designed to determine the source of oxidation which was found to occur during the reduction to UN in argon or helium. It can be seen that vacuum reductions (Experiments 4 and 6) resulted in uranium nitride powder which showed no oxide phase in the x-ray analysis.

2. Fabrication of Uranium Mononitride

The pellets used in these experiments were cold pressed at 16,000 pounds per square inch using Carbowax 6000 dissolved in trichlorethylene as temporary binder. The UN powder was milled for 36 hours in rubber-lined ball mills with stainless steel balls. Table No.II gives a typical analysis of this material.

TABLE NO. II

UN Powder Before Sintering

Chemical Analysis		X-ray Analysis
Total U	94.73%	Major UN
N_2	5.24	Faint UO_2, UN_2
Fe	.13	
Total Carbon	.08	

In attempts to reduce oxidation occuring during sintering, pellets were placed in tantalum boats which were then sealed in plastic bags under an inert atmosphere for transference from the glove box to the sintering furnace. After carefully flushing out the sintering furnace, the plastic bags were allowed to decompose during the early stages of the heating cycle.

The pellets were heated at a rate of 300°C. per hour in flowing purified argon, holding at a maximum temperature of 1800°C. for 30 minutes. However, notwithstanding the precautions taken, the sintered pellets developed an oxide coating and also cracked.

In a second experiment, pellets were cold pressed from the UN powder produced in Experiment 6, Table No. I, omitting milling of the powder. The rate of heating was reduced to 100°C. per hour to remove the temporary binder more gradually and the sintering was carried out as previously described except that the pellets were in a closed graphite crucible having a tantalum lining. After sintering, these pellets were free of cracks and showed no evidence of surface oxidation. However, the density was low (10.5 grams per cubic centimeter). It is believed that milling under carefully controlled conditions, combined with the above fabrication procedure, will produce sound, oxide-free pellets of satisfactory density.

IV. PREPARATION AND FABRICATION OF URANIUM MONOCARBIDE

1. Preparation by Reduction of Uranium Dioxide

A large batch of uranium monocarbide has been synthesized to provide a stock of material from which bars and cylinders can be fabricated for physical testing. A typical x-ray and chemical analysis of this material is shown in Table No. III. Oxygen analysis is being obtained by the National Research Corporation.

2. Preparation by Reduction of Ammonium Diuranate

Experiments described in the last quarterly report suggest that uranium monocarbide can be made from ammonium diuranate after determining the proper amount of carbon required by this reaction. From previous work this amount was thought to be 10.34 percent and during the last quarter three experiments were undertaken to prove this point. The results are shown in Table No. IV. In all cases the

TABLE NO. III

Typical Analysis of Uranium Monocarbide

Chemical Analysis		X-ray Analysis
Total U	95.10%	Major UC
Total C	4.64	Indication of UO_2
Free C	.04	
Fe	.01	
N_2	Nil	

TABLE NO. IV

Synthesis of UC from Ammonium Diuranate

Experiment No.	1	2	3
Atmosphere	Vacuum	Argon	Argon
Time to Reach 700°C.	40 Min.	40 Min.	40 Min.
Time to Reach 1700°C.	1 Hr.	2 Hrs.	4 Hrs.
Total Carbon in Product, %	3.88	4.15	5.51
X-ray Analysis of Product			
UC	Major	Major	Major
UC_2	Weak	Weak	Mod./Strong
UO_2	Faint	Faint	Faint

pellets were cold pressed at 16,000 pounds per square inch using an ADU-carbon mixture of 10.34 percent carbon. These were heated to 1700°C. under varying conditions. The reaction product varies considerably and is apparently affected by variations in furnacing. The results indicate that stoichiometric UC could probably be obtained from ADU; however, considerable additional study would be required.

3. Preparation and Fabrication by Reaction of Uranium and Carbon While Hot Pressing

Several experiments have been carried out on this process which consists of hot-pressing mixtures of uranium metal and carbon. In all cases samples were pressed at 1500 pounds per square inch in a 1/2-inch diameter graphite mold. The heating rate and hold temperature, mixing procedure and uranium powder preparation have been varied.

Apparently the problem has been to produce a homogeneous mixture of the constituents, and to find the correct heating schedule to produce a complete reaction. Table No. V summarizes the hot pressing experiments. Experiments number 8 and 9 illustrate that with the proper conditions high densities can be produced by this method. However, it should be noted that metallographic examination disclosed small amounts of free uranium metal located at the grain boundaries; at present, it is not known if this is of serious consequence.

4. Fabrication of Uranium Monocarbide by Sintering

Further fabrication experiments have been carried out using the cold pressing and sintering technique described previously in the Third Quarterly Progress Report. The resulting pellets had a bulk density ranging from 93 to 96 percent of theoretical.

Initial experiments were made in cold pressing and sintering of bars, 3 inches by 1/2-inch by 1/4-inch, for physical testing. The procedure was identical to that used in fabricating the pellets with the exception that presintering was carried out at the slower rate of 50°C. per hour to prevent cracking due to binder removal.

The first bars were straight and crack-free but low in bulk density (10.25 grams per cubic centimeter). Further sinterings are in progress to increase the density, after which physical testing will be started.

TABLE NO. V

Preparation of UC by Simultaneous Reaction and Hot Pressing

No.	Mixing Method	Heating Schedule	Density g./cc.	Density % Theoretical	Remarks
1	Ball Milled	800°C. - 1 Hr. 1400°C. - 1 Hr.	13.3	97.7	This experiment described in Quarterly Report No. 2.
2	Ball Milled	800°C. - 1 Hr. 1100°C. - 1 Hr.	11.7	85.8	
3	Ball Milled	800°C. - 1 Hr. 1200°C. - 1 Hr.	11.7	85.8	
4	Ball Milled	800°C. - 1 Hr. 1200°C. - 1 Hr.	12.4	90.9	
5	Ball Milled	800°C. - 1 Hr. 1400°C. - 1 Hr.	12.25	90.0	
6	Ball Milled	1000°C. - 1 Hr. 1400°C. - 2 Hrs.	12.79	93.5	
7	Ball Milled	1070°C. - 1 Hr. 1400°C. - 2 Hrs.	12.58	92.4	
8	Vibrated ("Spex Mixer")	800°C. - 1 Hr. 1200°C. - 2 Hrs.	13.05	95.7	UH_3 used as starting material.
9	Vibrated ("Spex Mixer")	800°C. - 1 Hr. 1000°C. - 4-1/2 Hrs.	13.19	96.6	UH_3 used as starting material.

V. PREPARATION AND FABRICATION OF URANIUM SILICIDE (U_3Si_2)

1. Preparation of U_3Si_2

U_3Si_2 synthesis experiments have been continued using the non-quenching method. This involves heating to 1550°C. in either vacuum or inert atmosphere with no hold at top temperature. The furnace is then cooled as rapidly as possible. Several other crucible materials have been tested to complete the survey previously reported. The most promising materials appear to be BeO, ThO_2 and MgO. The results of synthesis experiments are shown in Table No. VI.

It can be noted from the x-ray analysis of the products that usually there are small amounts of UO_2 and Si present. To reduce the former impurity, it was felt that going to larger batches of reaction mix, thereby reducing the surface to volume ratio, would be effective. Experiments Nos. 4 and 5 were batches of one pound, or an increase of 4.5 times over the previous 100 gram batches. X-ray and metallographic analyses both indicate that this has successfully reduced the oxide impurity. Oxygen analysis is being obtained to substantiate this conclusion.

In an effort to reduce the silicon impurity, uranium in excess of the stoichiometric amount was added in Experiments 5 and 6. The success of this technique is in question, since x-ray analysis indicates little change in the amount of free silicon. Further study will be necessary to determine the significance of the silicon noted in the x-ray analysis.

2. Fabrication of U_3Si_2

Fabrication studies have been made by cold pressing and sintering of U_3Si_2 pellets. The silicide was first milled in a rubber-lined ball mill using stainless steel balls. The number of hours was varied to determine the optimum time. Pellets were pressed at 16,000 pounds per square inch using Carbowax 6000 dissolved in trichlorethylene as a temporary binder. This resulted in green densities of 65 to 70 percent of theoretical.

The pellets were sintered in a ceramic tube muffle furnace in a flowing atmosphere of argon. A variety of crucible materials and sintering rates were employed to determine optimum conditions. Table No. VII summarizes sintering experiments conducted during the last quarter.

TABLE NO. VI

U_3Si_2 Synthesis Experiments

Experiment No.	Batch Size, g.	Crucible Material	Furnacing Atmosphere	X-ray Analysis	Remarks
1 (a)	100	MgO	Argon	Mod. /Str. U_3Si_2 Weak/Mod. Si and UO_2	Did not wet crucible.
(b)	100	Ta	Argon	-	Reacted with Ta.
2	100	BeO	Argon	Mod. /Str. U_3Si_2 Weak/Mod. Si and UO_2	Did not wet crucible.
3	100	ThO_2	Argon	Mod. /Str. U_3Si_2 Weak/Mod. Si and UO_2	Did not wet crucible.
4	450	MgO	Vacuum	Mod. /Str. U_3Si_2 Weak/Mod. Si	Did not wet crucible.
5	450	MgO	Vacuum	Mod. /Str. U_3Si_2 Weak Si	+2.5% Excess uranium.
6	100	Al_2O_3	Vacuum	Mod. /Str. U_3Si_2 Weak Si and UO_2	+4% Excess uranium.

TABLE NO. VII

Sintering of U_3Si_2

Experiment No.	Milling Time, hrs.	Crucible Material	Density g./cc.	Density % Theoretical	Remarks
1	20	MgO	11.0	90.3	Cracked, oxidized.
2	20	MgO	11.40	93.5	" "
3	20	Graphite	11.0	90.3	" "
4	20	Al_2O_3	11.5	94.3	" "
5	20	Al_2O_3	11.4	93.5	+2% Excess uranium.
6	90	Al_2O_3	11.90	97.5	Cracked, oxidized.
7	48	ThO_2	11.82	97.0	No crack, surface oxidized.
8	48	ThO_2	11.70	96.0	" "
9	48	Graphite with Ta lining	12.0	98.4	No cracks or surface oxidation.
10	48	Graphite with Ta lining	11.8	96.8	Bars. No surface oxidation.

Three problems have existed; cracking, oxidation and low density. The cracking problem has been solved by keeping initial heating rates as low as 50°C. per hour during the removal of temporary binder. After 600°C. has been reached, the rate of temperature rise seems to have negligible effect.

A variety of crucible materials have been employed as well as the use of purified argon for the sintering atmosphere. By far the best crucible material studied has been graphite with a tantalum liner. In fact, this combination used in a flowing atmosphere of tank argon has produced the only pellets which were free from surface oxidation.

A milling time of 48 hours, coupled with sintering at 1300°C. for two hours, has produced highest densities. Experiment No. 9 represents the use of both of these conditions and yielded a bulk density of 98.4 percent of theoretical.

The sintering experiments have brought an additional problem to light, which is the appearance of traces of UO_2 in the sintered pellets. This is seen both in x-ray analysis and in metallographic examination. Examination of the reaction clinker discloses none of the UO_2 impurity; however, even those pellets which show no surface oxidation have traces of the UO_2 impurity. In view of this, it is felt that oxidation has occurred during the milling and cold pressing steps.

A bar having a nominal size of 3 inches by 1/2-inch by 1/4-inch has been fabricated from U_3Si_2 using previously described procedure of cold pressing and sintering in a tantalum-lined graphite crucible (Experiment 10, Table No. VII).

VI. PROCUREMENT OF EQUIPMENT

Delivery of the additional glove box for the current project is promised by August 15. All equipment to be used in the glove box has been received and includes a 20-ton hydraulic press, a ball mill and jars, low temperature muffle furnace, high temperature muffle furnace, a centerless grinder, a balance, and steel molds for pressing test specimens.

The modulus of rupture equipment has been completed and tested up to 2000°C. The inert atmosphere thermal expansion apparatus has been assembled and standardized up to 1400°C. The inert atmosphere thermal conductivity apparatus has been completed and is now being

calibrated. It is capable of making thermal conductivity measurements up to 1200°C.

VII. FUTURE WORK

Future work will consist primarily of fabrication of test specimens and the determination of the following physical properties of UC, UN and U_3Si_2: thermal conductivity, thermal expansion, modulus of rupture, modulus of elasticity, and resistance to thermal cycling. Also, as time permits, additional basic work will be done on the synthesis and fabrication of UN.