First Quarterly Report

SYNTHESIS AND FABRICATION OF REFRACTORY URANIUM COMPOUNDS

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FOREWORD

The work described in this report was done for the United States Atomic Energy Commission by The Carborundum Company under Contract No. AT (40-1)-2558, Modification No. 2. It is a part of the AEC Fuel Cycle Development Program, and covers the period of March 1, 1961 through May 31, 1961.

In addition to the authors, the following persons contributed to the work described in this report: L. N. Hailey and T. J. Keaty.

I. INTRODUCTION

The object of the investigation is to develop refractory uranium materials possessing sufficient advantages over uranium dioxide to warrant their use as reactor fuels. The specific objectives under the modified contract are to determine the effect of certain impurities (O, N, C, U, and Fe) and porosity upon the irradiation behavior of high density uranium monocarbide, and insofar as time permits, to study further the synthesis, fabrication and properties of uranium silicides.

The work described in this report was done in an effort to define optimum conditions for obtaining high density sintered pellets of essentially stoichiometric UC, and UC plus certain added impurities. It includes a study of the effect of the following factors on the density of the sintered pellets: thermal history of the UC powder prepared by reacting UO_2 and carbon for various times and at various temperatures, sintering time and temperature for the pellets, and added impurities.

The work is divided into three phases: synthesis studies of UC, vacuum sintering, and atmospheric pressure sintering.

II. SYNTHESIS OF URANIUM MONOCARBIDE

The synthesis study was designed to determine the effect of the thermal history of the UC powder (time and temperature used in synthesis) on its subsequent sinterability. However, it also generated information regarding the effect of time and temperature on the completeness of the UO_2-carbon reaction.

The materials used were depleted UO_2 supplied by Oak Ridge National Laboratory and Thermax Thermatomic Carbon obtained from the R. T. Vanderbilt Company. Table No. I shows a spectrographic analysis of the carbon.

In each synthesis experiment 453.6 g of UO_2 and 60.5 g of carbon were ball-milled together for 24 hours in a rubber-lined mill with stainless steel balls. At the end of this period the average particle size of the mixture was less than one micron.

The UO_2 and carbon mixes were then cold pressed into 1-5/8 inch diameter pellets, placed in a graphite crucible and heated in the vacuum furnace under the conditions of temperature and time indicated in Table No. II.

TABLE NO. I

Spectrographic Analysis of Thermax Thermatomic Carbon, %

Ag	N.D.*
Al	.001 - .005
B	N.D.
Ca	.001 - .005
Co	N.D.
Cr	< .001
Cu	.001
Fe	.001 - .005
Ga	N.D.
Mg	.001 - .005
Mn	< .001
Na	.01 - .05
Ni	< .001
Si	.01 - .05
Ti	< .001
V	N.D.
W	N.D.
Zr	.001 - .005

*N.D. - Not detected.

TABLE NO. II

Effects of Time and Temperature on the Synthesis of UC from Stoichiometric Mixtures of UO_2 and Carbon

Experiment No.	Time, Min.	Temperature, °C.	Chemical Analysis, %						X-Ray Analysis
			U	Total Carbon	Free Carbon	Fe	O_2	N_2	
1	43	1460	88.73	7.20	3.59	0.01	3.8	<.01	Major UO_2 Strong UC Moderate UC_2
2	107 (Duplicate Analysis:	1460	94.01 93.80	5.17 5.21	0.55 0.94	0.13 0.15)	0.865	<.01	Major UC Weak UO_2 Faint UC_2
3	75	1600	95.04	4.88	0.08	0.02	0.412	<.01	Major UC Faint UO_2 Faint UC_2
4	75	1600	95.21	4.72	0.06	<0.01	0.350	<.01	Major UC Faint UO_2 Faint UC_2
5	43	1740	95.04	4.81	0.06	<0.01	0.449	<.01	Major UC Faint UO_2
6	107 (Duplicate Analysis:	1740	95.14 94.90	4.73 4.68	0.08 0.23	<0.01 <0.01)	0.564	<.01	Major UC Faint UO_2 Faint UC_2

The reaction product of furnacing at 1740°C. for 107 minutes was a hard clinker of silvery gray color. As time and temperature decreased the clinker became softer and darker in color.

The reaction products were crushed in a tool steel mortar to pass an 80 mesh screen. At this point samples for analysis were withdrawn by passing the material through a riffle until the desired sample size was obtained.

Each batch was analyzed chemically for total uranium, total carbon, free carbon, iron, nitrogen and oxygen. An x-ray analysis was also performed on each batch. A summary of these experiments is shown in Table No. II.

The data of Table No. II was analyzed mathematically, using the percent total carbon as a response to the variables of time and temperature. This treatment indicates that the two reactions at 1460°C. have not reached a state of completion (4.80 percent carbon). However, there is no significant difference chemically in products from the remaining four conditions of reaction and therefore, in these instances, no indication that higher temperature or longer reaction times at the same temperatures would yield a purer product. In regard to the first two experiments, longer reaction times at 1460°C. would probably yield a better product.

The oxygen content of the products of the last four experiments is abnormally high since total carbon is nearly theoretical and free carbon is quite low. This is being investigated.

III. VACUUM SINTERING OF URANIUM MONOCARBIDE

This phase was designed to measure the effects of several factors on pellet density resulting from vacuum sintering. The UC powders employed had different thermal histories, and different levels of impurity. It should thus be possible to determine the optimum time and temperature for sintering the various powders, the most readily sinterable UC powder, and the effect of common impurities on sintered density.

The UC powders used were those described in Table No. II. Each of these six materials were split into six portions and mixed with impurities to give the 36 compositions shown in Table No. III.

TABLE NO. III

Composition of UC Powders for Vacuum Sintering Experiments

1. Six UC powders shown in Table No. II
2. Six UC powders shown in Table No. II plus 10% UH_3
3. Six UC powders shown in Table No. II plus 5% UC_2
4. Six UC powders shown in Table No. II plus 5% UO_2
5. Six UC powders shown in Table No. II plus 10% UN
6. Six UC powders shown in Table No. II plus 0.5% Fe

These samples were then sintered according to the schedule shown in Table No. IV.

TABLE NO. IV

Time and Temperature Used in UC Sintering Experiments

Temperature, °C.	Time, Min.
1940	81
1800	60
1660	39
1800	60
1600	81
1940	39

Thus, in each sintering there were 36 pellets representing six UC powders with different thermal histories and different added impurities.

In preparing the above mixes for sintering the following procedure was used: Each batch of minus 80 mesh UC powder from the synthesis

phase was ball-milled for 24 hours in a rubber-lined mill using stainless steel balls. At the end of this time each batch of UC was split into six portions and the various impurities added as shown in Table No. III. The mixtures were then milled for an additional two hours to an average particle size of one to two microns.

The sources of the various impurities added to the mixes were as follows: The depleted UO_2 obtained from Oak Ridge National Laboratory was ball-milled for 24 hours in a rubber-lined ball mill with stainless steel balls to an average particle size of less than one micron. The UC_2 was synthesized at The Carborundum Company from UO_2 and carbon and was ball-milled to an average particle size of one to two microns. Its analysis is shown in Table No. V. The UN was synthesized at The Carborundum Company by nitriding uranium metal and was milled to an average particle size of less than one micron. Its analysis is seen in Table No. VI. The UH_3 powder was produced at The Carborundum Company by hydriding normal uranium metal shot obtained from the National Lead Company. The iron was minus 325 mesh powder obtained from the J. T. Baker Chemical Company and had the specifications shown in Table No. VII.

TABLE NO. V

Analysis of UC_2 Powder

Chemical Analysis		X-Ray Analysis
Uranium	90.68%	Major UC_2
Total Carbon	8.96%	Weak UC
Oxygen	0.27%	Faint UO_2
Nitrogen	0.37%	Faint Graphite

TABLE NO. VI

Analysis of UN Powder

Chemical Analysis		X-Ray Analysis
Uranium	94.50%	Major UN
Nitrogen	5.25%	Faint UO_2 and U_2N_3
Iron	0.01%	
Total Carbon	0.10%	
Free Carbon	0.07%	

TABLE NO. VII

Analysis of Iron Powder

Fe	96.20%
Insoluble in H_2SO_4	0.20
Soluble in H_2O	0.004
Nitrogen	0.003
Sulfide	0.014
Arsenic	$<$ 0.0005

Pellets, 0.6 inches in diameter by 0.25 inches thick, of the various mixes were formed for sintering studies by pressing at 16,500 pounds per square inch, using 0.5 percent carbowax as the temporary binder. The average bulk density for each of the six different batches of UC pellets (without additives), before sintering, is shown in Table No. VIII.

TABLE NO. VIII

Densities of UC Pellets Before Sintering

Batch No.	Synthesis Reaction Conditions		Green Density, g/cc
	Time, Min.	Temp., °C.	
1	43	1460	7.19
2	107	1460	8.33
3	75	1600	8.32
4	75	1600	8.31
5	43	1740	8.33
6	107	1740	8.26

The lower bulk density of the No. 1 batch may be a reflection of the incomplete reaction between the UO_2 and carbon (see Table No. II).

These pellets, as well as those containing added impurities, were sintered in a tantalum-lined graphite crucible with a tantalum spacer between each pellet. The furnacing was carried out in two stages, the first to remove temporary binder, followed by the second which was vacuum sintering. In the first stage the pellets were heated at a rate of 50°C. per hour to 600°C. and then rapidly to 1250°C., in flowing helium in an Inconel muffle tube furnace. The pellets were then cooled, transferred to a vacuum furnace, evacuated to a pressure of 5 to 10 microns of mercury, and heated to a predetermined temperature. The sintering times and temperatures are shown in Table No. XI.

On removal from the furnace all pellets had a silver-gray surface. The condition of the pellets was generally excellent except for those made from UC powder No. 1 (Table No. II). As can be seen in Table No. II, this material was only partially reacted and during sintering the reaction of UO_2 and carbon apparently continued, resulting in the generation of carbon monoxide which ruptured the pellets.

The bulk density of each pellet was calculated from its volume (as measured by a mercury displacement method) and weight. Results are shown in Table No. IX. These densities may show an error as large as plus or minus .09 g/cc. This is due to the difficulties in obtaining an accurate volume measurement.

The percent open porosity of the stoichiometric UC samples sintered at 1940°C. for 39 and 81 minutes were determined by boiling the pellets in ethyl benzene and weighing the amount of absorbed liquid. The results which are shown in Figure 1 indicate that as the pellets approach a density of 12.6 g/cc, 92 percent of theoretical, and the remaining porosity becomes closed within the pellet.

The data from the vacuum sintering experiments are being analyzed statistically. While the analysis is not complete at this time, several general preliminary statements can be made. The first observation concerns the sinterability of UC powders with different thermal histories. The powder synthesized at the highest temperature (1740°C.), for the longest reaction time (107 minutes), yields significantly lower densities than the other five UC powders when exposed to the same sintering treatment. Mathematically we cannot differentiate between the sinterability of UC powders Nos. 1, 3, 4 and 5. Batch No. 2 is slightly contaminated with iron and cannot be compared with the other UC powders.

Consideration of the effect of sintering time and temperature indicates that temperature is more significant than holding time at sintering temperature. Plots of sintering temperature versus sintered density are not straight lines.

There is some indication of a beneficial effect of certain impurities placed in these UC samples. Iron, in particular, is effective.

Although the analysis of these experiments is not complete, the results indicate that some additional sinterings at higher temperatures are needed to establish optimum conditions.

TABLE NO. IX

Summary of Experiments on Sintering UC Pellets in Vacuum

Sintering		UC	Synthesis of UC		Sintered Bulk Density, g/cc					
Temp., °C.	Time, Min.	Batch No.	Temp., °C.	Time, Min.	UC	UC + 10% UH_3	UC + 5% UC_2	UC + 5% UO_2	UC + 10% UN	UC + 0.5% Fe
1660	39	1	1460	43	9.61	9.84	9.25	9.62	9.67	9.47
		2	1460	107	8.22	8.70	9.45	8.95	9.14	9.37
		3	1600	75	8.16	9.26	8.36	8.66	8.29	8.96
		4	1600	75	8.63	9.76	8.54	8.70	8.22	10.79
		5	1740	43	8.52	9.52	8.87	8.28	8.32	9.24
		6	1740	107	8.41	8.63	8.44	8.47	8.26	8.71
1660	81	1	1460	43	10.23	10.55	10.47	10.23	10.54	10.11
		2	1460	107	9.72	9.84	9.44	10.08	9.73	9.92
		3	1600	75	8.72	9.37	8.65	9.02	8.51	10.54
		4	1000	75	8.75	11.52	8.90	8.96	8.42	11.06
		5	1740	43	8.77	8.70	9.20	9.00	8.92	10.47
		6	1740	107	8.59	8.84	8.53	8.57	8.15	10.08
1800	60	1	1460	43	11.66	10.37	11.46	10.19	11.32	10.64
		2	1460	107	12.36	11.89	11.96	12.78	11.84	11.82
		3	1600	75	9.81	10.27	10.02	10.56	9.76	12.02
		4	1600	75	9.23	10.21	9.16	9.73	9.32	11.77
		5	1740	43	10.52	10.93	11.12	11.56	11.81	12.13
		6	1740	107	9.15	9.25	9.34	9.08	8.70	11.73

TABLE NO. IX (cont'd)

Summary of Experiments on Sintering UC Pellets in Vacuum

Sintering		UC	Synthesis of UC		Sintered Bulk Density, g/cc					
Temp., °C.	Time, Min.	Batch No.	Temp., °C.	Time, Min.	UC	UC + 10% UH_3	UC + 5% UC_2	UC + 5% UO_2	UC + 10% UN	UC + 0.5% Fe
1800	60	1	1460	43	10.48	10.90	10.88	11.13	11.42	10.67
		2	1460	107	12.15	11.72	12.11	12.48	12.26	12.04
		3	1600	75	9.89	10.03	9.88	10.88	9.89	11.96
		4	1600	75	9.80	9.68	9.79	9.88	9.28	11.64
		5	1740	43	10.50	10.80	10.85	11.47	11.58	11.84
		6	1740	107	9.51	9.37	9.44	9.30	8.93	11.98
1940	39	1	1460	43	11.48	11.86	11.81	12.05	12.05	10.67
		2	1460	107	12.50	12.11	12.45	12.71	12.91	12.41
		3	1600	75	10.64	11.11	10.18	11.71	10.92	12.77
		4	1600	75	11.04	10.69	11.34	11.00	10.14	12.14
		5	1740	43	11.96	11.41	11.96	12.16	12.16	12.16
		6	1740	107	11.10	10.16	10.72	10.16	9.45	12.26
1940	81	1	1460	43	11.78	12.27	11.78	11.47	11.66	10.68
		2	1460	107	12.29	12.28	12.65	12.80	12.62	12.65
		3	1600	75	11.47	11.15	11.11	12.06	11.52	12.40
		4	1600	75	12.19	11.25	12.44	11.95	10.94	12.27
		5	1740	43	12.09	11.50	12.15	12.50	12.51	11.94
		6	1740	107	12.14	11.55	12.22	11.77	10.42	12.47

IV. ATMOSPHERIC PRESSURE SINTERING OF URANIUM MONOCARBIDE

These experiments were designed to explore the sinterability of UC in helium at atmospheric pressure. Higher densities might be achieved by this method as the result of lower weight losses due to vaporization.

In addition to the stoichiometric compound, UC samples containing 10 percent UH_3, 1.0 percent iron, and 0.1 percent iron were studied simultaneously.

The UC employed in this study was produced from a UO_2-carbon reaction and had the analysis as shown in Table No. X.

TABLE NO. X

Analysis of UC Powder Used in Sintering at Atmospheric Pressure in Helium

Chemical Analysis		X-Ray Analysis
Uranium	95.02%	Major UC
Total Carbon	4.78%	Faint UO_2
Free Carbon	0.06%	Faint UC_2
Iron	$<$ 0.01%	
Nitrogen	0.03%	
Oxygen	0.25	

The procedure used in preparation of the mixes for sintering, including ball milling the powders and cold pressing the pellets, was the same as described above under "Vacuum Sintering of Uranium Monocarbide." The stoichiometric UC, after ball milling, contained less than 0.01 percent iron.

Sintering was carried out in an alumina tube muffle furnace in a flowing helium atmosphere. The pellets were contained in a tantalum-lined graphite crucible. The initial heating rate during removal of temporary binder was 50°C. per hour to 600°C. After this, the temperature was raised as rapidly as possible to the desired sintering temperature.

Each sintering included four pellets as follows: stoichiometric UC, UC plus 10 percent UH_3, UC plus 1.0 percent iron, and UC plus 0.1 percent iron. These experiments are summarized in Table No. XI.

TABLE NO. XI

Summary of Experiments on Sintering UC Compositions in Helium at Atmospheric Pressure

Composition	Bulk Density (g/cc) After Sintering Under the Following Conditions		
	1600°C. 4 hrs.	1800°C. 1-1/2 hrs.	1800°C. 4 hrs.
UC	10.20	11.65	12.30
UC + 10% UH_3	10.55	11.70	12.33
UC + 0.1% Fe	10.90	12.24	12.60
UC + 1.0% Fe	11.50	12.12	12.50

Referring to Table No. XI, it will be seen that density increases with both sintering temperature and time. The maximum densities obtained by sintering at atmospheric pressure and in vacuum were about the same (see Tables Nos. IX and XI). Metallographic examinations disclose some differences in the microstructure of the various compositions. Those with iron additions experienced greater grain growth than the stoichiometric UC. This was particularly pronounced in the samples sintered at 1800°C. for four hours. While the crystal size in the UC samples sintered at 1600°C. for four hours and 1800°C. for 1-1/2 hours was less than ten microns, the crystal size in the samples sintered at 1800°C. for four hours was 40 to 60 microns in diameter.

The addition of 10 percent UH_3 seems to have but little effect on the sintered density of UC. The reason for this is not clear. However, metallographic examination failed to disclose any free uranium metal in the structure. This problem will be given further study.

V. SUMMARY

In order to obtain fuel UC pellets of maximum density for irradiation testing, a statistically designed experiment was employed to study the effect of the following factors on the sinterability of UC: thermal history of the UC powder, time of sintering, temperature of sintering, and additives.

The following tentative conclusions are based on a preliminary evaluation of the results:

1. The UC powder synthesized under the most severe conditions of temperature and time (1740°C., 107 min.) was less sinterable than powders prepared at lower temperatures, or at the same temperature for shorter time.

2. Although both temperature and time of sintering pellets affect density, temperature is more significant than time.

3. Small additions of iron (0.1 - 1.0 percent) improve sinterability and at the same time promote grain growth in the UC pellet.

4. The final density obtained on sintering in a vacuum was about the same as that resulting for sintering in helium at atmospheric pressure.

VI. FUTURE WORK

The evaluation of vacuum sintered samples will be completed. This will include metallographic, x-ray and chemical analyses of the highest density samples.

The fabrication of enriched UC samples for irradiation testing will begin as soon as the enriched uranium dioxide is received.

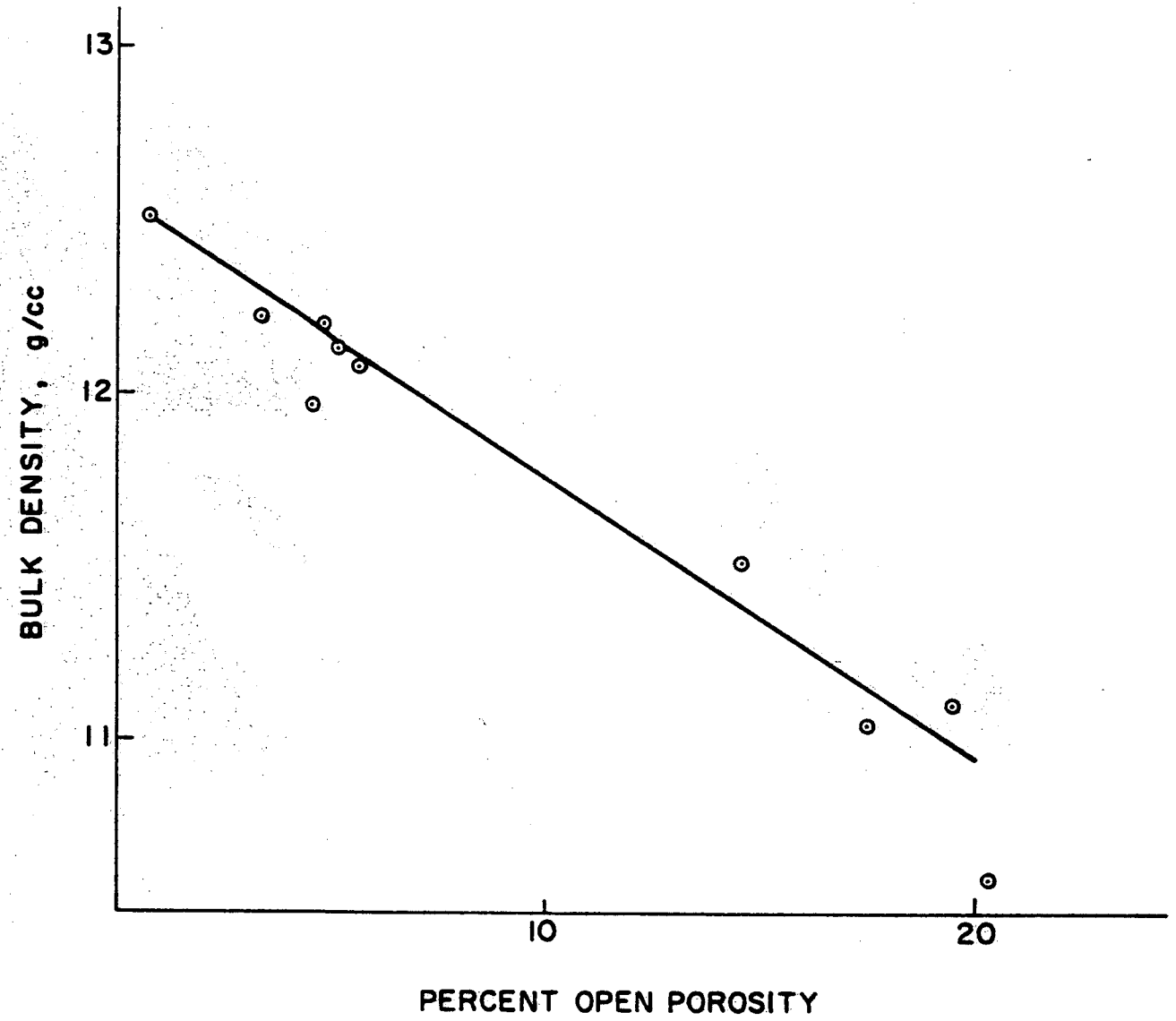

FIGURE I. PERCENT OPEN POROSITY VS. BULK DENSITY OF VACUUM SINTERED UC

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