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OLIN MATHIESON
CHEMICAL CORPORATION

ENERGY DIVISION

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NUCLEAR FUEL RESEARCH

FUEL CYCLE DEVELOPMENT PROGRAM

QUARTERLY PROGRESS REPORT

JULY 1 TO SEPTEMBER 30, 1960

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Nuclear Fuel Research Laboratory
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CONTENTS

SUMMARY

This report presents the progress made by Olin Mathieson Chemical Corporation under Contract No. AT-(30-1)-2374 during the period July 1 to September 30, 1960.

Under Task I, work was continued on the development of a UO_2 pellet fabrication process based on low temperature sintering in an inert atmosphere.

A study of the chemical and physical characteristics of several ADU oxides on hand was carried out to determine the cause of poor sinterability as compared with Davison Lot O. The latter has consistently sintered to densities exceeding 95% of theoretical in this process. The properties investigated included (1) particle size distribution, (2) surface area, (3) microscopic appearance, (4) hydrogen sinterability, and (5) chemical analysis. No clear distinguishing difference among the various oxides lots has yet been found which accounts for the observed variation in sinterability.

A program aimed at improving sinterability by activation techniques was initiated and, of the methods employed, oxidation-reduction cycling was by far the most effective. After only one cycle, consisting of oxidation to U_3O_8 at 500°C and reduction to UO_2 at 525°C, all production lot oxides could be densified to at least 95% of theoretical at temperatures not exceeding 1300°C. The enhancement of sinterability is so pronounced that such densities have been achieved after sintering at as low as 1100°C for only one hour in nitrogen. High temperature hydrogen sinterability has been similarly improved.

Under Task II, extensive chemical analyses of uranium carbide prepared by the methane reaction indicated that improvements are necessary in the control of heating rate and time at temperature for the carburizing step to achieve adequate carbon compositional control. It was observed that the analyses of the uranium carbide product was not affected by increasing the carburizing gas flow rate in the retort from about 1-1/2 to 16 times the amount required to achieve stoichiometry. Thus, gas flow in excess of the minimum required, based on approximately a 60% to 70% efficiency, has no effect. Using methane, it appears that the average of nitrogen, oxygen and free carbon contents are 0.43%, 0.77% and 0.25%, respectively.

A preliminary study was made of the use of propane for carburizing uranium. The results indicated that the free carbon was slightly higher than that obtained with methane, but that the nitrogen and oxygen contents were significantly lower, viz., 0.06% nitrogen and 0.22% oxygen. Further work is planned, using propane as the carburizing gas.

Further work on the cold pressing and 1800°C vacuum sintering of uranium carbide produced by the methane reaction indicated that the best densities that could be achieved by this method with essentially stoichiometric uranium monocarbide was 11.2 to 12.2 g/cm^3. Nitrogen and oxygen appear to form an isomorphous solid solution in the uranium monocarbide structure and do not appear to enhance the sinterability. It was found that the presence of free uranium is essential and that approximately 51 a/o or more of uranium must be present in the composition in order to achieve a high sintered density. Densities approaching the theoretical were obtained when an adequate quantity of free uranium was

present, either because of the composition of the product as produced from the methane-uranium reaction or when adjusted in composition by the addition of uranium in the form of uranium hydride to the powder mixture prior to cold pressing and sintering.

Significant improvements were made in the skull arc melting and casting technique by utilizing a ten-turn water-cooled coil inserted beneath the crucible in the skull furnace. This provided sufficient magnetic field at 400 amperes to prevent arc deflection during melting uranium carbide at 2,500 amperes melting current. Good melting and pouring were achieved consistently, by utilizing this method. Although crack-free castings were obtained, surface quality must be further improved by optimizing the graphite mold temperature.

Encouraging results were obtained by arc melting uranium oxide graphite mixtures, blended to yield, after reaction, uranium monocarbide. Pelletized charge material was reacted and melted in the arc furnace which yielded a product containing 4.71% carbon, 0.084% oxygen and 0.06% nitrogen. Work was carried out, also, on the use of pre-reacted uranium oxide graphite mixtures to form a consumable electrode. An electrode, pre-reacted by vacuum induction heating at 2000°C, was consumably arc melted successfully.

I. THE DEVELOPMENT OF A LOW COST FABRICATION PROCESS FOR URANIUM OXIDE FUEL (TASK I)

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A. Introduction

In the Quarterly Progress Report for April 1 to June 30, 1960 (NYO-2689), the development of a two-stage version of the low temperature Inert Atmosphere Sintering Process for UO_2 pellet production was described. The method involved sintering first in nitrogen to densify the oxide and next in hydrogen to remove excess oxygen, the objective being to produce high density stoichiometric uniform pellets in the shortest overall sintering cycle. Attempts to optimize the sintering conditions with respect to time and temperature, however, were hampered by the large variation in sinterability of the ADU oxide lots available for the program. Only one oxide raw material, Davison Lot 0, could be sintered to as high as 95% of theoretical by either the low temperature process or a conventional high temperature hydrogen sintering process. A study of the physical and chemical characteristics of the oxides was then initiated with the aim of determining the cause of poor sinterability. During the reporting period, this study was continued and methods of activating the oxide lots on hand to improve sinterability were investigated.

B. Process Development Studies

1. Characterization of ADU Oxide Lots

a. Particle Size Distribution Analyses

The sub-sieve particle size distribution of three Davison oxides, Lots 0, IV and V, was determined using the procedure of ASTM Designation No. D-433-54T entitled, "Tentative Method for Grain Size Analysis in Soils." The method involves the dispersal and sedimentation of the UO_2 in a column of water and the use of a special hydrometer (Bouyoucos type) to measure sedimentation rate. It assumes the applicability of Stokes' Law, so that the size measured is the equivalent spherical diameter. The procedure was tested until reproducible results were obtained. The particle size distributions determined for the Davison lots in the as-received condition are shown in Fig. I-1. Lot V appears to have a distribution similar to that of Lot 0, whereas Lot IV contains a relatively large weight fraction of coarse material (greater than 10 microns).

b. Surface Area Measurements

Samples of Davison Lots 0, IV and V, as-received, were submitted to the Perkin-Elmer Corporation for surface area measurements employing the Model 212 Perkin-Elmer-Shell Sorptometer, an instrument recently ordered for work on this program. The method involves a dynamic measurement concept instead of the static approach normally used in connection with a BET plot. The data needed for the standard BET plot is obtained from the thermal conductivity increase of helium-nitrogen mixtures caused by adsorption of nitrogen from the mixture as it passes over the liquid nitrogen cooled sample. Prior to adsorption measurement, the samples were degassed for 2 hours in helium at 150°C. The following results were obtained based on a 3-point calculation in conjunction with the BET equation:

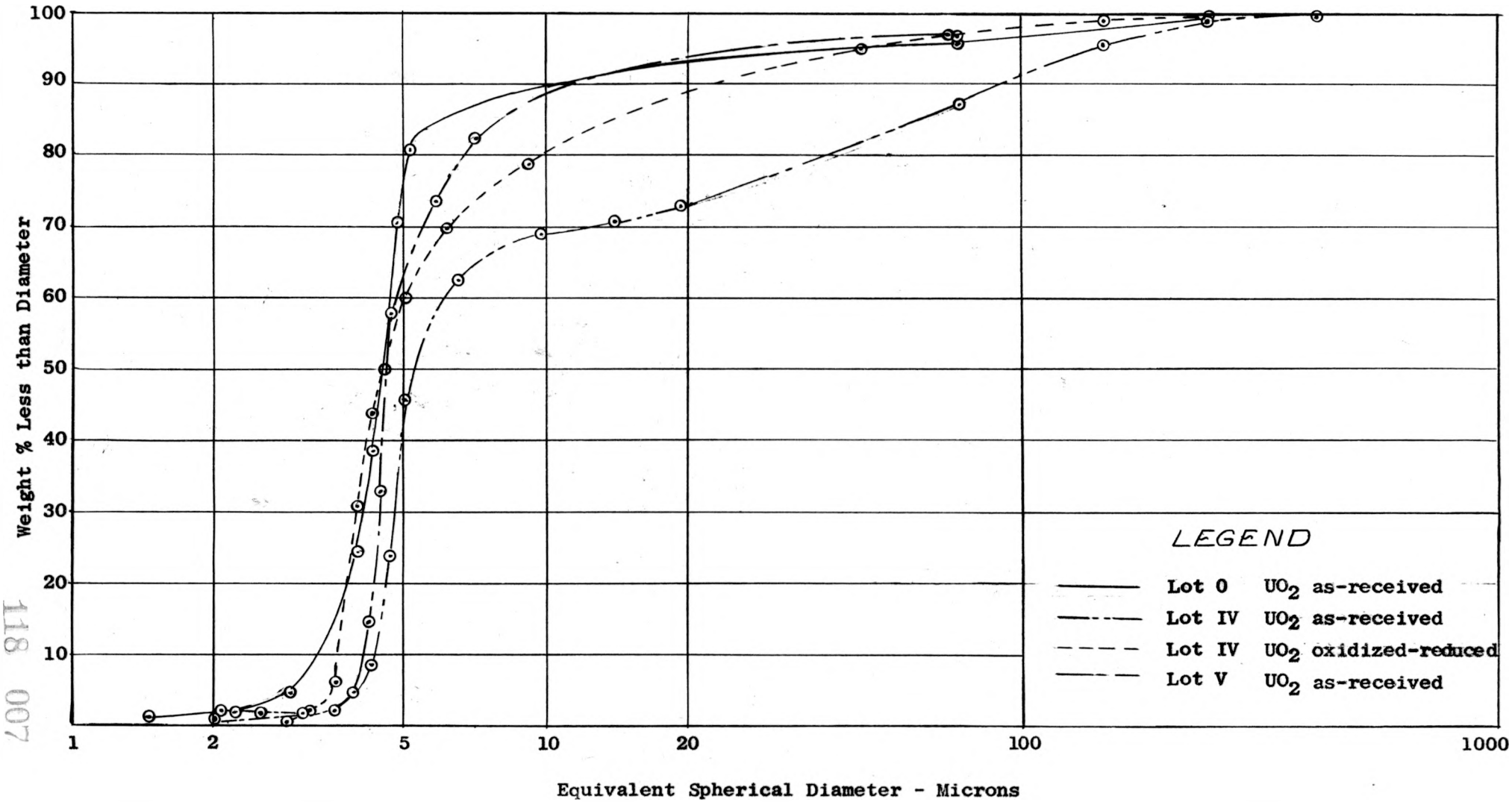

Fig. I-1 Particle Size Distribution of Davison UO_2

Davison Oxide	Surface Area Sq. meters/gm
Lot 0	3.14
Lot IV	2.20
Lot V	3.11

Although the order of decreasing surface area is the same as anticipated from the particle size distribution curves, the actual values are quite similar and show very little difference among the three oxides. The observed variations in sinterability reported in NYO-2689 cannot be attributed solely to such a small spread of surface area values.

c. Electron Microscopy

An investigation of oxide particle size and shape was also undertaken by means of electron microscopy. Samples of Davison Lots 0 and IV, for this work, were obtained by forming a suspension of the oxide in water as prescribed for particle size analysis by sedimentation and withdrawing a portion of the suspension after particles larger than approximately 10 microns had settled out. Initial sample preparation employed sodium pyrophosphate as a dispersing agent, but a clear view of the oxide was apparently obscured by the pyrophosphate residue. Samples of the two oxides, therefore, were prepared without dispersing agent and the resulting electron micrographs are shown in Fig. I-2 to I-5. A comparison of the edges of the agglomerates, shown in the lower magnification plates, suggests that the Lot 0 oxide particles may have finer grained surface irregularities than those of Lot IV. However, no significant difference can be observed between the two oxides at the higher magnification. Additional work is apparently needed, utilizing a replica technique, to reveal more detail of the particle surface and to show a possible difference in surface texture.

d. Hydrogen Sinterability

To establish whether the variation in sinterability from lot to lot was characteristic of the nitrogen sintering process or of the raw material itself, a series of high temperature hydrogen sintering experiments were carried out. All of the compacts were prepared by the same procedure with 0.4% PVA, a forming pressure of 19 tsi, and sintered in a conventional molybdenum-wound hydrogen furnace. In several cases the sintering temperature and time were varied to determine the effect on pellet density. A summary of all the high temperature sintering data on as-received oxides obtained to date is presented in Table I-1. All the sintered pellets were black and fairly uniform dimensionally. The variation in pellet density obtained for each oxide is quite consistent with respect to the anticipated influence of sintering time and temperature. The results with Lot 0 again demonstrate the unusual activity of this material. A surprising result was the density of 10.2 gm/cc attained by Lot V after sintering at 1550°C for 6 hours. Previous low temperature nitrogen sintering experiments with this material have yielded relatively poor pellet densities, the highest being 9.5 gm/cc after sintering at 1300°C in nitrogen for 2 hours followed by soaking in hydrogen for 1 hour.

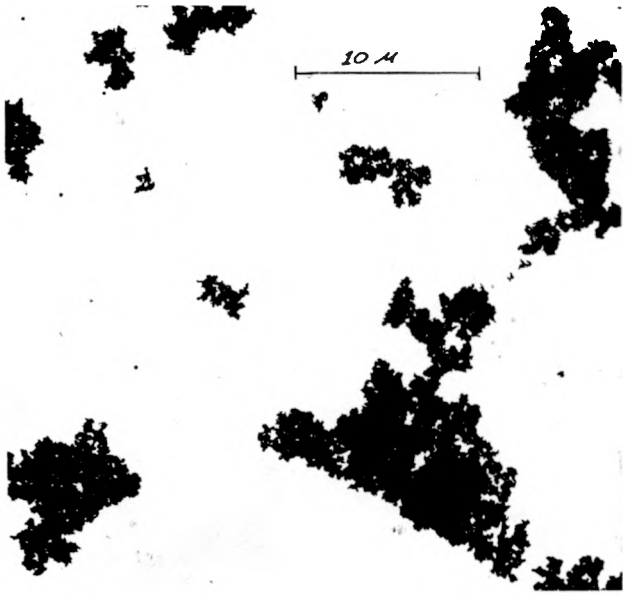

Fig. I-2 Davison Lot 0 UO_2
2,300X
1 mm = 0.43 μ
1 mm shadow = 0.26 μ height

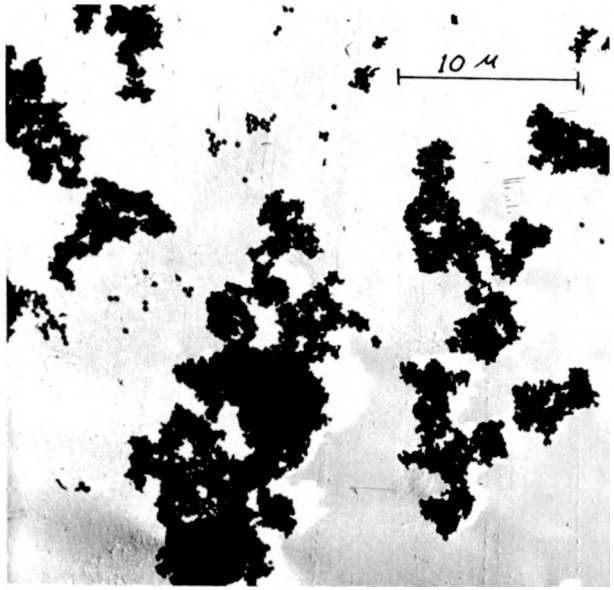

Fig. I-3 Davison Lot IV UO_2
2,300X
1 mm = 0.43 μ
1 mm shadow = 0.26 μ height

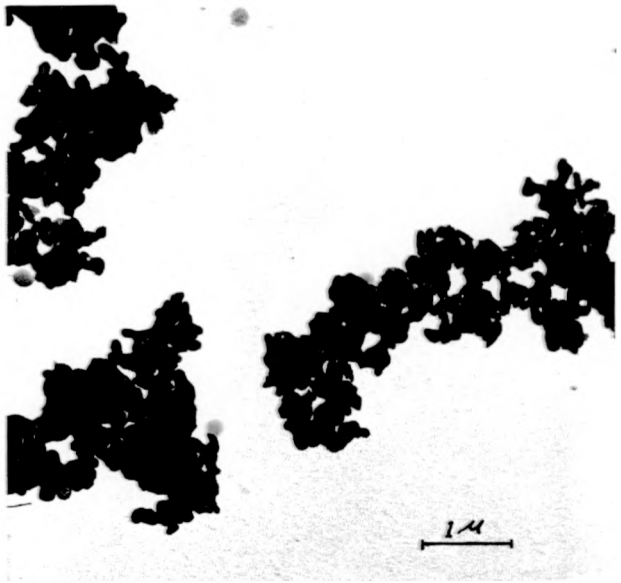

Fig. I-4 Davison Lot 0 UO_2
11,000X
1 mm = 0.09 μ
1 mm shadow = 0.05 μ height

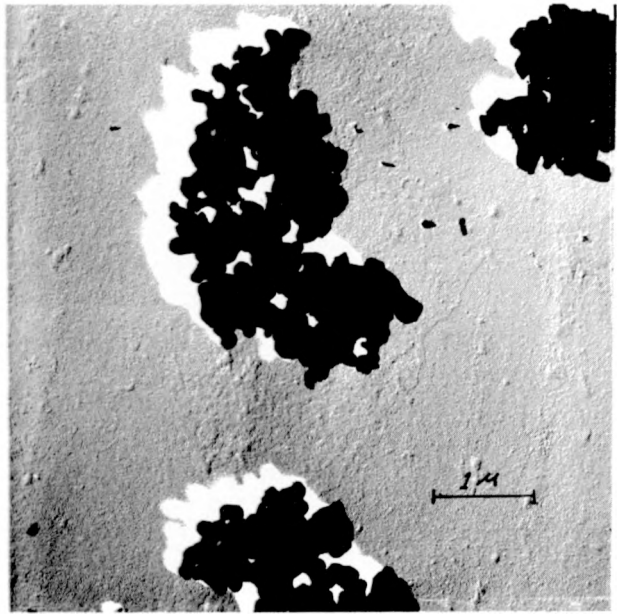

Fig. I-5 Davison Lot IV UO_2
12,000X
1 mm = 0.08 μ
1 mm shadow = 0.05 μ height

TABLE I-1

SUMMARY OF HYDROGEN SINTERING DATA

Material	Initial O/U Ratio	Sintering Cycle Temp. ° C	Sintering Cycle Time, Hr.	Geometric Sintered Density, gm/cc
Davison Lot O	2.09	1,650	6	10.6
	2.12	1,550	6	10.6
	2.05	1,550	6	10.6
	2.12	1,550	2	10.5
	-	1,550	2	10.4
	2.12	1,400	6	10.2
Davison Lot III	-	1,650	6	10.3
Davison Lot IV	2.09	1,650	6	10.0
	2.03	1,550	6	9.9
	2.08	1,550	2	9.4
	-	1,500	2	9.1
	2.08	1,400	6	8.6
Davison Lot V*	2.03	1,550	6	10.2
	2.09	1,400	6	9.1
Numec Lot 1	2.10	1,650	6	9.8
	2.10	1,550	2	9.0
	2.10	1,400	6	8.5
Spencer Lot 2	-	1,650	6	10.5
Mallinckrodt Lot 3	-	1,650	6	10.1

*Limited work has been done with this small lot of non-production type material. Sintering data at 1,650° C is not available.

Of the production type ADU oxides, only Davison Lot O and Spencer Lot 2 have densified to 95% of theoretical at 1650°C for 6 hours. Under these conditions the other oxides yielded densities from 9.8 to 10.3 gm/cc, a range comparable to their best results from low temperature nitrogen sintering. Davison Lot O, of course, has consistently produced densities 95% of theoretical in the latter process. The Spencer oxide, therefore, exhibits anomalous behavior, since such a high density has not yet been achieved with it in the low temperature nitrogen sintering process.

The bulk of the data in Table I-1, along with earlier results on nitrogen sintering, tend to support the conclusion that the variation in sinterability encountered is related to the individual characteristics of the oxide rather than the method of pelletizing and sintering.

e. Chemical Analysis

All of the ADU oxide lots on hand were submitted for extensive quantitative chemical analysis. The results reported are shown in Table I-2. Although there appear to be substantial differences in the concentration of some of the impurities, all the values are believed to be below levels considered detrimental to UO_2 sintering. This has since been borne out in experiments to be discussed below in which essentially all these oxides have been activated without changing chemical composition to produce high density pellets by nitrogen sintering.

The high fluorine content of Davison Lot V is probably related to the fact that it is a special non-production scale lot and normal quality control procedures were not used in its preparation. Of greater significance is the fluorine content of pellets made from Davison Lot IV by both the nitrogen sintering and hydrogen sintering processes. These were 20 ppm and 30 ppm, respectively, indicating that fluorine is effectively removed at low temperatures as well as high temperatures. Fluroine must be reduced to such levels to assure the suitability of UO_2 for application in water cooled reactors employing zirconium as a fuel clad.

2. Activation of ADU Oxides

a. Effect of Excess Oxygen

At the beginning of the reporting period, sintering experiments were performed with the objective of clarifying the effect of excess oxygen introduced by air roasting. Previous results with wet ball-milled Davison Lot III had shown an increase in pellet density which could be attributed to either the activation treatment or to a higher initial O/U ratio than normally employed.

This investigation, as well as subsequent work to be reported below, was conducted with the small furnace used in previcus work. In each experiment the loading of green compacts was introduced into the cold furnace and heated under pure nitrogen to the sintering temperature. After a given interval at this temperature, the nitrogen was normally displaced by hydrogen and the loading was soaked for an additional period before being cooled to room temperature in nitrogen.

TABLE I-2

QUANTITATIVE ANALYSES ON ADU UO_2 LOTS
(in ppm)

Elements	Davison Lot 0	Davison Lot III	Davison Lot IV	Davison Lot V	Spencer Lot 2	MCW Lot 3	Numec Lot 1
Cd	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
B	0.41	0.35	0.37	<0.2	1.1	1.1	>1.2
Si	73	>125	76	131	>125	>125	24
Mo	<1	<6	<1	<2	<6	<6	<6
Mn	<6	<6	<6	<6	<6	<6	<6
V	<20	<10	<20	<20	<10	<10	<10
Cu	<12	<12	<12	<20	<12	<12	<12
Fe	52	>100	51	80	22	39	<20
Ni	30	>125	102	98	<20	47	<20
Cr	17	>50	13	52	25	36	12
C	70	120	130	170	240	160	140
F	190	400	850	2200	n.a.	n.a.	n.a.
N	20	20	30	n.a.	n.a.	n.a.	n.a.

n.a. - not available

For this study, Davison Lots III and IV were roasted to two levels of excess oxygen content. Davison Lot 0 was introduced as a control and Numec Lot 1 was also included. The results of two-stage sintering at 1300°C, 2 hours in nitrogen and 1 hour in hydrogen, are summarized as follows:

Oxide	Initial O/U Ratio	Linear Shrinkage, %	Geometric Sintered Density, gm/cc
Davison Lot III	2.26	15.1	9.9
Davison Lot IV	2.26	15.1	9.7
Davison Lot IV *	2.26	14.5	9.8
Davison Lot III	2.35	16.0	10.1
Davison Lot IV	2.35	15.7	9.9
Numec Lot 1	2.37	16.9	9.9
Davison Lot 0	2.27	18.3	10.5

*Hammer-milled in Mikro-Pulverizer and air roasted.

All pellets exhibited a black color and good dimensional integrity. It is apparent that an increase in excess oxygen leads to a corresponding increase in pellet density. The values achieved with Lots III and IV, however, are not considered satisfactory. The effect of even higher O/U ratios should be investigated.

The green compacts for the pellets described above were pressed at 19 tsi after the usual granulation treatment incorporating 0.4% PVA. Compacts of Lots 0 and IV, formed by a "slugging" technique, were also sintered under these conditions. "Slugging" involved pressing compacts at 15 tsi, crushing and passing through a 20 mesh sieve, then repressing compacts at 30 tsi. The pellet densities obtained were 1 to 2% greater than those reported for normally compacted material of the same initial O/U ratio.

b. Oxidation-Reduction Cycling

The major effort on improving low temperature sinterability involved the use of oxidation-reduction cycling of the oxides. Such a pretreatment is reported[1] to have a pronounced activating effect on ceramic grade UO_2. In this investigation, the oxides were treated batchwise in Inconel boats instead of employing a fluidized bed reactor as in the work cited.

Davison Lots III and IV were selected for the initial test since these oxides have not sintered well in the low temperature process. The as-received materials were oxidized to U_3O_8 in air over a period of 1-1/2 hours at 500°C, and was reduced in hydrogen over a period of 1 hour at 525°C. An air roasting step followed to introduce excess oxygen.

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(1) D. R. Stenquist and R. J. Anicetti "Fabrication Behavior of Some Uranium Dioxide Powders," General Electric Hanford Atomic Products Operation, December 1, 1957, HW-51748.

These materials were then granulated, compacted and sintered in the usual manner. The sintered pellets from both oxides had densities of 97.5% of theoretical, in striking contrast to the previous results obtained with these materials. The sintering conditions and the resulting pellet data are shown in Table I-3.

Several additional experiments were then conducted to determine (1) the degree of activation obtained by oxidation-reduction cycling, (2) the reproducibility of the pretreatment procedure, and (3) its applicability to other oxide lots on hand. The data on these experiments are summarized in Table I-3. In Sinters No. 4-II and 6-II, the two initial oxidized-reduced batches of Davison Lots III and IV were employed. Second batches of these lots were subjected to this activation treatment and used in Sinters 7-II, 11-II and 13-II. In the case of each of the other oxide lots, sintering experiments were conducted with only one batch of oxidized-reduced material. All the pellets produced were black and dimensionally uniform.

The remarkable enhancement in sinterability for all these oxides can be seen in the following comparison of the pellet densities obtained with the highest densities previously achieved in low temperature nitrogen sintering using roasting only as a pretreatment:

Oxide	Highest Density, gm/cc	
	Roasting Only	Oxidized-Reduced
Davison Lot III	10.1	10.7
Davison Lot IV	9.9	10.7
Spencer Lot 2	9.9	10.5
Numec Lot 1	9.9	10.4
Mallinckrodt Lot 3	8.7	10.6

The data in Table I-3 indicate that the method of activation and pellet fabrication is reproducible to within 1% with respect to the pellet density attained. This is best illustrated by comparing the results of Sinters No. 2-II and 11-II.

The effect of higher initial O/U ratios on pellet density can be found by comparing Sinter No. 4-II with 6-II and Sinter No. 7-II with 11-II. The activation treatment has so improved sinterability that the effect is almost obscured. The results of the application of oxidation-reduction cycling on the remaining oxide production lots on hand are presented under Sinters No. 10-II and 15-II. Again high densities were obtained and the beneficial effect of increasing initial O/U ratio is more clearly shown.

The degree of activation achieved is apparent from an examination of the pellet densities obtained in Sinter No. 13-II. Densities of 95% of theoretical were attained by sintering Davison Lots III and IV for only one hour in nitrogen at 1100°C. A one hour soak in hydrogen was added, as usual, to remove the excess oxygen. In comparison, Davison Lot 0 (roasted only), which was considered previously to be an unusually reactive material, sintered to a density of 93% of theoretical under the same conditions.

TABLE I-3

NITROGEN SINTERING OF UO_2 ACTIVATED BY OXIDATION-REDUCTION CYCLING

Sinter No.	UO_2 Source	Initial O/U Ratio	Sintering Cycle, hr. N_2	Sintering Cycle, hr. H_2	Sintering Temp. ° C	Geometric Sintered Density, gm/cc
2-II	Davison Lot III[a]	2.38	2	1	1,300	10.7
	Davison Lot IV [a]	2.38	2	1	1,300	10.7
	Davison Lot 0 *	2.27	2	1	1,300	10.6
4-II	Davison Lot III[a]	2.28	1	1	1,200	10.5
	Davison Lot IV [a]	2.28	1	1	1,200	10.4
	Davison Lot 0 *	2.27	1	1	1,200	10.5
6-II	Davison Lot III[a]	2.38	1	1	1,200	10.6
	Davison Lot IV [a]	2.38	1	1	1,200	10.6
7-II	Davison Lot III[b]	2.25	2	1	1,300	10.6
	Davison Lot IV [b]	2.26	2	1	1,300	10.6
	Davison Lot 0	2.34	2	1	1,300	10.7
10-II	Spencer Lot 2	2.28	2	1	1,300	10.3
	Numec Lot 1	2.34	2	1	1,300	10.4
	Mallinckrodt Lot 3	2.31	2	1	1,300	10.5
	Davison Lot 0 *	2.27	2	1	1,300	10.6
11-II	Davison Lot III[b]	2.37	2	1	1,300	10.6
	Davison Lot IV [b]	2.37	2	1	1,300	10.7
	Davison Lot 0 *	2.27	2	1	1,300	10.5
13-II	Davison Lot III[b]	2.37	1	1	1,100	10.5
	Davison Lot IV [b]	2.37	1	1	1,100	10.4
	Davison Lot 0 *	2.27	1	1	1,100	10.2
15-II	Spencer Lot 2	2.38	1	1	1,200	10.5
	Mallinckrodt Lot 3	2.39	1	1	1,200	10.6

a First oxidized-reduced batch.

b Second oxidized-reduced batch.

* Roasted only, used for experimental control.

c. Effect of Oxidation-Reduction Cycling on Oxide Characteristics

It is of interest to note that although the sinterability of Davison Lot 0 did not appear to improve after an oxidation-reduction treatment (see Sinter No. 7-II, Table I-3), the oxidation rate of this oxide increased as demonstrated during the subsequent roasting step. The pertinent data are shown in the following table along with similar information for other oxides. The effect of wet ball milling for 24 hours is also indicated.

TABLE I-4

O/U RATIOS AFTER AIR ROASTING 6 HOURS at 140°C

Oxide	As Received	Oxidized-Reduced	Ball Milled - 24 hr.
Davison Lot 0	2.27	2.34	--
Davison Lot III	2.14	2.25	2.21
Davison Lot IV	2.18	2.26	2.22
Spencer Lot 2	2.23	2.28	--

In addition to this chemical property, the effect of oxidation-reduction cycling on the bulk density of the oxides, as measured by the Scott Volumeter, was also investigated. The following table summarizes this information:

TABLE I-5

BULK DENSITY OF UO_2 LOTS, gm/cc

Oxide	As Received	Oxidized-Reduced
Davison Lot III		
Batch 1	1.79	1.33
Batch 2	1.79	1.36
Davison Lot IV		
Batch 1	2.12	1.52
Batch 2	2.12	1.50
Mallinckrodt Lot 3	1.21	0.97
Spencer Lot 2	1.29	1.06
Numec Lot 1	1.76	1.50

All the values represent an average of three determinations. Davison Lot IV exhibited the greatest reduction in bulk density (28%), while the Numec oxide showed the smallest (15%).

The activation mechanism is believed to involve the destruction and regeneration of the fluorite lattice which occurs during the oxidation-reduction cycle and results in fracturing and fragmentation of the agglomerates. This is confirmed, in part, by a sedimentation analysis of oxidized-reduced Davison Lot IV indicating that an appreciable particle size reduction had taken place. The particle size distribution of the activated oxide is plotted in Fig. I-1 where it may be compared with that of the as-received material.

Two high temperature sintering experiments were conducted to determine the effect of this activation method on sinterability in hydrogen. The data are presented in Table I-6 and the marked enhancement of sinterability is clearly demonstrated by the pellet density increase from 9.1 gm/cc to 10.4 gm/cc for Davison Lot IV achieved by this treatment in Sinter No. 40-M. It is noteworthy that the densities obtained for the oxidized-reduced material sintered at 1500°C for 2 hours are the same as those obtained for these oxides when sintered in nitrogen for 1 hour at 1200°C (see Sinter No. 4-II, Table I-3).

d. Wet Ball Milling

Several two-stage nitrogen sintering experiments were conducted during the reporting period on oxides subjected to a wet ball milling treatment to improve sinterability. The data collected are shown in Table I-7. For Sinter No. 3-II, the ball milled oxide was not roasted but was simply granulated and compacted. All the sintered pellets in this experiment were brown and exhibited relatively poor densities including those from Davison Lot 0 which had not been ball milled.

In an attempt to increase pellet densities, all the ball milled oxides were roasted to introduce more excess oxygen except Numec Lot 1. Sinter No. 5-II, with these materials, also yielded poor densities. Again, all pellets were brown.

A final effort was made to obtain high densities by introducing still more excess oxygen. The oxides were sintered in 9-II. In this case, the pellet density of Davison Lot 0 reverted to its usually high level, but no improvement was achieved with the other oxides.

The results of the above experiments have since been attributed mainly to a pickup in milling of as much as 3000 ppm carbon which is more than twice the normal carbon content of granulated oxide containing 0.4% PVA. It is believed that the excess oxygen required for nitrogen sintering is removed by the carbon before the sintering temperature is reached. Apparently, in the first two experiments the high carbon content of adjacent pellets inhibited the sintering of Davison Lot 0 oxide, which had not been wet ball milled.

To reduce the amount of carbon pickup, the procurement of a more abrasion resistant rubber-lined mill is being explored. The effect of changing the mill charge, such as decreasing the number of ceramic balls used, is also being investigated.

TABLE I-6

HYDROGEN SINTERING OF OXIDIZED-REDUCED UO_2

Sinter No.	Oxide	Sintering Cycle		Geometric Sintered Density, gm/cc
		Temp. ° C	Time, Hr.	
39-M	Davison Lot III	1,650	6	10.7
	Davison Lot IV	1,650	6	10.7
	Davison Lot O *	1,650	6	10.6
40-M	Davison Lot III	1,500	2	10.5
	Davison Lot IV	1,500	2	10.4
	Davison Lot IV *	1,500	2	9.1
	Davison Lot O *	1,500	2	10.4

* As-received material.

TABLE I-7

NITROGEN SINTERING OF BALL MILLED UO_2

Sintering Cycle - 2 hr. in N_2, 1 hr. in H_2 at 1,300° C

Sinter No.	UO_2 Source	Initial O/U Ratio	Ball Milling Time, hr.	Geometric Sintered Density, gm/cc
3-II	Davison Lot III	2.17	24	9.4
	Davison Lot IV	2.19	24	9.5
	Mallinckrodt Lot 3	2.16	24	8.9
	Numec Lot 1	2.31	24	9.3
	Davison Lot IV	2.13	12	7.4
	Davison Lot O	2.12	0	7.6
5-II	Davison Lot III	2.21	24	9.2
	Davison Lot IV	2.22	24	9.3
	Mallinckrodt Lot 3	2.25	24	7.7
	Numec Lot 1	2.31	24	8.6
	Davison Lot IV	2.19	12	8.2
	Davison Lot O	2.27	0	9.6
9-II	Davison Lot III	2.31	24	8.1
	Davison Lot IV	2.31	24	7.4
	Mallinckrodt Lot 3	2.38	24	9.3
	Davison Lot O	2.27	0	10.5

C. Conclusions

The oxidation-reduction cycling activation treatment appears to have general applicability in improving the sinterability of ADU oxides from several sources. With sufficient excess oxygen introduced by air roasting, all production lot oxides can be densified to at least 95% of theoretical at temperatures not exceeding 1300°C with a corresponding sintering time of 2 hours in nitrogen. The experimental results suggest that considerably milder sintering conditions, in conjunction with a particular initial O/U ratio, can be employed to yield pellets in a desired high density range. Further development of the Inert Atmosphere Sintering Process, therefore, need not be hampered by raw material variability. As anticipated, the factors responsible for the enhancement of low temperature sinterability in nitrogen also operate to improve high temperature hydrogen sinterability.

D. Work Plan for the Next Quarter

Optimization of the sintering conditions for the two-stage low temperature sintering operation will be completed. This will involve an investigation to determine the minimum time required to remove the excess oxygen from the sintered pellets with hydrogen during the second elevated temperature stage.

The sintering step of the process will be scaled up, so that a large number of pellets for an irradiation program can be prepared under identical conditions.

Since the oxidation-reduction cycling treatment appears applicable to all ADU oxides, no problem is expected in sintering an enriched oxide lot to high density. Work on the irradiation testing program, therefore, will be initiated. Capsule designs will be submitted to the Westinghouse Testing Reactor for approval and enriched material will be procured for the program.

II. THE DEVELOPMENT OF URANIUM CARBIDES AS A NUCLEAR FUEL FOR LOWERING THE COST OF NUCLEAR POWER (Task II)

H. S. Kalish, F. B. Litton, J. Crane

A. Introduction

The objective of research concerned with the methane reaction during this period was an attempt to define the variables which were affecting the chemical composition of uranium carbide powders prepared by reacting uranium with methane, and to attempt to control the variables which were believed to be affecting the composition. A determination was also made of the factors affecting sintered densities and the structures were studied relative to the composition variables, particularly carbon, oxygen, nitrogen and free uranium contents.

The work on the arc melting of uranium carbide was directed toward the improvement in the skull melting and casting operation, by utilizing a direct current coil in the furnace to control the arc during the melting cycle.

An important phase of work which was initiated during this report period was the use of reacted and unreacted uranium oxide-carbon mixtures as a charge for the skull furnace. Based on this method, a charge in the form of pellets, or as a consumable electrode, was studied.

B. Uranium Monocarbide by the Methane Reaction

1. Analysis of Uranium Monocarbide Product

Experimental work was continued on the preparation of uranium carbide made by the procedure described in Quarterly Report, NYO-2689, July 27, 1960. The method is reviewed briefly as follows: One pound of extruded uranium rod was pickled in nitric acid, rinsed in water, dried with alcohol, and placed in the retort on the top tier of the uranium support. The retort was sealed and flushed with argon; deoxidized and dried hydrogen was flushed through the system for 15 minutes prior to heating. The uranium was hydrided at 250°C in a closed system under a pressure of hydrogen of 3 psig until the reaction was complete. After hydriding, the 4 to 1 methane to hydrogen carburizing gas mixture was flowed through the system at 5 liters/min. The reactions were carried out for two hours at 750°C. After the carburizing reaction, the retort was flushed with argon, sealed, cooled to room temperature and discharged in the dry box.

The carburizing gas mixture consisting of a 4 to 1 mixture of methane to hydrogen was analyzed by mass spectroscopy. The analysis was 81% CH_4, 0.60% N_2 and 0.01% O_2. The dew point of the methane was -32°F; and of the hydrogen -56°F. The 4 to 1 carburizing gas mixture had a dew point of -44°F.

The chemical analysis of uranium carbide powders prepared using identical experimental conditions are shown in Table II-1. In these

six samples, the carbon content varied from 4.30% to 4.62%. The average carbon content was 4.49%. The average free carbon content was 0.25% and the oxygen 0.77%. These analyses indicate that improvements must be made in the method to obtain reproducibility of composition.

The average nitrogen analysis as shown in Table II-1 was 0.43%. The nitrogen results were biased by the low values obtained by the Kjeldahl method for analysis on the first two specimens. The Kjeldahl method was not accurate for determining nitrogen in relatively pure uranium mononitride prepared for standards during the course of this experimental work. Doubt was cast on the nitrogen values previously reported where nitrogen was determined in combination with carbon in the uranium carbide. As a result, a modified Dumas procedure was developed by the Analytical Laboratories to cope with this problem. The results by the Dumas procedure for nitrogen in uranium nitride was checked out using synthesized standards as well as x-ray diffraction analyses and metallography. The nitrogen values reported in samples after run 3C-HM-31 were determined by the modified Dumas procedure.

In order to increase the carbon content to a value above the 4.49% average, shown in Table II-1, three additional runs were made using a two and one-half-hour time instead of the two-hour time. The average analysis of these three runs was 4.29% carbon and 0.74% nitrogen, showing that the expected increase in carbon content did not occur, and further indicating the difficulty in reproducing composition by this reaction.

2. Effect of Carburizing Gas Flow on Product Analysis

As a start in determining the variables which were affecting the carbon content in the methane-uranium reaction, a study was embarked upon of the effect of the methane gas flow on the product analysis. A series of experiments were made using a 4 to 1 methane to hydrogen carburizing gas mixture in which the methane flow was progressively decreased from 4 to 0.5 liters/min. In each carburizing experiment in this series, 400 grams of uranium rod was hydrided for approximately eight hours at 250°C and 3 psig hydrogen pressure to form uranium hydride powder. The carburizing was carried out for two hours at 750°C. The chemical analyses are recorded in Table II-2.

The analyses show conclusively that the methane flow rate did not affect the carbon composition of the product. In each run, however, the amount of methane that flowed through the system was above that required to form stoichiometric uranium monocarbide. These results indicated that the efficiency in utilization of carbon from the methane when the reaction is under optimum control is as high as 60% to 70% when the minimum amount of methane is utilized. Excessive methane above the minimum appears to have no effect upon the reaction. In order to better define the efficiency, a run was made in which 600 grams of uranium were hydrided and heated up to the carburizing temperature of 750°C in a hydrogen atmosphere. A flow of 0.5 liters/min. was then introduced to the retort and continued for two hours.

TABLE II-1

CHEMICAL ANALYSES OF URANIUM MONOCARBIDE PRODUCED BY THE METHANE REACTION IN A RETORT

Sample No.	Composition, per cent			
	Total Carbon	Free Carbon	Nitrogen*	Oxygen
3C-HM-28	4.56	0.40	0.26	0.16
3C-HM-31	4.57	0.20	0.17	0.64
J-2	4.62	0.33	0.54	0.36
J-3	4.30	0.08	0.69	0.94
J-4	4.46	--	0.49	0.74
J-12	4.47	--	--	--
Average	4.49	0.25	0.43	0.77

* Nitrogen was determined by the Kjedahl Method for samples 3C-HM-28 and 3C-HM-31; the modified Dumas Method was used for determining nitrogen in subsequent samples in this report.

TABLE II-2

EFFECT OF RATE OF CARBURIZING GAS FLOW ON CARBON CONTENT OF URANIUM CARBIDE

Methane Flow, Liters/min.	Composition, per cent	
	Carbon	Nitrogen
4.0	4.86	--
3.0	5.10	0.82
2.0	5.20	0.35
1.0	5.67	0.25
0.5	5.36	--

This was sufficient only to result in a product of 4.8% carbon, if all the carbon available had been utilized. The product analyzed 3.2% carbon indicating, in this case, an efficiency of 68%. The product caked during this experiment because of sintering of the uranium powder when it decomposed from the hydride above the temperature of 400°C, prior to the introduction of the methane at 750°C. Because of the caking which occurred it was decided, in subsequent runs, to revert to the method which had been used of heating the hydride powder to the carburizing temperature in a methane atmosphere rather than in a hydrogen atmosphere. A subsequent run was performed under these conditions, using a flow of 0.7 liters/min. of methane. The product of this carburizing run analyzed 4.79% carbon and, as had been observed previously, there was no caking of the powder. Work is now in process with the methane reaction in an attempt to finally pin down conditions which yield the optimum compositional control and to determine degree of compositional control which is feasible with this method. This is being done by reinvestigating the temperature variable in the range of 650°C to 750°C, using a precise control of methane flow, time and heating rate.

3. Carburization of Uranium with Propane

Experiments were started on the use of propane for carburizing uranium. This work was initiated because propane is commercially available in a purer state and at a lower cost than methane. During this report period one carburizing experiment, No. J-5, was completed. The experiment was carried-out in the same manner as described in the previous section except that a carburizing time of one hour at 700°C was used. The analysis of the uranium carbide product was as follows:

5.0% Carbon
0.41% Free Carbon
0.22% Oxygen
0.06% Nitrogen

This run, using propane, is extremely promising, in view of the low oxygen and nitrogen contents which were obtained. The free carbon appears to be on the high side, but may be controlled by reducing the carburizing temperature. In view of these promising results, additional work will be done to determine if the propane is a superior carburizing gas to methane for producing uranium carbide.

C. Consolidation of Uranium Carbide Powder

1. Investigation of Sintering Variables

Compacts were produced from each of the carburizing runs under an argon atmosphere using a pressure of 35 tsi. No mold lubricant or additive to the powder was used for these compacts. The cold-pressed bars, 2-1/4" long by 1/2" wide by 1/4" thick were vacuum sintered for three hours at 1800°C. The compacts were heated at a slow rate to maintain a pressure below one micron during the vacuum sintering.

In all cases, the sintered density of the compacts was relatively low, ranging from 10.8 to 12.2 g/cm^3 for the ten different batches of uranium carbide powder. There was no clear trend between composition and sintered density, except that the highest density compact, viz., 12.2 g/cm^3, was produced from the batch having a significantly lower carbon content than the others. The carbon content of that batch was 3.27, but the nitrogen and oxygen values were high, so that there was still less than 50 a/o uranium in the sintered product. These results gave further indication that high sintered density cannot be obtained from methane-carburized powders which are subsequently cold pressed and sintered, unless they have free uranium present. A typical metallographic structure of a stoichiometric carbon content, relatively high purity, cold pressed and sintered compact produced from methane-carburized powder is shown in Figure II-1.

Attempts were again made to increase the sintered density of these near-stoichiometric uranium monocarbide compacts, by increasing the sintering temperature. A series of samples was cold pressed under argon without lubricant at 35 tsi and sintered for three hours at 1800°C and 2200°C in vacuum. The sintered densities of specimens, which are representative of three different batches of methane-produced uranium carbide powder, are shown in Table II-3. The densities of these, as well as other relatively porous samples, are being determined by weighing in air and determining the volume by immersion in mercury. The data indicate that a significant increase in density can be obtained by going up to 2200°C, but there has been pronounced evidence indicating uranium volatilization at this temperature. The extent of the uranium volatilization was not determined during this experiment, but uranium volatilization at 2000°C is discussed in another section of this report.

Examination of the metallographic structures of these samples indicated that it was essentially the same as that shown in Figure II-1. The structures indicated that the material was substantially the isomorphous solid solution of uranium monocarbide containing oxygen and nitrogen. A few platelets, which appeared to be uranium dicarbide, were observed, particularly at the surface of samples sintered at 2200°C. There appeared to be somewhat less voids in the specimens sintered at 2200°C, compared to those sintered at 1800°C, verifying the density results.

2. Effect of Additions of Nitrogen and Uranium on Sintered Densities of Methane Produced Powder

It was demonstrated in previous reports of this investigation that high density sintered products could be obtained from methane powders, containing less than stoichiometric carbon and relatively high nitrogen and oxygen contents. For example, the chemical analysis of a high density carbide material shown in Figure 6 of NYO-2688 contained 4.61% carbon, 0.72% oxygen and 0.09% nitrogen. The x-ray diffraction analysis showed evidence only of uranium monocarbide. These data indicate, therefore, that the stoichiometry of sintered uranium carbide was influenced by the total carbon, nitrogen and oxygen contents.

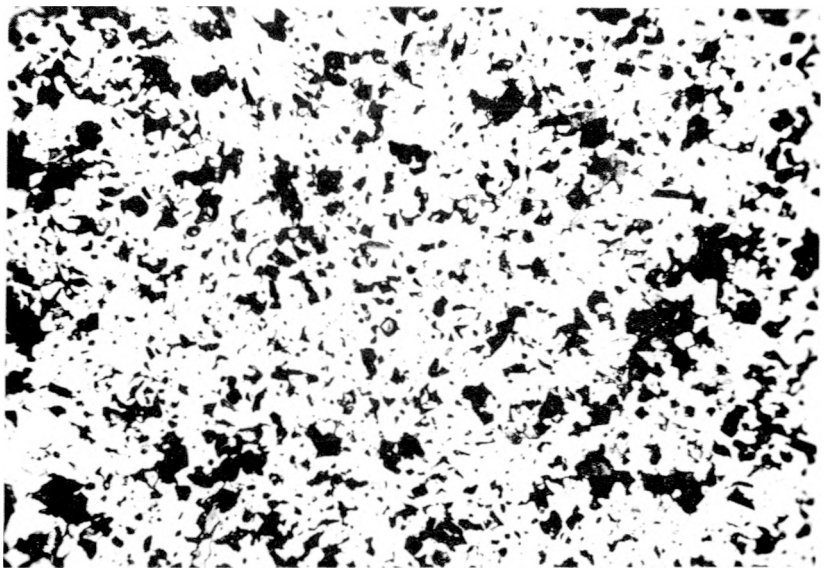

Fig. II-1. Typical Structure of Essentially Stoichiometric Uranium Monocarbide Produced from Methane Reaction Powder.

Specimen No. J-13
Sintered Density - 11.25 g/cm^3
Carbon Content - 4.86 per cent
Structure - Unetched; 250 mag.

TABLE II-3

THE DENSITY OF SPECIMENS PRODUCED BY COLD PRESSING AT 35 TSI AND VACUUM SINTERING COMPACTS FROM THREE DIFFERENT BATCHES OF METHANE PRODUCED URANIUM CARBIDE POWDER

Sintering Temperature	Sintered Densities, g/cm^3 1800°C	2200°C
Powder Batch No.		
J-2	10.81	11.24
J-3	10.90	11.58
J-4	11.13	11.57
Average	10.94	11.46

In order to determine the effect of nitrogen on the structure of uranium carbide, a sample of uranium carbide analyzed to contain 4.6% carbon was prepared by arc melting uranium and graphite under argon. One-half of this material was melted under an atmosphere of nitrogen. The metallographic structures are shown in Figures II-2 and II-3 before and after arc melting under nitrogen. Figure II-2 shows a cast structure of uranium carbide containing free uranium at the grain boundaries. Figure II-3, after melting in nitrogen, shows that the free uranium combined to form a hyper-stoichiometric structure with a precipitate, presumably dicarbide, within the monocarbide grains. Chemical analysis indicated that the material shown in Figure II-3 contained 4.04% carbon and 1.08% nitrogen. These structures are conclusive evidence that uranium nitride is isomorphous with carbide and replaces carbon in the monocarbide structure.

The adjustment to a one-phase uranium monocarbide structure of low carbon uranium carbide by the addition of nitrogen was investigated. A sample was prepared to contain 3.2% carbon and repeatedly melted under nitrogen for a total of 21 one-minute melts. After this melting procedure the sample contained 1.36% nitrogen. In another experiment, melting under nitrogen for five times at one-minute melts each time, the nitrogen was increased from 0.065% to 1.52%. The metallographic structure of a 3.23% carbon sample, melted under nitrogen five times, is shown in Figure II-4. The structure is essentially a one-phase uranium carbide nitride isomorphous solid solution. There is evidence of some free uranium at the grain boundaries, which would be expected on the basis of the atomic per cent of carbon and nitrogen per cent in comparison to the uranium. Thus, it is possible to produce a single-phase structure of the uranium monocarbide type which consists of an isomorphous solid solution of carbon, nitrogen and, probably, oxygen. The control of composition, however, appears to be a problem, also, in this method and, perhaps, of exceeding complexity. This is brought out by the fact that whereas a sample, in one case, melted for 21 one-minute melts, resulted in 1.36% nitrogen, and another one, which was melted only five times, showed a nitrogen increase from 0.065% to 1.52%.

A determination was then made of the effect of either uranium or nitrogen addition on the sintered densities of methane-produced uranium carbide. Additions of the nitrogen and uranium were made separately. Three batches of powder, containing 4.1% carbon - 0.81% nitrogen, 4.23% carbon - 0.75% nitrogen and 4.53% carbon - 0.66% nitrogen were each blended with a sufficient quantity of uranium hydride powder such that the uranium metal content of the product would be adjusted to 51 a/o. The blended powders were compacted at 35 tsi and sintered for three hours at 1800°C in vacuum. The resultant sintered compacts were of relatively high density, about 13 g/cm^3, and as shown in the photomicrograph of Figure II-5, had a limited amount of porosity and the usual uranium in the grain boundaries. The only apparent difference between this material and that produced, where the composition is not adjusted but is controlled by having the necessary amount of free uranium present from the methane reaction, is that the synthesized mixture appears to yield a coarser grain size.

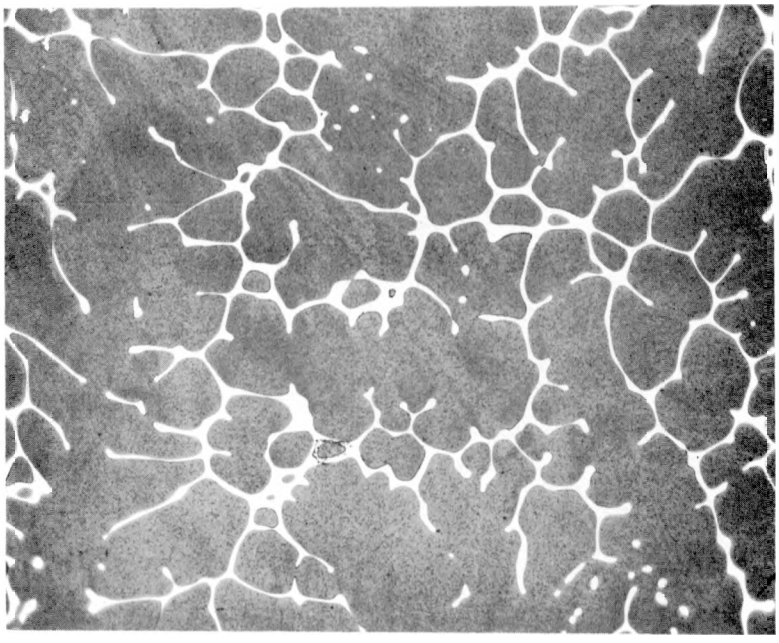

Fig. II-2. Arc Melted Uranium Carbide Containing 4.6% Carbon Showing Uranium at the Grain Boundaries.

Etched 250 mag.

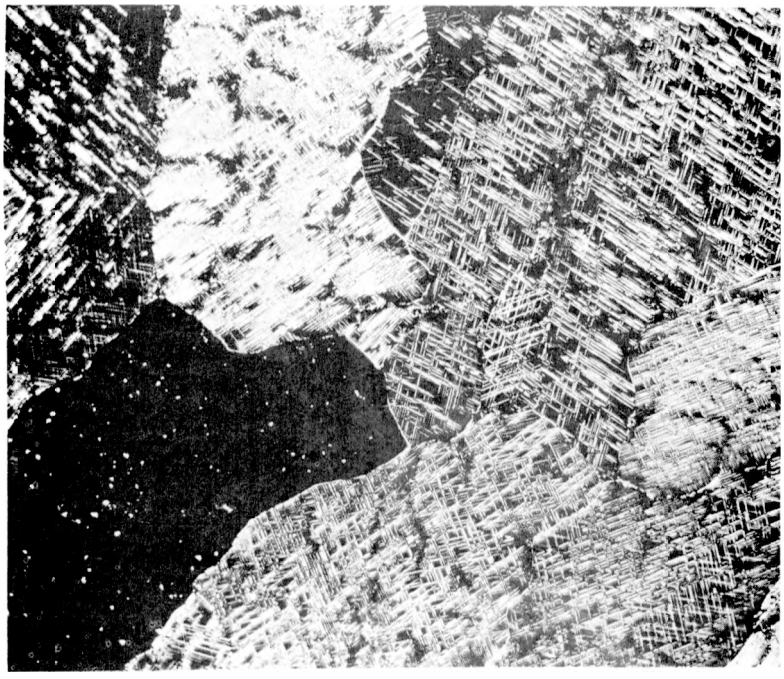

Fig. II-3. Hyper-stoichiometric Carbide Structure After Arc Melting Material Shown in Fig. II-2 Under Nitrogen. (Polarized Light.)

Analysis: 4.4% C, 1.08% N_2

Etched 250 mag.

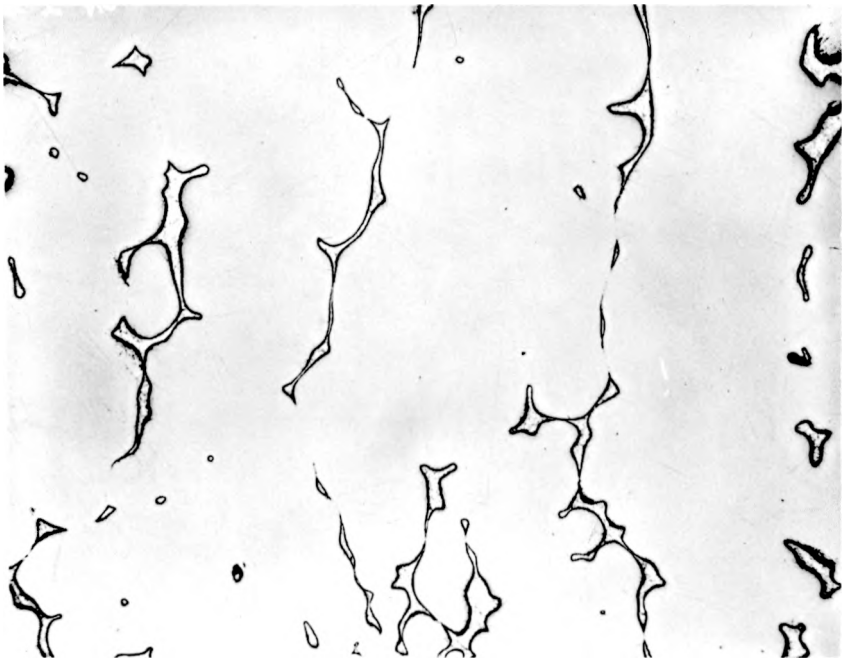

Fig. II-4. Structure of Uranium Carbide After Melting for Five Minutes Under a Nitrogen Atmosphere.

Analysis: 3.23% C, 1.52% N_2

Etched 250 mag.

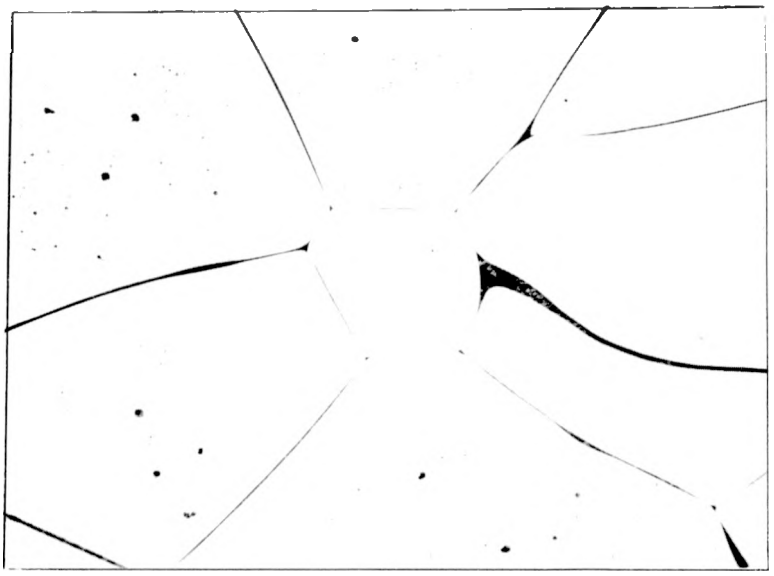

Fig. II-5. Structure of Sintered Uranium Carbide. The Composition was Adjusted to 51 Atom Per Cent Uranium Based on Carbon, Nitrogen and Oxygen Content.

Etched 250 mag.

Fig. II-6. Structure of Sintered Uranium Carbide. The Composition was Adjusted to 50 Atom Per Cent Uranium and 3 Weight Per Cent Carbon by Adding U_2N_3.

Etched 250 mag.

To determine the effect of nitrogen on a single-phase uranium monocarbide type structure, uranium sesquinitride (U_2N_3) was added to a batch of methane-produced powder which contained 4.23% carbon and 0.75% nitrogen. The powder was mixed and blended with the uranium sesquinitride so that it would contain about 3% carbon and 2% nitrogen, which would result in a material containing 50 a/o uranium. The compact was pressed at 35 tsi and sintered for three hours at 1800°C in vacuum. No substantial grain growth occurred and a porous specimen resulted, as shown in Figure II-6, typical of sintered stoichiometric uranium monocarbide. These data indicate that the free uranium is the essential component to the attainment of a high sintered density and that the presence of nitrogen in even substantial quantities will not enhance the sintered density, unless free uranium is present. The role of nitrogen in enhancing the sintered density, when free uranium is present, has not yet been determined.

The data on this phase of the work shows that high density structures are obtained on sintered methane-produced powders containing uranium in excess of that required to satisfy the stoichiometry of the composition, based on the carbon, oxygen and nitrogen contents. At this time it is not known whether the nitrogen and oxygen contents are critical in obtaining high density structure. Further work will be carried out to determine these composition variables.

3. Volatilization of Uranium on Sintering

As pointed out previously, the graphite susceptor used for vacuum sintering uranium carbide in the induction furnace showed that the uranium was volatilized from the uranium carbide during sintering. The loss of uranium was particularly pronounced at temperatures above 1800°C. Work was performed to determine the weight loss at this temperature. Several specimens that had been sintered previously in vacuum at 1800°C for three hours were reheated in vacuum at 2000°C for a three-hour period. As shown in Table II-4, there is a significant weight loss at 2000°C for those samples containing free uranium. It appears that where the uranium is tied up as uranium monocarbide the weight loss diminishes markedly and where the carbon content is well above stoichiometric the weight loss is almost insignificant.

D. Arc Melting and Casting Uranium Carbide

1. Skull Furnace

Although full-sized castings 5/8" dia. by 6" long were made in the skull furnace, arc deflection was a continual problem. The melting cycle was not consistent and required special adjustment during every melt. Attempts were made to melt at amperages where arc deflection was not a serious problem, but it was found that insufficient superheated material was generated to completely fill the mold cavities of 3/8" dia. by 3" long. Relocation of power return cables and

TABLE II-4

THE EFFECT OF CARBON COMPOSITION ON THE VOLATILIZATION OF URANIUM FROM URANIUM MONOCARBIDE. WEIGHT LOSS SHOWN IS AFTER REHEATING THREE HOURS AT 2000°C. BARS TESTED WERE PRODUCED BY SINTERING THREE HOURS AT 1800°C.

Carbon Content w/o	Weight Loss on Reheating %
3.56	6.4
3.61	7.9
4.10	4.5
4.23	1.9
4.23	2.3
4.53	1.4
4.86	0.7
5.67	0.03

positioning of mold pre-heat power cables succeeded in minimizing arc deflection up to about 2000 amperes, but this effect was not entirely reliable and was not more than superficially effective at amperages above 2000. Effort was then made to eliminate the cause of arc deflection.

It was found that the mild steel housing for the ladle assembly was developing a magnetic field with the passage of high arc current assymetrical with respect to the electrode axis. The effect of this magnetic field was to deflect the arc. It was decided to overcome arc deflection with a magnetic field from a suitably wound coil rather than to attempt to eliminate a rather complex magnetic field within the furnace. After tests were made to determine the field strength required to eliminate arc deflection, a ten-turn coil using 1/4" dia. copper tubing was made and positioned beneath the ladle. Figure II-7 shows the coil positioned beneath the ladle.

Six preliminary melts were made using the coil. In all cases deflection was eliminated by use of a maximum current of 400 amperes at five volts to the coil. It was found that after establishing any given arc voltage and amperage, these settings could be maintained without adjustment. Pool position was also good in all cases. The six melts resulted in five full-sized castings 3/4" dia. by 6" long, each about 500 grams when cropped; the total pour was about 700 grams. Melting time was six minutes. A typical casting is shown in Figure II-8. The castings showed no external surface cracks.

All of the above castings were made without mold pre-heat, and no significant effort was made to control surface quality, a factor which needs improvement. The prime purpose of these tests was to establish whether a uniform, easily controlled short-time melting procedure capable of making uranium carbide castings about 1/2" to 3/4" dia. by 6" long was feasible with this skull furnace. These casting tests established that it was feasible to consistently produce castings in the skull furnace with the coil installed for arc control.

2. Consumable Melting

Experiments were continued on the preparation of consumable electrodes for arc melting uranium carbide. The reaction of UO_2 with graphite to produce suitable bars is now being investigated as a method for consumable electrode preparation. The immediate objective of this work, then, is to establish a method for obtaining bars of suitable strength, electrical conductivity and shock resistance to enable them to be handled, mounted and consumably melted. The analyses of the starting materials are shown in Table II-5.

Bars compacted from a mixture of UO_2 and graphite were found to have electrical resistivity of several hundred ohm-cm, so it was obvious that such an electrode could not satisfactorily conduct the necessary current and it was apparent that the charge material would have to be reacted prior to its use in the form of a consumable electrode.

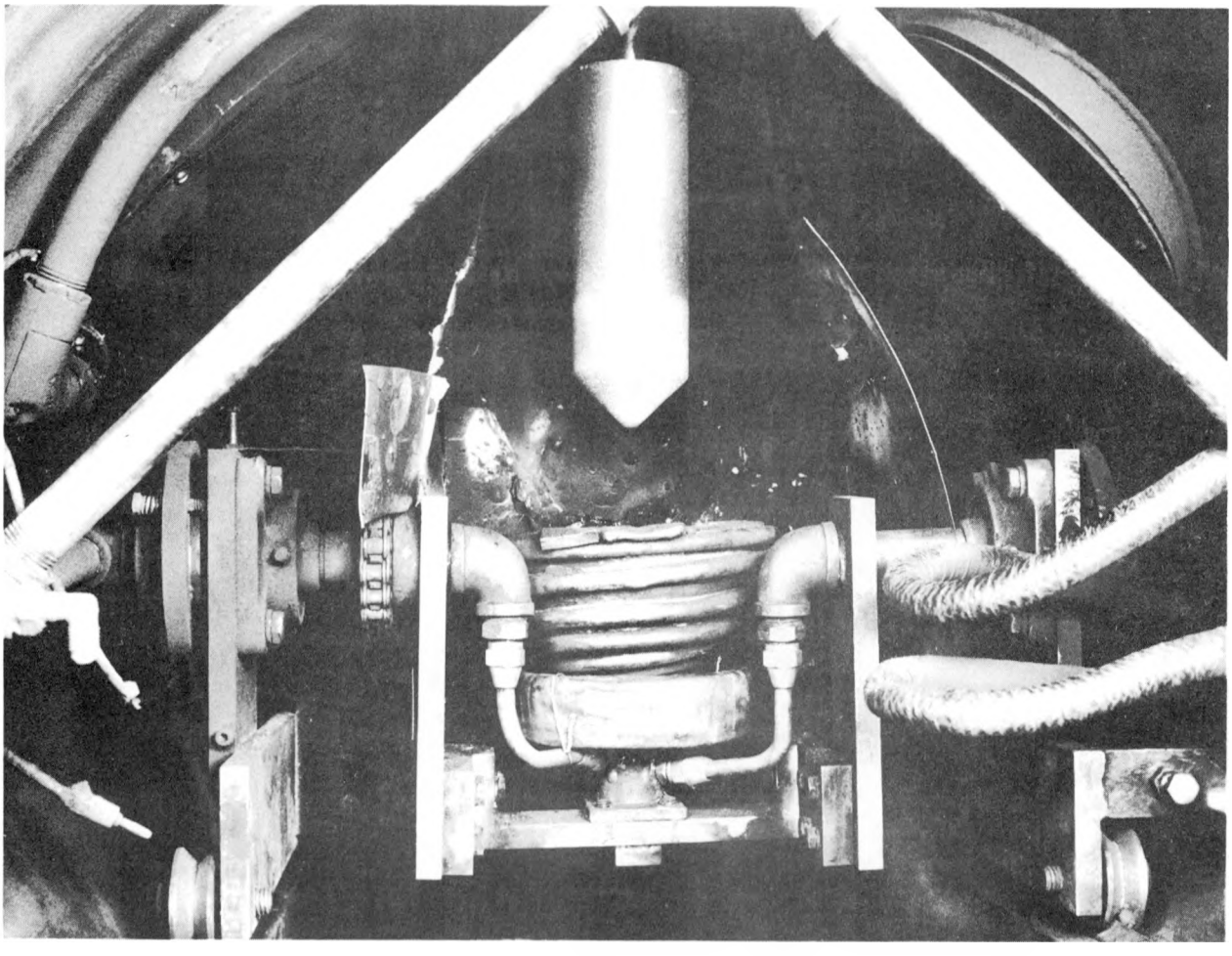

Fig. II-7. View of Ladle Assembly Showing Coil Positioned at Base of Ladle. Flexible Leads in Lower Right Foreground Carry Power and Water To and From the Coil.

1/3X

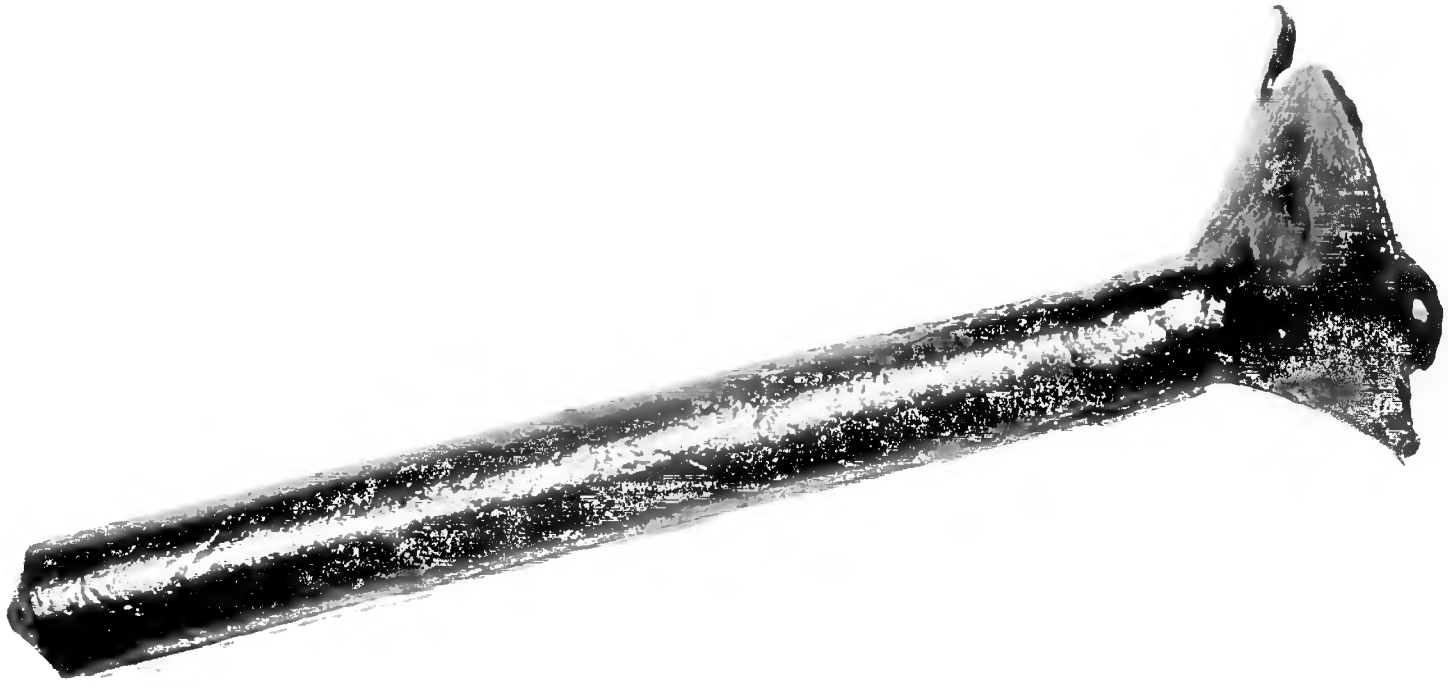

Fig. II-8. Skull Casting Representative of Castings Made Using the Coil to Control Arc Deflection.

Actual Size

TABLE II-5

ANALYSES OF UO_2 AND GRAPHITE POWDERS USED FOR PREPARATION OF CONSUMABLE ELECTRODE MATERIAL

Analysis of UO_2

Typical Chemical Analyses of UO_2

U	- 87.8	B	- 0.4 ppm
UO_2	- 94.8	Cr	- 20 ppm
Fe	- 50 ppm	Cu	- 1 ppm
Mo	- 1 ppm	Ni	- 60 ppm
Si	- 60 ppm	Pb	- 1 ppm
F	< 50 ppm	Sn	- 1 ppm
Ag	< 0.01 ppm		

Dry Screen Analysis

Sieve No.	Per Cent Retained	Cumulative Per Cent
60	0.13	0.13
100	0.43	0.56
200	0.34	0.90
325	0.51	1.41
Minus 325	98.59	100.00

Bulk Density of UO_2 - 1.208 g/cm^3

Analysis of Graphite

Graphite Analysis (NC grade 48)

Sieve Analysis: 99% -200 mesh
Maximum Ash: 0.08%
Average Ash: 0.03%

Analysis of Ash

Element	S	Cu	Fe	Si	Ti	V	Total
Minimum %	0.003	0.002	0.0025	0.0007	0.0005	0.0025	0.010
Maximum %	0.006	0.011	0.013	0.004	0.002	0.013	0.049
Typical %	0.004	0.004	0.005	0.0014	0.001	0.005	0.021

Bars with green strength suitable for handling were obtained by compacting a mixture of UO_2 and graphite powders with 0.75% polyvinyl alcohol binder. The compacts were dried by baking at 650°C for one-half hour in nitrogen. Compacting pressures from 7 to 35 tsi were investigated. These bars were 2-1/2" long with a cross-section about 1/2". Variation of density with compacting pressure is shown in Table II-6.

The baked bars were sintered for two hours in vacuum at 1500°C and 2000°C. In both cases, the carbothermic reaction, as judged by weight change, was essentially complete in accordance with the equation $UO_2 + 3C \rightleftarrows UC + 2CO$. The density of the bar sintered at 2000°C rose from 3.2 g/cm^3 before sintering to 9.5 g/cm^3 after sintering. Cracking of the bar sintered at 1500°C precluded density measurement. Resistivity after sintering ranged from 70 micro-ohm-cm for the higher sintering temperature to 125 for the lower temperature. Chemical analyses are shown below:

Sintering Temperature	Analyses (w/o)			
	Total Carbon	Free Carbon	Oxygen	Nitrogen
1500°C	4.71	Trace	0.359	0.10
2000°C	4.96	Trace	0.265	0.33

An attempt was made to arc melt each bar consumably, the bar being clamped at one end in a split graphite threaded rod. The bar sintered at 1500°C did not disintegrate when an arc was struck, but a piece about 1/2" at the tip did break off at amperage too low to cause melting of the bar. Because of the short length of the electrode available for melting, the test had to be discontinued. The bar sintered at 2000°C was found to be capable of melting uranium carbide striker as a non-consumable electrode up to 500 amperes. At 500 amperes the electrode melted rapidly at the tip. After about 3/4" was melted, the test was discontinued. No fragmentation or disintegration occurred during the test and heat-up and eventual melting took place at the tip. The results of these tests do indicate that it is possible to produce an electrode which is essentially UC, which will support an arc and which can be consumably melted with sufficient power. Sintering at other temperatures is planned prior to preparation of a large electrode suitable for use in the skull furnace.

3. Non-Consumable Melting

Although consumable melting has an advantage over non-consumable melting because contamination of the melt by the non-consumable electrode is avoided, the decreased melt time and advances in skull melting technology which have been made in this program should minimize if not eliminate carbon increase from the graphite electrode. Extensive investigation of non-consumable melting along the lines described below is, therefore, underway.

TABLE II-6

EFFECTIVE COMPACTING PRESSURE ON THE DENSITY OF UO_2 AND GRAPHITE BARS AFTER BAKING FOR ONE-HALF HOUR AT 650°C IN NITROGEN

Compacting Pressure (tsi)	Calculated Density (g/cm^3)
35	3.87
25	3.68
12	3.50
7	3.30

The non-consumable melting of massive charge materials, such as uranium metal plus graphite and chunks of sintered carbide bars, has been extensively investigated. On the other hand, the use of UO_2-graphite mixtures as a charge material for non-consumable melting does not appear to have been investigated. This approach is quite promising, since UO_2 can be readily mixed with powdered graphite, compacted and charged in pellet form simplifying the continuous addition of the charge during melting and casting and avoiding the problems in handling material which is reactive prior to the melting operation. It also appears to have potential economic advantages and is a good way to achieve good homogeneity and composition control. One disadvantage in directly arc melting the UO_2-graphite mixture, however, is the evolution of large quantities of CO during the reaction and the time for the reaction to go to completion. Two approaches are being investigated. One involves the pre-reaction of compacted UO_2-graphite pellets by induction heating in vacuum and the other the direct charging of the compacted UO_2-graphite pellets to the skull melting furnace. While the former method involves an added step, it does avoid the problem of gas evolution during the arc melting operation.

As a preliminary investigation, arc melting of un-reacted pellets in a button furnace has been investigated. Pellets of UO_2 and graphite powders compacted at 35 tsi and baked at 650°C were reacted and melted on a copper hearth, using both argon and helium atmospheres and tungsten and graphite electrodes. The atmospheres used were dynamic: the pressure was maintained by balancing the incoming flow of the inert gas with evacuation of the chamber by a mechanical pump at 5" Hg absolute pressure. It was found that although the pellets were electrically non-conductive at the beginning, as the reaction progressed, the pellets became conductive and this was accompanied by evolution of gas, an erratic arc and much sputtering. There was no significant difference in arc behavior between the two electrode materials, but reaction in helium atmosphere was more rapid than in argon, and coalescence occurred sooner in helium.

Analyses of these buttons for carbon, oxygen and nitrogen showed that they contained no free carbon, total carbon from 4.66 w/o to 4.76 w/o, oxygen from 0.075 w/o to 0.093 w/o and nitrogen 0.06 w/o. Metallographic examination at lower magnification revealed that the material was single-phase uranium monocarbide. At magnifications of 1500X and above, there was some evidence of dispersed particles which may have been complex carbides or oxides not completely reacted.

Preparation is now being made to skull cast uranium monocarbide, using UO_2 + graphite pellets as charge material. Conditions established by work in the button furnace are expected to serve as a guide in establishing the various parameters for the skull furnace operation. Work is also in progress to skull melt and cast, using pellet charges of reacted UO_2 + graphite.

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