NYO-2691

NUCLEAR FUEL RESEARCH FUEL CYCLE DEVELOPMENT PROGRAM

Quarterly Progress Report [Covering the Period]
October 1 to December 31, 1960

February 10, 1961

Olin Mathieson Chemical Corporation
New Haven, Connecticut

UNITED STATES ATOMIC ENERGY COMMISSION • OFFICE OF TECHNICAL INFORMATION

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NYO-2691

METALS, CERAMICS, AND MATERIALS

NUCLEAR FUEL RESEARCH

FUEL CYCLE DEVELOPMENT PROGRAM

QUARTERLY PROGRESS REPORT

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Date of Issuance: February 10, 1961

Nuclear Fuel Research Laboratory
E. Gordon, Technical Manager
Contract AT(30-1)-2374

OLIN MATHIESON CHEMICAL CORPORATION
New Haven, Connecticut

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SUMMARY

This report presents the progress made by Olin Mathieson Chemical Corporation under Contract No. AT(30-1)-2374 during the period October 1 to December 31, 1960.

Under Task I, work was continued on the development of a laboratory scale process for the fabrication of UO_2 pellets based on low temperature sintering in nitrogen.

Using several ceramic grade oxide lots activated by oxidation-reduction cycling, the major effort was devoted to optimizing the sintering conditions. With the initial O/U ratio kept constant, the relationship between pellet density and sintering temperature was established. The effect on pellet density of variations in the quantity of excess oxygen initially introduced was also determined. It was found that a density of 95% of theoretical can be readily attained in the 1200°C to 1300°C temperature range with a minimum initial O/U ratio of 2.25. Sintering times of one to two hours in nitrogen were employed. A study of the hydrogen soaking conditions for the excess oxygen removal step indicates that at least a one-hour exposure in hydrogen is required at 1200°C to 1300°C to obtain complete reversion to stoichiometry.

An investigation of the influence of fluoride impurity on the low temperature sinterability of UO_2 demonstrated that the introduction of approximately 3000 ppm fluorine seriously inhibits sintering. Oxidation-reduction cycling of the contaminated oxide restores the original activity.

A two-month corrosion test on sintered UO_2 pellets was completed successfully without any indication of oxidation of the UO_2 in 680°F water.

Work was initiated on the UO_2 pellet irradiation testing program. Steps were taken to obtain approval for the experiments from the test reactor operator.

Under Task II, the study of the effects of reaction temperature on the carbon content of methane-produced uranium monocarbide indicated that the carbon content of the powder can be reduced from 4.8 w/o to 4.4 w/o by reducing the carburizing temperature from 750°C to 650°C. These tests were all performed by holding at carburizing temperatures for two hours; carburizing at 650°C without the two-hour hold time produced a carbide having a carbon content of 3.9 w/o.

Investigation with propane indicated that it will be a superior carburizing medium. It was found that the high free-carbon concentration reported previously resulted from the pyrolytic decomposition of propane on the retort walls. This deposit was isolated and a carbide powder was produced with the free carbon reduced to less than 0.2 w/o and the nitrogen less than 0.01 w/o. This has been done up to 4.3 w/o carbon. Investigations are now under way to increase the carbon content to stoichiometric while maintaining the purity.

Compacting tests on propane-produced uranium monocarbide are reported in which 3 w/o cetyl alcohol was found effective as a binder-lubricant when the compacts were pressed at 35 and 50 tsi. Lower cetyl alcohol additions proved unsuccessful, producing compacts which broke upon removal from the compacting die.

The yields and chemical analyses of castings produced by reacting uranium dioxide-graphite pellets in vacuum prior to melting are reported. Virtually no losses in reacting the pellets have been noted; approximately 99% of the theoretical uranium monocarbide yield is obtained after reacting the pellets in a vacuum furnace. Up to a maximum of 7% recoverable, but not remeltable, loss occurs during skull arc melting. The chemical analyses indicate good homogeneity in carbon content between the top and bottom of the castings. The parameters of the melting process have been established, and the actual cycle requires only five minutes.

Experimental work is also reported for castings made using uranium dioxide-graphite pellets charged directly into the skull furnace without being previously reacted. This work is still in progress. Data obtained thus far show good homogeneity regarding carbon content is attainable in the final casting without pre-reacting the uranium dioxide-graphite mixtures, but longer melting times are required and greater material losses appear likely.

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

R. B. Holden, N. Fuhrman, L. D. Hower, Jr.

A. Introduction

As noted in the Quarterly Progress Report for July 1 to September 30, 1960 (NYO-2690), activation of the oxide lots on hand by oxidation-reduction cycling had removed the major obstacle to further development of the low temperature Inert Atmosphere Sintering Process. It was clearly demonstrated that the sinterability of all production lot oxides could be enhanced to produce a density of at least 95% of theoretical at temperatures not exceeding 1300°C. Attempts to optimize the sintering conditions with respect to time and temperature, therefore, were no longer hampered by large variations in oxide sinterability. Moreover, the irradiation testing program could now be initiated.

At the beginning of this reporting period, work was well under way on establishing the relationship between pellet density and sintering temperature as well as that between pellet density and initial O/U ratio. This study was completed during the period and an investigation involving optimization of the hydrogen soaking conditions of the second stage of the two-stage process was also completed.

B. Process Development Studies

1. Pellet Density vs. Sintering Temperature

With the initial O/U ratio kept constant, two-stage nitrogen sintering experiments were conducted with several oxide lots at four sintering temperatures, 1000, 1100, 1200 and 1300°C. The as-received materials used in this work were activated by oxidation to U_3O_8 in air at 500°C, followed by reduction to UO_2 in hydrogen at 525°C. The activated oxides were then air-roasted to introduce excess oxygen. Compacts were cold pressed at 19 tsi from roasted material previously granulated with 0.4% PVA. The green compacts were sintered in nitrogen for one hour and soaked in hydrogen for an additional hour to remove the excess oxygen. The pellet densities arising from this study are plotted as a function of sintering temperature in Figure I-1. Data for Davison Lot O, as received, is included for comparison. In developing the data, final O/U ratio measurements were made to assure that the excess oxygen had been removed from the pellets during the hydrogen soak. In only one case, Spencer Lot 2 at 1100°C, was it necessary to correct the density to stoichiometric composition.

It is noteworthy that the activation effect was sufficiently pronounced in the case of one oxide, Davison Lot 3, to permit the attainment of 95% of theoretical density at a temperature as low as 1000°C. Although there is a wide variation in the sintered density at 1000°C, all of the oxides exhibited essentially the same density of 10.5 to 10.6 g/cm^3 at 1200°C. Upon increasing the sintering temperature to 1300°C, there appears to be a density decrease which is most pronounced in the case of the Spencer oxide. In fact, the Spencer plot displays a comparatively sharp maximum in the 1100°C to 1200°C range. With the exception of the Spencer oxide, the observed density decrease with increasing sintering temperature is believed to be associated with the use of different activated batches in the 1300°C experiments.

The effect of a longer nitrogen soaking period at 1300°C was shown when the activated batches used in the lower temperature experiments were sintered for two hours in nitrogen followed by one hour in hydrogen. The densities obtained are compared in the following table with the one hour in nitrogen data for 1200°C and 1300°C plotted in Figure I-1:

	Density, g/cm^3		
	@ 1200°C	@ 1300°C	
Oxide	1 hr. in N_2	1 hr. in N_2	2 hr. in N_2
Davison Lot 3	10.6	10.5	10.7
Davison Lot 4	10.6	10.5	10.7
Mallinckrodt Lot 3	10.6	10.4	10.6
Spencer Lot 2	10.5	10.0	9.9

As anticipated, the densities obtained at 1300°C with a sintering period of two hours are greater than those obtained with the one-hour period. The one hour at 1300°C values, unexpectedly, are less than the corresponding 1200°C values. This anomaly, as noted earlier, is attributed to the normal batch-to-batch variation encountered in the activity imparted to these oxides by the oxidation-reduction treatment.

The Spencer oxide behavior, however, cannot be explained by such variations in processing. To verify the peaking of the density vs. temperature curve, several sintering experiments were conducted with four different batches of oxidized-reduced Spencer Lot 2. Pellets were prepared using similar sintering conditions - initial O/U ratio of 2.38, soaking for one hour in nitrogen followed by one hour in hydrogen at 1200°C. Three of the four batches produced a pellet density of 10.5 g/cm^3, which is the value obtained with the original batch as plotted in Figure I-1. As a result of a 1300°C sintering of one of these batches, a pellet density of 9.8 g/cm^3 was obtained which is in fair agreement with the 10.0 g/cm^3 originally found. The pronounced maximum exhibited by the Spencer oxide pellet density as a function of sintering temperature, therefore, definitely appears to be real.

2. Pellet Density vs. Initial O/U Ratio

A series of sintering experiments were conducted with these activated oxides as part of a systematic study to establish the effect of initial O/U ratio variation on pellet density. The oxides were processed and compacted as described in the above section, except that each material was oxidized to produce three different initial O/U ratios. All of the data were obtained under identical sintering conditions involving heating at 1300°C for two hours in nitrogen followed by one hour in hydrogen. The results of the study are shown in Figure I-2.

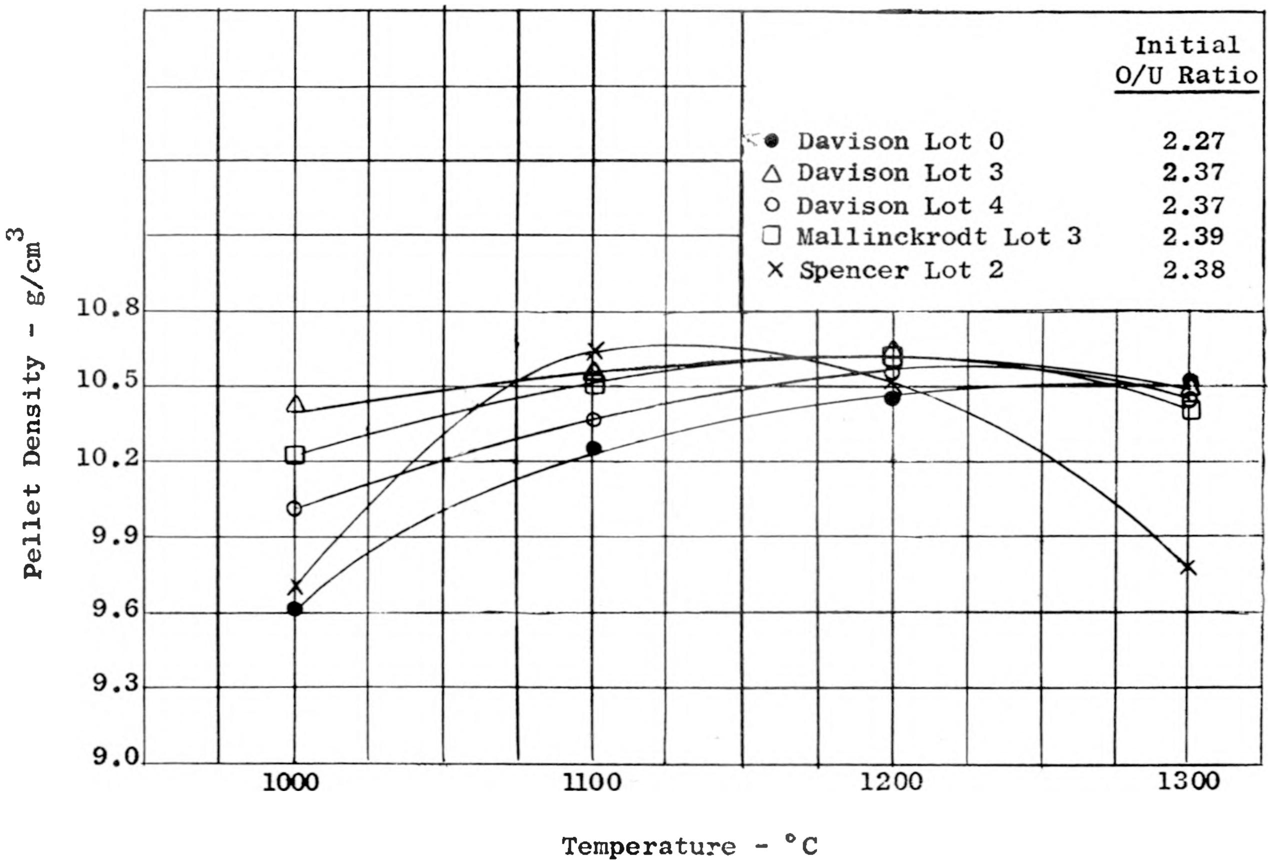

Fig. I-1 Pellet Density vs. Sintering Temperature
Active UO_2 Sintered for 1 Hour in N_2
Followed by 1 Hour in H_2

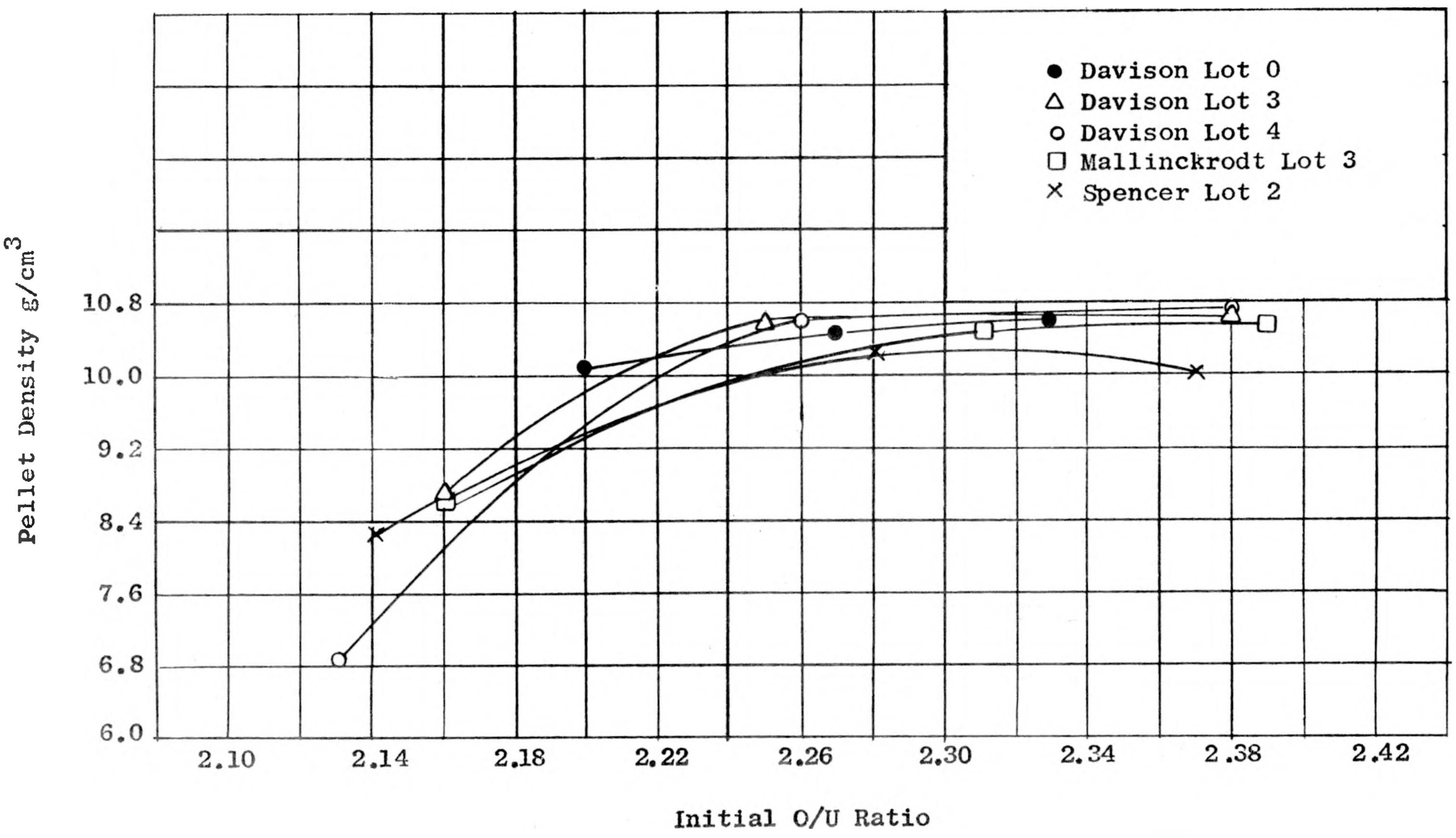

Fig. I-2 Pellet Density vs. Initial O/U Ratio
Active UO_2 Sintered at 1300°C for
2 Hours in N_2, 1 Hour in H_2

As expected, the pellet densities increase with increasing excess oxygen levels, the Spencer oxide again being the only exception. The fall-off in density shown in the low initial O/U ratio range is attributed to the heightened deleterious effect of the carbonaceous binder which removes oxygen leaving very little excess to enhance sinterability.

This binder inhibitor effect was clearly demonstrated when Spencer Lot 2, having an initial O/U ratio of 2.14, was inadvertently sintered without binder to produce a density of 10.3 g/cm^3. With 0.4% PVA binder present, on the other hand, the density attained was only 8.3 g/cm^3 as shown in Figure I-2. Further evidence corroborating this finding on the role of carbon was reported in the Quarterly Progress Report for July 1 to September 30, 1960 (NYO-2690), in which it was noted that carbon pickup during wet ball milling led to a deterioration of oxide sinterability.

3. Wet Ball Milling Experiments

Further work on wet ball milling was performed employing shorter grinding times (4 hours instead of 24 hours) and a reduction in grinding media to minimize the carbon pickup. Milled oxides were roasted to introduce excess oxygen, formed into green compacts by the standard procedure, and sintered at 1300°C. Although chemical analysis showed a significant decrease in carbon contamination (800 ppm instead of 3000 ppm), the resulting pellet densities were still inferior, ranging from 8.3 to 10.0 g/cm^3. Apparently the milder grinding conditions did not sufficiently activate the oxides.

4. Effect of Forming Pressure

The use of higher forming pressures was investigated as a means of improving pellet density without resorting to an activation treatment. Preliminary work had shown that compacts containing the standard binder addition (0.4% PVA) could not be formed at pressures above 20 tsi without the formation of laminar cracks; consequently, an arbitrary binder addition of 1.0% PVA was used in this study. As-received Davison Lot 3 was roasted to produce an initial O/U ratio of 2.35 and compacts were formed at several pressures. After a dewaxing step at 325°C for 3-1/2 hours in nitrogen, two compacts were removed for carbon analysis. The remainder were sintered at 1300°C for two hours in nitrogen followed by one hour in hydrogen. The experimental data are summarized as follows:

Binder Concentration, %	Forming Pressure, tsi	Geometric Sintered Density, g/cm^3
0.4	19	9.9
1.0*	19	9.8
1.0	30	10.3
1.0	40	10.1
1.0	50	10.2

*Carbon Content after Granulation - 4550 ppm
Carbon Content after Dewaxing at 325°C - 4100 ppm

All pellets exhibited the normal black luster and good dimensional integrity. The results suggest that by using an intermediate quantity of binder and high forming pressures, satisfactory densities may be attainable with unactivated Davison Lot 3 UO_2.

5. Optimization of Hydrogen Soaking Conditions

The use of comparatively mild sintering conditions with the activated oxides gives rise to the possibility of incomplete removal of residual excess oxygen in the second stage of the process. Until now the criterion for temperature selection was based on the minimum required to reach 95% of theoretical density after sintering for one hour in nitrogen. This temperature may not necessarily be optimum for complete excess oxygen removal. Several two-stage sintering experiments were conducted, therefore, with the objective of determining the role of time and temperature in the hydrogen soaking stage of the process.

To avoid any ambiguity, the study was restricted to a single well-behaved representative material, oxidized-reduced Davison Lot 3, and the use of one nitrogen sintering temperature, 1200°C. The procedure for the experiments involved the preparation of compacts in the usual manner from the oxide, previously roasted to produce an initial O/U ratio of 2.36. The compacts were sintered in nitrogen for one hour. After this stage, samples were taken for O/U ratio measurements and the remaining pellets were soaked for varying periods in hydrogen at 1000, 1100, 1200 and 1300°C. Final O/U ratios were determined on pellet cores after at least 40% had been removed by grinding. The final O/U ratios are plotted in Figure I-3 as a function of soaking time at each temperature. As shown in the plot, the O/U ratio of the pellets had been reduced from 2.36 to 2.20 in the nitrogen sintering step.

The pellet densities obtained in this study were 95% to 97% of theoretical. As the excess oxygen was removed from the pellets, the observed densities, calculated as per cent of theoretical using Gronvold's* data, were fairly constant indicating that no further densification was occurring in the hydrogen soaking step.

As seen in Figure I-3, the higher the soaking temperature, the shorter the time interval to effect complete removal of excess oxygen. It appears that at least a one-hour exposure is required for reversion to stoichiometry at 1200°C or below. In view of these results, it is possible that in the sintering of very active oxides, a higher temperature may be required for soaking in hydrogen than for the densification step in nitrogen.

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*Gronvold, F., "High Temperature X-ray Study of Uranium Oxides in the UO_2 - U_3O_8 Region", J. Inorganic and Nuclear Chemistry, 1, 357 (1955)

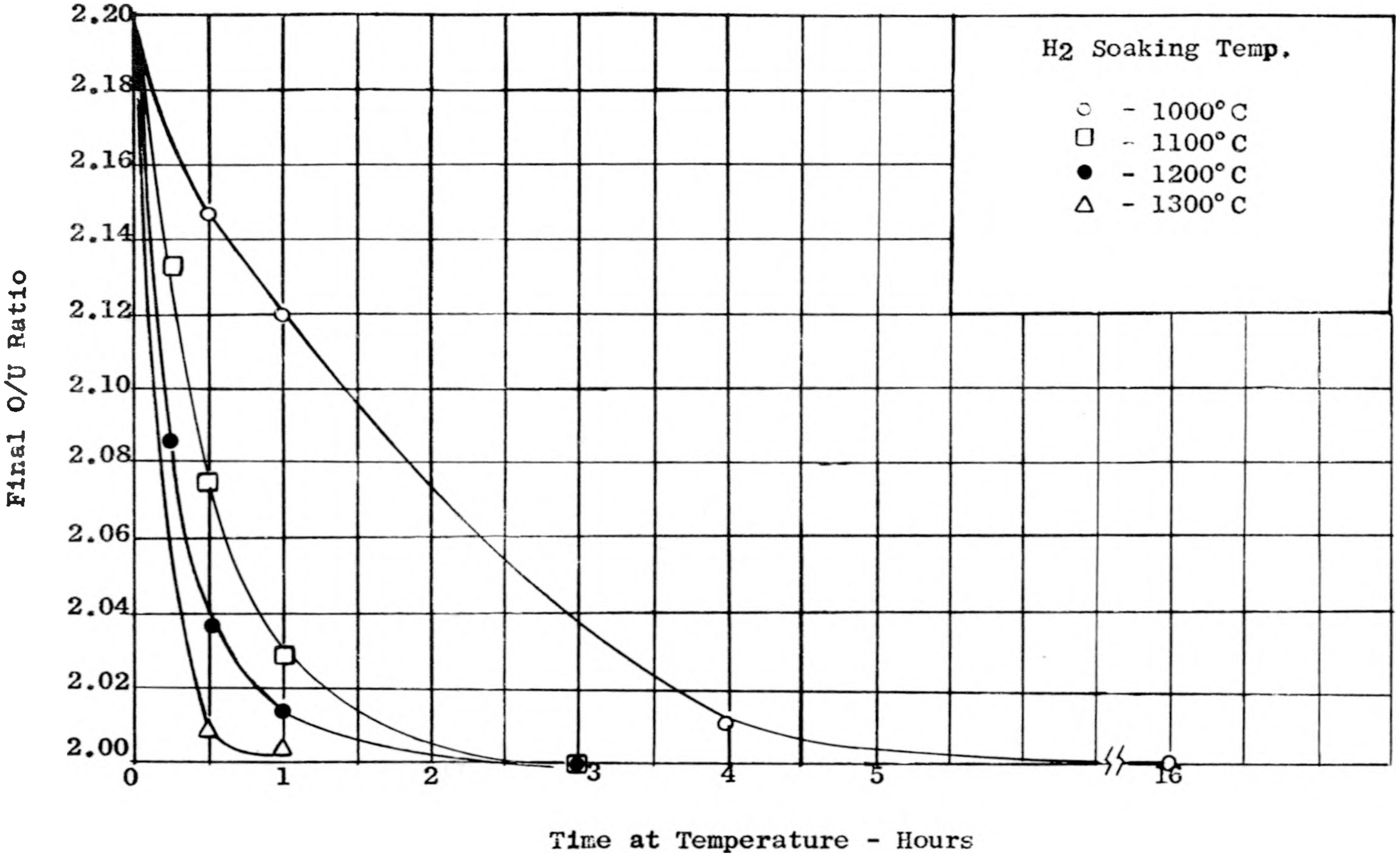

Fig. I-3 Final Pellet O/U Ratio vs. Hydrogen Soaking Time
Davison Lot 3 $UO_{2.36}$
First Sintered in N_2 for 1 Hour at 1200° C

It is worth noting that the determination of the final O/U ratio on the pellet core gives a somewhat higher value than would have been obtained on the entire pellet. This arises from the excess oxygen concentration gradient which exists in non-stoichiometric pellets as was demonstrated by separate analyses of the outer surface and the core of a pellet. The outer surface, constituting 65% of the pellet, had an O/U ratio of 2.098, whereas that of the core was 2.120. The difference is significantly larger than the normal experimental error of the determination.

6. Effect of Fluoride Impurity on UO_2 Sinterability

Toward the end of the reporting period, an investigation was initiated to determine the effect of fluoride impurity on the low temperature inert atmosphere sinterability of UO_2. This was prompted by the fact that, of the Davison oxides studied in the program to date, the most sinterable, Lot 0, has substantially less fluoride impurity than the others. In addition, the relative activity of the as-received oxides exhibits an inverse relationship with the fluorine content, as shown in the following table which compares the density attained with these materials in the two-stage sintering process with their fluorine levels:

Material	Maximum* Pellet Density, g/cm^3	Fluorine Content, ppm
Lot 0	10.7	190
Lot 3	10.1	400
Lot 4	9.9	850
Lot 5	9.5	2200

*With air-roasting as the only pretreatment

For this work, a 200-gram batch of Lot 0 was mixed with a dilute HF solution and dried at room temperature. The amount of HF used was calculated to raise the fluoride impurity level to a maximum of 3000 ppm. One-half of the resulting material was air-roasted at 140°C for six hours, granulated, pressed at 19 tsi and sintered at 1300°C for two hours in nitrogen followed by one hour in hydrogen. The remaining half was subjected to one oxidation-reduction cycle (1-1/2 hours in air at 500°C, followed by one hour in hydrogen at 525°C). This material was processed and sintered in the same manner as described for the first half of the batch. The following table compares the initial O/U ratios and pellet densities obtained with those of untreated Lot 0 processed under similar conditions:

Material	Initial O/U Ratio	Geometric Density, g/cm^3
Lot 0, as-received	2.27	10.5
Lot 0 +HF	2.20	8.1
Lot 0, as-received, oxidized-reduced	2.34	10.8
Lot 0 +HF, oxidized-reduced	2.28	10.7

It is clear that the fluoride introduction has inhibited the activity of the oxide as indicated by the lower O/U ratio resulting from the roasting step, as well as by the much poorer density obtained. On the other hand, oxidation-reduction cycling appears to have reactivated the oxide to the point where it compares favorably with oxidized-reduced unfluoridated Lot O.

To elucidate the mechanism of fluoride removal and oxide reactivation, samples of the as-received oxide and material resulting from each processing step have been submitted for fluorine analysis. In addition, a batch of fluoridated Lot O oxide will be heated to 500°C in a stream of pure nitrogen and processed into pellets. The results should aid in establishing the role of temperature and atmosphere in the activation of the fluoride contaminated oxide.

C. Corrosion Test of Sintered UO_2

A test to determine the stability in water of UO_2 pellets sintered by the two-stage process was conducted during the reporting period. The test was carried out over a two-month period in an autoclave containing degassed water at 680°F. Five nitrogen sintered pellets fabricated from different oxides, two of which were activated, and four high temperature hydrogen sintered pellets, also fabricated from different oxides, were tested. The latter were included for comparison purposes. The pellets had a diameter of approximately 0.4 inch and their weights ranged from 6.8 to 10.3 grams. Other pertinent experimental data are summarized in Table I-1.

No visible physical changes were observed after the exposure. The weight changes listed in Table I-1 are very low and, since no significant weight gains occurred, it is apparent that the high density UO_2 pellets are stable to oxidation in high temperature water regardless of the method of fabrication.

D. Irradiation Testing Program

On November 22, a conference was held with Westinghouse Testing Reactor personnel to review the irradiation capsule design. The experiments planned involve the irradiation of three uninstrumented capsules containing 1/4 inch diameter enriched UO_2 pellets. One capsule is to be irradiated to a fuel burnup of 10,000 megawatt days per ton of uranium and two capsules are to be irradiated to a burnup of 20,000 megawatt days per ton of uranium. The objective is to determine the dimensional stability and fission gas retentivity of UO_2 pellets fabricated by the low temperature nitrogen sintering process.

Hydraulic data based on coolant flow experiments with three dummy capsules having different outside diameters were obtained from the WTR to assist in finalizing the aspects of the capsule design related to heat transfer and test location in the reactor. A Hazards Evaluation Report incorporating this information is being prepared for submittal to the WTR Safeguards Committee as the first step in obtaining approval for the experiments from the reactor operator.

TABLE I-1

UO_2 PELLET CORROSION TEST DATA

Code	Oxide	Treatment	Sintering Temp. °C	Density g/cm^3	Weight Change %	Final O/U Ratio
Low Temperature Nitrogen Sintered Pellets						
19P75-1	Davison Lot O	Roasted	1250	10.6	0	-
19P89-1	Davison Lot 3	Roasted & Ball Milled	1250	10.4	+0.013	2.00
24P65-2	Davison Lot O	Roasted	1300	10.5	-0.011	-
27P14-5	Davison Lot 4	Oxidized-Reduced	1200	10.4	+0.002	-
26P81-5	Davison Lot 3	Oxidized-Reduced	1300	10.7	+0.002	2.00
High Temperature Hydrogen Sintered Pellets						
21P89-2	Davison Lot O	As Received	1650	10.6	-0.013	-
26P76-5	Davison Lot 3	Oxidized-Reduced	1650	10.7	-0.009	-
27P20-8	Davison Lot 4	Oxidized-Reduced	1500	10.4	0	-
-	Mallinckrodt	Sintered by MCW	-	10.7	-0.007	-

E. Conclusions

The relationships developed for UO_2 pellet density as a function of sintering temperature and initial O/U ratio indicate that (1) all active oxides studied can be sintered to at least 95% of theoretical density at 1200°C to 1300°C with a corresponding sintering time of only one hour in nitrogen, and (2) the minimum initial O/U ratio required to achieve such a density is 2.25. To assure complete removal of excess oxygen, a hydrogen soaking period of at least one hour is required in the 1200°C to 1300°C range.

The sinterability of active UO_2 deteriorates as a result of the addition of fluoride impurity. Oxidation-reduction cycling appears to reactivate such contaminated oxide.

The results of a two-month corrosion test demonstrate that UO_2 pellets fabricated by the low temperature nitrogen sintering process are stable to oxidation in 680°F water.

F. Work Plan for the Next Quarter

The study of the effect of fluoride impurity on UO_2 sinterability and the role of oxidation-reduction cycling in restoring activity will be completed.

The design of the UO_2 capsule experiments will be finalized and approval will be obtained from the AEC and the WTR for the irradiation. Suitably enriched ceramic grade oxide will be procured and fabricated into 1/4-inch diameter pellets. An attempt will be made to fabricate very high density pellets (greater than 98% of theoretical) as well as 95% T.D. pellets for the program, so that radiation behavior may eventually be correlated with a density variation in this range. It is planned to insert the capsules into the WTR at the end of the next reporting period.

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, M. L. Kohn

A. Introduction

The experimentation on the production of uranium monocarbide was continued in an attempt to relate the carbon content to the carburizing temperature using methane as the carburizing medium. In these tests, the carburizing temperature was varied, maintaining the heat-up rate, the gas flow and carburizing time constant. Additional work on gas carburization was performed using propane as the carburizing medium in a manner similar to the previous methane sequences. This program is designed to develop the procedures necessary for the production of uranium monocarbide low in nitrogen and oxygen. Methods are being developed to consolidate the fine, fluffy uranium monocarbide powder produced by reacting uranium hydride with propane.

Two processes utilizing uranium dioxide-graphite pellets as the starting material for skull melting and casting uranium monocarbide are being evaluated. In the first process, the uranium dioxide-graphite charge material is blended, compacted and then reacted to uranium monocarbide in a vacuum sintering furnace. These reacted pellets are then used as the feed material for arc melting and casting. In the second process, the pellets are not reacted to uranium monocarbide, instead, they are charged directly to the skull furnace. The reaction of the uranium dioxide and graphite to uranium monocarbide occurs in the skull furnace and is followed immediately by the melting and pouring of the material into the mold. After establishing parameters for both methods, two series of five castings to be made by each method were started. The examination of castings from the first series is described. The second series of five castings is currently in progress. A comparison of the two methods based on these two series will be made at the conclusion of the second series.

B. Uranium Monocarbide by Gas Carburizing Methods

Experimental work on the gas carburization of uranium hydride was performed using both methane and propane as the carburizing media. The procedures employed were detailed in the Quarterly Reports, NYO-2689 and NYO-2690, July 27, 1960 and November 11, 1960, respectively. Changes in the experimental conditions are described in the following sections.

1. Methane Reaction

A sequence of tests were performed using the 4 to 1 ratio of methane to hydrogen carburizing mixture in which the carburizing temperatures were reduced from 750°C to 650°C in 25°C steps. In all cases, the heat-up to carburizing temperature was controlled to produce similar time-temperature relationships. The methane flow was held constant in all tests at 0.7 liters/min., and the hydrogen at 0.2 liters/min. The charge was approximately 600 grams of extruded uranium rod, and the hydriding was performed at 250°C under a positive hydrogen pressure until the reaction was completed.

The chemical analyses of the carburized material made in these experiments are reported in Table II-1. The conditions for Test No. J-27 were similar to those of Test No. J-26, except that the reaction vessel was cooled and the carburizing gas replaced with argon as soon as the carburizing temperature was reached. In the case of Tests No. J-21 to J-26, inclusive, the chemical analyses showed the variation in carbon concentration obtained by changing the carburizing temperature. Comparing the carbon contents of Test No. J-27 with those of Tests No. J-21 to J-26, inclusive, it became apparent that the most efficient use of the carburizing medium occurs during the heat-up period. In this test, 88 per cent of the total carbon content (as compared with the data of Test No. J-26) was produced during heating of the hydride from 250°C to 650°C.

In all tests except for Test No. J-27, the nitrogen content was relatively high, ranging from 0.24 to 0.40 w/o. In Test No. J-27, performed without holding at carburizing temperature for two hours, the nitrogen content was 66 per cent of the next lowest reported nitrogen value. The lower nitrogen concentration in Test No. J-27 was explained on the basis of the decreased exposure time of this material to the methane in the carburizing gas.

In these runs as in previous ones with methane, there was no occurrence of a free-carbon deposit on the walls of the reaction vessel from a pyrolytic decomposition of the carburizing gas as reported below for propane. The total nitrogen concentration noted for this material comes from the uranium carbide powder, and is not partitioned primarily to the free-carbon deposition as in the case of propane-produced uranium monocarbide.

2. Propane Reaction

The use of propane as a carburizing medium is attractive because of the high concentration of carbon per mole of gas, the lower residual nitrogen concentration, and the lower unit cost of the gas. The carburizing equipment was altered to employ the use of propane as a carburizing medium. Hydrogen was not mixed with the propane, as it was in the case of the methane, because of the lower residual oxygen content of the propane. The nitrogen and oxygen concentrations were determined by mass spectrometry to be 0.032 and 0.073 w/o, respectively.

In exploratory tests using propane it was found that propane is adsorbed on the activated alumina desiccant of commercial gas dryers. The carbide made in these initial tests had high total-carbon and free-carbon concentrations. Furthermore, they exhibited a high degree of agglomeration. After altering the gas system as previously described, the product was a very fine, fluffy powder.

In subsequent experimental work, a series of runs were made using two liters/min. propane flow through the retort, and a one-hour carburizing period at decreasing carburizing temperatures. The carburizing temperature was decreased from 550°C to 450°C. The

TABLE II-1

EFFECT OF CARBURIZING TEMPERATURE ON THE CARBON CONTENT OF METHANE-PRODUCED URANIUM MONOCARBIDE

Test No.	Carburizing Temperature	Chemical Composition, w/o Total Carbon	 Nitrogen
J-21	750	4.8	ND
J-23A	725	4.5	0.40
J-24	700	4.6	0.30
J-25	675	4.4	0.24
J-26	650	4.4	0.36
J-27	650	3.9	0.15

ND - Not Determined
Reaction time was two hours at temperature except for Test No. J-27 which was not held at temperature.

carburizing was carried out on derby uranium rather than extruded rod as was used for the methane sequence.

Chemical analyses for the first three of an extensive series of tests under controlled conditions, to obtain the optimum carbon content, are shown in Table II-2. Initially, it was observed after completion of the run that there was a significant deposit of carbon on the wall. In order to avoid mixing the wall deposit with the carbide on the tiered trays, the carbide was carefully removed from the center of the retort and the wall deposit removed, subsequently. Analyses of the three runs showed, conclusively, that the wall deposit contained a high percentage of carbon. Furthermore, the carbon analyzed as wall deposit material was all free carbon. It was also shown that the high nitrogen content is associated with the wall deposit. Having done this, the uranium carbide, as demonstrated by the three runs, can be obtained which is very low in nitrogen and free carbon, using the temperatures and times shown. In fact, as shown in Table II-2 by decreasing the temperature to 450°C the wall deposit was virtually eliminated, but the carbon content of the carburized powder was only 3.1 w/o. Further experimental work is in process to develop a method for obtaining the desired carbon content without the excess of free carbon deposit in the propane-reacted powder. Two methods are being investigated, the first is to use a long-time, low-temperature carburization cycle, and the second is to find a material which will inhibit the decomposition of the propane so that it can decompose only to react with the uranium hydride already in the vessel.

C. Consolidation of Uranium Carbide Powder

The very fine, fluffy uranium carbide powder produced by the propane reaction requires the development of proper compacting techniques. In initiating this work, uranium carbide containing 3.9 to 4.3 w/o carbon was used for the preparation of bar-shaped compacts. The compacting was performed at pressures of 25 to 50 tsi; varying amounts of cetyl alcohol, up to three w/o, were used as a lubricant and/or binder for the material.

It was found that satisfactory compacts were produced using three w/o cetyl alcohol. At 35 and 50 tsi compacting pressure, the green densities were 8.32 and 8.70 g/cm^3, respectively. At lower concentrations of cetyl alcohol, all the compacts fractured in the die except for that one produced at 35 tsi from powders containing two w/o cetyl alcohol. This specimen had a green density of 8.30 g/cm^3. An attempt was made to compact uranium monocarbide using a die-wall lubricant without the use of cetyl alcohol which proved unsuccessful. Additional tests are in process in which camphor is being used as the lubricant binder. The initial tests will be performed using three and two w/o camphor additions.

D. Arc Melting and Casting Uranium Carbide

In experimental work reported in Quarterly Report, NYO-2690, it was shown that the reduction of uranium dioxide by carbon could be carried out in an arc furnace. Since then experiments were carried out to scale up and

TABLE II-2

EFFECT OF TEMPERATURE ON THE CARBON CONTENT OF PROPANE-PRODUCED URANIUM CARBIDE, CARBURIZED FOR ONE HOUR

		Chemical Composition, w/o				
		Uranium Monocarbide Product			Wall Deposit	
Test No.	Carburizing Temperature °C	Total Carbon	Free Carbon	Nitrogen	Carbon	Nitrogen
5K-P550-1	550	4.3	Trace	<0.01	21.1	0.13
5K-P500-1	500	3.5	Trace	ND(a)	10.5	ND
5K-P450-1	450	3.1	Trace	ND	(b)	(b)

(a) ND - Not Determined

(b) No wall deposit present

transpose the preliminary work to a skull melting operation. The charges consisted of either uranium dioxide-graphite pellets (unreacted pellets) or of uranium carbide pellets prepared by reacting uranium dioxide-graphite pellets at 1700°C for two hours in vacuum (reacted pellets).

The preparation of the pellets was the same for both charges and consisted of the following steps: (a) Weighing uranium dioxide and graphite powders in the proportion to yield stoichiometric uranium carbide based on the reaction: $UO_2 + 3C \rightarrow UC + 2CO$. (b) Blending the powders in a rotary mill. The current practice is to blend for two hours in inclined containers providing lateral motion. (c) Compacting at 35 tsi pressure. The pellets weigh from five to seven grams each and are approximately 1/2 inch diameter by 1/2 inch long.

Each charge of pellets was made from one or an integral number of mixes to insure that the composition was that required for stoichiometric uranium monocarbide despite minor variations in chemical composition from pellet to pellet. The pellets were melted in a uranium carbide skull weighing from five to six kilograms.

After establishing the necessary parameters from a number of trial melts, a program was initiated to prepare five castings from each of the two types of charge material using identical conditions for each series. The purpose of this work was to provide an indication of compositional control and yield of uranium carbide and the cycle of operations required for the two methods.

1. Reacted Uranium Dioxide-Graphite Charges

Initial experiments indicated that carbothermic reduction of uranium dioxide was essentially complete at temperatures above 1500°C after two hours in vacuum. Charges reacted at 1700°C for two hours in a vacuum induction furnace were then loaded in the skull furnace. A typical lot of uranium dioxide-graphite pellets of 1000 grams yielded about 850 grams of carbide pellets which was the limit for batch loading of the present skull. To minimize oxidation of the charge, the reacted pellets were removed from the induction furnace under argon in a closed graphite container, and immediately charged into the skull furnace under argon.

The yield of uranium carbide in cast form from reacted uranium dioxide-graphite charges is shown in Table II-3. The data from Table II-3 indicate that the production of uranium carbide according to the equation $UO_2 + 3C \rightarrow 2CO + UC$ has gone to completion. The small differences between the theoretically computed yields and the actual yield is associated with losses due to handling of the pellets when charging the sintering furnace and possible volatilization. The data of Specimens No. 10D-1SM16 and 11D-1SM17 show a casting weight greater than the charge weight. This gain from charge to casting results in a corresponding weight loss of the skull; a portion of the skull becomes molten during every melt. Aside from losses, a decrease in weight from charge to casting, signifies a corresponding increase in the weight of the skull. Losses tabulated in the last column of Table II-3 were

TABLE II-3

YIELD OF URANIUM CARBIDE - REACTED CHARGE

Specimen No.	Charge Weight, gms.	Theoretical UC in charge (1), gms.	Weight After Reacting, gms.	Yield, (2) per cent	Casting Weight(3) gms.	Gross Wt. Before Melting (4), gms.	Gross Wt. After Melting, (5) gms.	Loss During Casting, gms.
10D-1SM11	980.3	800.9	793.0	99.0	556.9	--	--	--
10D-1SM16	987.2	806.5	803.0	99.6	906.0	6281	6222	59
11D-1SM17	941.0	768.8	762.0	99.1	920.0	5960	5952	8
11D-2SM1	979.5	800.3	795.0	99.3	643.0	6518	6485	33
11D-2SM3	979.0	799.8	796.0	99.5	647.5	6628	6577	51

(1) Calculation of the quantity of uranium monocarbide which should result from charges assuming all reactants are fully reacted and no losses occur.

(2) Based upon theoretical uranium monocarbide in charge.

(3) Total weight of casting, including sprue.

(4) Skull weight before melting plus weight of pellets.

(5) Skull weight after melting plus weight of casting.

determined by the difference between the total material before melting (skull plus pellets) and after casting (skull plus casting). These losses represent material which is, in the main, recoverable, but not immediately returnable to the process as charge material. For example, most spatter which occurs during melting can be reclaimed from the spatter shields and adjacent furnace walls but not in a usable form; whereas, most splash during pouring is simply charged back into the skull prior to loading for the next melt. The fine spatter, therefore, is shown as a recoverable, but non-remeltable loss in the last column of Table II-3. The maximum loss of this type in the five melts was seven per cent. It may be feasible to significantly reduce this in future work. The remeltable splash which occurs during pouring is included as part of the final skull weight.

The melt cycle was established at five minutes, after preliminary runs showed a longer time was unnecessary. The atmosphere consisted of a 2:1 helium - argon mixture at ten-inch Hg absolute pressure. Molds were outgassed prior to casting but were not heated at the time of the pour. The system was evacuated at the conclusion of the casting cycle to aid in slow cooling of the castings.

Melting of these charges was accomplished without arc instability and without excessive spatter. The reacted pellet charges have good electrical conductivity. The pellet charges, from initial compacting to loading in the skull furnace, were handled without significant breakage and no fines were found to develop to cause difficulty during melting. The analyses of the five castings prepared from reacted charges are recorded in Table II-4.

These data indicate a high degree of uniformity of the carbon content of the casting. The greatest difference in carbon content between the top and the bottom of the castings was 0.3 w/o (11D-2SM3), and the maximum difference between the average carbon content for a charge and its corresponding casting was 0.3 w/o (11D-2SM1). Since these were the first two castings prepared from a new skull there is some suggestion that the above variations were influenced by heterogeneity of the skull. The homogeneity of the charge as evidenced by the carbon analyses reported shows that the blending operation produces pellets with a high degree of uniformity of carbon content.

2. Unreacted Uranium Dioxide-Graphite Charges

Previously reported work on the carbothermic reduction of uranium dioxide in the button furnace indicated that the use of a dynamic helium atmosphere accelerated reduction and melting of the charge while maintaining reasonable arc stability. Hence, a dynamic helium atmosphere was used in the skull furnace during the reduction phase. Further, it was previously demonstrated that if the arc was provided a ground path adjacent to rather than through the charge, reaction of the charge proceeded from radiation heating rapidly enough so that in a short time some of the pellets would conduct. Therefore, a uranium carbide slug was loaded as a striker in the center of the pellet charge to allow the current to flow from the electrode through

TABLE II-4

ANALYSES OF CAST URANIUM CARBIDE FROM REACTED URANIUM DIOXIDE-GRAPHITE CHARGES

	Chemical Composition, w/o (1)								
	Reacted Charge (2)					Casting			
	Total Carbon		Nitrogen		Skull, prior to Melt	Total Carbon		Nitrogen	
Specimen No.	Top	Bottom	Top	Bottom	Total Carbon	Top	Bottom	Top	Bottom
10D-1SM11	-	-	<.01	<.01	4.7	4.6	4.6	<.01	<.01
10D-1SM16	4.8	4.8	<.01	<.01	4.6	4.8	4.8	<.01	<.01
11D-1SM17	4.7	4.7	<.01	<.01	4.8	4.9	4.7	<.01	<.01
11D-2SM1	4.8	5.0	<.01	<.01	5.0	4.5	4.6	<.01	<.01
11D-2SM3	4.4	4.3	<.01	<.01	4.4	4.3	4.6	<.01	<.01

(1) All results are averages of duplicate samples.

(2) Samples for analyses of the charge were obtained by taking one pellet at the top of the crucible and one at the bottom of the crucible.

TABLE II-5

ANALYSES OF CAST URANIUM CARBIDE FROM UNREACTED URANIUM DIOXIDE-GRAPHITE CHARGES

	Chemical Composition, w/o				
	Skull prior to Melt	Casting			
		Total Carbon		Nitrogen	
Specimen No.	Total Carbon	Top	Bottom	Top	Bottom
10D-11-B-1SM4	4.6	4.7	4.7	<.01	<.01
10D-12-1SM10	4.5	4.7	4.6	<.01	<.01
*11D-21-2SM6	4.6	4.6	4.6	<.01	<.01

* First casting of the current series of five being made under identical conditions

the striker to the skull. Once the carbide striker becomes molten, reaction of the pellets occurs and the reacting pellets join the molten pool and completely react. The reaction can be quite violent and, as had been anticipated from the previous work done on the button furnace, spatter was much greater than that experienced with other charge materials. To minimize spatter during reaction, the amperage is reduced and voltage maintained as high as is consistent with continuous reaction and arc stability.

The optimum charge to the skull furnace for preparing a 600 to 700 gram casting was 600 to 700 grams of pellets and about 250 grams of cast uranium carbide striker. With the batch-type loading, a melting time of 18 minutes was required for each charge; during the first 13 minutes a dynamic helium atmosphere and amperages of 500 to 1500 were used, the final five minutes of melting time represented the standard casting cycle, which is performed in a static atmosphere of helium and argon. Having established the necessary parameters, a series of five castings are being prepared under identical conditions in order to provide data on the compositional control and yield for this process. Analytical data for the first casting of this series of five castings as well as for two castings made when the parameters for this method were being established are shown in Table II-5.

Castings 1SM4 and 1SM10 were prepared using different charge size and melting time: the former was made from a charge almost twice that from which the latter was prepared. The smaller charge was found to provide smoother continuous operation in the present skull; however, only about five minutes more melting time was required for 1SM4. Casting 1SM10 was prepared under conditions almost the same as those which are being used for the series now in progress.

The data in Table II-5 show that the maximum variation of carbon content between the bottom and top of each of the three castings was 0.1 w/o. There have not been sufficient data to date to clearly show the yield for this process, but the indication at present is that losses are much higher for this process than those shown in Table II-3 for the other method (reacted pellet).

3. Metallographic Examination

Cross-sections were taken from each casting at both top and bottom and were examined metallographically over a range of magnifications up to 2000X. Uniform structure throughout each sample and general agreement with chemical analyses were observed.

Typical structures are shown in Figures II-1 and II-2. Figure II-1 shows the etched microstructure of a casting made from unreacted charge material at 200 magnification. Figure II-2 shows the microstructure of the same material at 1500 magnification. These structures are typical uranium monocarbide containing uncombined uranium. No significant difference was discernible between

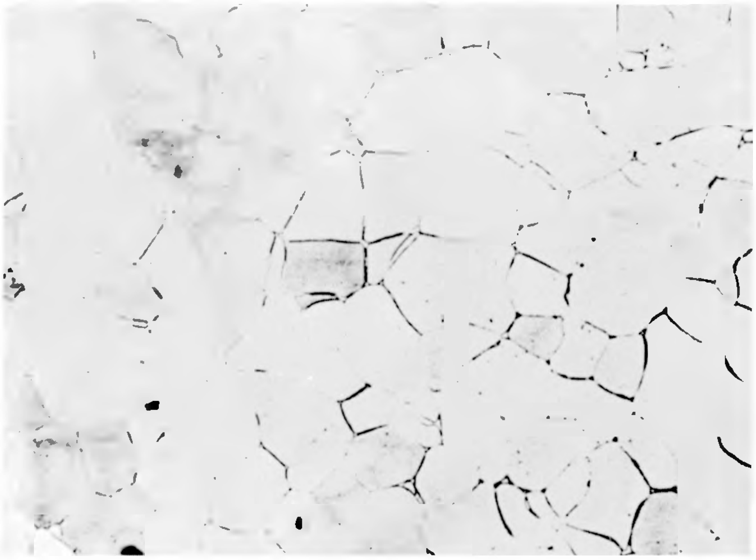

Fig. II-1 Typical microstructure of cast hypostoichiometric uranium carbide (4.7 w/o C) prepared from uranium dioxide-graphite (unreacted) charge material.

Etchant: Equal parts of Nitric Acid, Acetic Acid, and Water X200

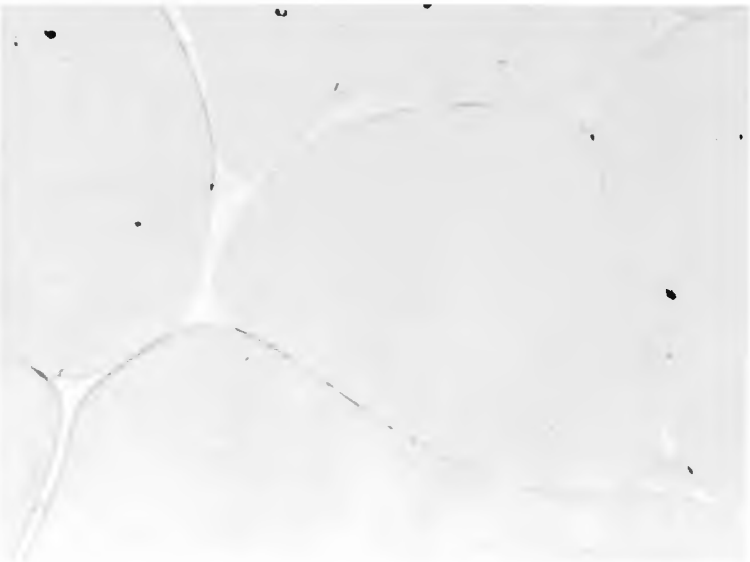

Fig. II-2 Detail of microstructure of material shown in Fig. II-1. Note free uranium at the grain boundaries.

Etchant: Equal parts of Nitric Acid, Acetic Acid, and Water X1500 castings made from either of the two types of charge material. These microstructures are further proof that the uranium dioxide-graphite reaction is complete by arc melting and that there is no uranium dioxide or free carbon present.