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FUEL CYCLE DEVELOPMENT PROGRAM

QUARTERLY PROGRESS REPORT

APRIL 1 TO JUNE 30, 1961

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Nuclear Fuel Research Laboratory
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CONTENTS

SUMMARY

This report presents the progress made by United Nuclear Corporation, Fuels Division (formerly Olin Mathieson Chemical Corporation, Nuclear Fuels Operation) under Contract No. AT(30-1)-2374 during the period April 1 to June 30, 1961.

Under Task I, work on the fabrication and encapsulation of the 4.95% enriched UO_2 pellet specimens for irradiation testing was completed. Five groups of pellets prepared by low temperature nitrogen sintering and one group prepared by high temperature hydrogen sintering were sealed in three irradiation capsules which were transferred to the Westinghouse Testing Reactor for irradiation commencing on June 1. The specimens are to be tested to burnups as high as 20,000 MWD/T to determine their radiation behavior as a function of sintering temperature (1000°C to 1300°C), pellet density (95% T.D. to 98% T.D.), and initial grain size (5 μ to 10 μ).

Pre-irradiation examination, consisting of O/U ratio determination and micrographic investigation, was performed on representative enriched pellets to assure that reversion to stoichiometric composition had occurred and to characterize the microstructure of the sintered oxide.

Several depleted oxide pellets produced from a particular raw material were also micrographically examined to determine the effect of processing variables on grain size. The sintering temperature appears to be the most influential factor governing the magnitude of this property. Pellets sintered at 1650°C and 1500°C in hydrogen exhibited average grain sizes of 37 μ and 18 μ, respectively, whereas a pellet sintered at 1300°C in nitrogen had a grain size of 12 μ.

Further investigation of the role of oxidation-reduction cycling in removing fluoride impurity from UO_2 indicates that the presence of moisture in the furnace atmosphere is the major factor responsible for fluoride removal.

Under Task II, the reproducibility of the carbon content in uranium monocarbide made by the propane reaction was determined. In a series of twelve carburizing runs in which time and temperature were held constant but the heating rate varied, the carbon content ranged from 4.0 w/o to 4.9 w/o. The average carbon content was 4.6 w/o in this series. Better carbon control was obtained by duplicating the thermal cycle. In a series of six carburizing runs in which the carburizing cycle was duplicated, the carbon content was reproduced to within plus or minus 0.1 w/o; the carbon content varied from 4.6 w/o to 4.8 w/o.

Additions of either cetyl alcohol or camphor had no effect on the sintered density of uranium carbide. On sintering rectangular bars of 4.0 w/o and 4.4 w/o carbon uranium carbide for three hours at 1800°C, cored structures were obtained due to uranium volatilization. Porosity was observed in the microstructure of uranium carbide containing more than 4.3 w/o carbon. The structure of sintered material containing less than 4.3 w/o carbon was dense and free from porosity.

At 1200°C, a 4.4 w/o carbon material was sintered to 13.2 g/cm^3 density (95% theoretical). Uranium segregation occurred in compacts processed with lower carbon content. A much higher sintering temperature was required for sintering 4.7 w/o carbon uranium carbide. A 4.7 w/o carbon carbide sintered to 12.3 g/cm^3 density (90.5% theoretical) at 1800°C in three hours. This density was not increased by sintering either at higher observed temperature or for longer periods of time.

The variables in the consolidation of uranium carbide by skull melting were investigated. In a series of fifteen 7/16-in. diameter x 6-in. long castings, mold pre-heat did not appear to improve the surface characteristics of the casting; reaction with the mold occurred at temperatures above 700°C. Flow-lines in the surface cleaned up when the casting was ground to remove about 0.060 in. from the diameter.

The preparation of 7/16-in. and 3/4-in. diameter castings indicated the desirability of maintaining charge and skull weight constant to obtain compositional control. A three-mold cluster was fabricated and several three-rod castings poured. The cluster mold will be used for the preparation of irradiation test specimens and maintaining the weight of pour at approximately one kilogram.

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

In the previous quarter, simple modifications of the oxidation-reduction activation technique, such as multiple cycling, permitted the attainment of depleted oxide pellet densities of 98% of theoretical. It was found also that the sinterability of the enriched oxide procured for the irradiation testing program was similarly enhanced by such a treatment. The testing objectives were, therefore, broadened to include a study of the effects on radiation behavior of variations in pellet density (95% T.D. to 98% T.D.) and sintering temperature (1000°C to 1300°C).

The major effort during this reporting period was devoted to completion of the encapsulation phase of the irradiation testing program. This work included (1) the preparation of enriched oxide pellets having suitable properties, (2) the fabrication and assembly of the irradiation capsules, and (3) pre-irradiation examination and testing of enriched pellet specimens. In addition, pellets from a representative depleted oxide lot were subjected to systematic micrographic examination with the objective of characterizing grain growth behavior as a function of sintering conditions and subsequent annealing.

B. Irradiation Testing Program

1. Preparation of Enriched Oxide Pellets

The fabrication of 4.95% enriched UO_2 pellets for irradiation testing was completed early in the quarter. In reviewing and summarizing the experimental data developed in this phase of the program, it should be noted first that approximately 1,500 grams of a representative Mallinckrodt ceramic grade enriched oxide lot (MCW designation - Lot J36GZ, total weight - 400 pounds) were processed into nine separate batches activated by oxidation-reduction cycling. The activation treatment employed and the pertinent properties of each batch are presented in Table I-1.

The results of preliminary sintering experiments with Batches No. 1 and 2, described in the Quarterly Progress Report for January 1 to March 31, 1961 (NYO-2692), had shown that the sinterability enhancement imparted by the activation treatment would permit (1) the use of a sintering temperature as low as 1000°C and (2) the attainment of 98% T.D. Similar scoping tests were conducted with Batches No. 3 and 4 to find the exact sintering conditions for fabricating pellets with desired pellet properties, such as density and diameter, at several sintering temperatures.

Pellets tentatively selected for the irradiation were produced from Batches No. 5, 6, 8 and 9. The properties of these pellets and the sintering conditions used in their fabrication are summarized in Table I-2. Sufficient pellets were provided to fill ten specimen tubes, of which six were encapsulated for the

TABLE I-1. DATA ON MCW ENRICHED (4.95%) OXIDE BATCHES ACTIVATED FOR PELLET FABRICATION

Oxide Batch No.	Oxide Wt.	Oxidation-Reduction Activation Conditions			Bulk Density After Activation	O/U Ratio After Roasting 16 Hours in Air at 160°C
		Time, Hours		No. of Cycles		
		In Air at 500°C	In H_2 at 530°C		g/cm^3	
1	102.0	1.5	1	1	2.210	2.387
2	105.0	16.0	1	1	2.156	2.389
3	103.9	1.5	1	1	2.188	2.394
4	101.8	1.5	1	3	1.405	2.396
5*	216.1	1.5	1	1	2.190	2.379
6*	211.1	1.5	1	1	2.036	2.382
7	208.5	16.0	1	1	2.093	2.381
8*	200.4	1.5	1	3	1.337	2.377
9*	210.5	1.5	1	3	1.425	2.384

* Source of pellets selected for irradiation test.

TABLE I-2. PROPERTIES OF GROUPS OF PELLETS FABRICATED FROM MCW ENRICHED (4.95%) OXIDE AND TENTATIVELY SELECTED FOR IRRADIATION TESTING

Sinter Code No.	Oxide Batch No.	Final O/U Ratio	Average Density		Sintering Conditions			Total Length of Group in.	Average Pellet Dia. in.	Specimen Tube No.
			Geometric g/cm^3	T.D. %	Temp. °C	Hours N_2	Hours H_2			
38P91	6	2.003	10.43	95.1	1300	1	1	1.376	0.253	1*
			10.44	95.2	1300	1	1	1.416	0.253	2*
38P96	6	1.993	10.45	95.3	1300	1	1	1.613	0.253	9
			10.45	95.3	1300	1	1	1.626	0.253	10
39P05	8	2.001	10.75	98.1	1200	1	1	1.384	0.249	7*
			10.73	97.9	1200	1	1	1.374	0.249	8*
39P09	9	1.996	10.67	97.3	1000	1	3	1.469	0.251	5
			10.66	97.3	1000	1	3	1.454	0.251	6*
40P02	5	2.003	10.55	96.3	1550	0	4	1.613	0.251	3*
40P04	9	2.009	10.74	97.9	1550	0	4	1.383	0.248	4

* Specimen tubes ultimately selected for encapsulation and testing.

irradiation test. In the preparation of the specimens, ten additional pellets were produced in each sintering run for pre-irradiation micrographic examination and O/U ratio determination.

The 95% T.D. pellets shown under Sinter Codes No. 38P91 and 38P96 of Table I-2 were prepared in accordance with the fabrication procedure developed the previous quarter with enriched oxide subjected to one standard oxidation-reduction cycle. This involved compacting with a relatively low forming pressure of 15 tsi.

In an attempt to produce pellets of very high density, two variations of the procedure were tested. The first, with Oxide Batch No. 7, involved a very long oxidation-reduction cycle (sixteen hours of oxidation) and resulted in pellets averaging 96.9% T.D. The second involved the use of three standard oxidation-reduction cycles, rather than one, and produced pellets averaging 98.0% T.D., as shown in Table I-2 under Sinter Code No. 39P05.

The initial sintering experiment with this triple-cycled material produced pellets having a small circumferential fissure near the base. To eliminate this defect, a slugging technique was used consisting of (1) pressing a green compact at 5 tsi, (2) breaking up the compact, and (3) repressing at 20 to 30 tsi. This procedure was employed with only limited success in the sintering run to prepare 98% T.D. pellets for the irradiation test in that only seven defect-free pellets resulted. Microscopic examination of each of the thirteen remaining pellets revealed the presence of a small fissure. The defect was believed to be insignificant and three from this group were selected for irradiation testing.

The surprisingly high average pellet density of 97.3% T.D. obtained with a sintering temperature of only 1000°C (see Sinter Code 39P09) also resulted from the use of oxide activated by three standard oxidation-reduction cycles (Oxide Batch No. 9). The slugging technique with a final forming pressure of 35 tsi was employed and defect-free pellets were produced.

Two hydrogen sintering runs were conducted to produce pellets from oxide batches subjected to one standard oxidation-reduction cycle and three standard oxidation-reduction cycles, respectively (Table I-2, Codes No. 40P02 and 40P04). The hydrogen sintered pellets are to serve as experimental controls in the irradiation program. It is noteworthy that none of the pellets from the latter oxide batch exhibited the crack observed after low temperature nitrogen sintering to the same density. The absence of this defect is attributed to the use of a dewaxing step at 1000°C before sintering in hydrogen at 1550°C.

2. Fabrication of Irradiation Capsules

The enriched pellet test specimens, two of which are shown in Fig. I-1, were sealed in three capsule assemblies, constructed of Type 304 stainless steel and fabricated in accordance with the design illustrated in the previous quarterly report, NYO-2692. Briefly, a capsule assembly consists of an outer capsule within which is an inner capsule containing two stacked specimen tubes.

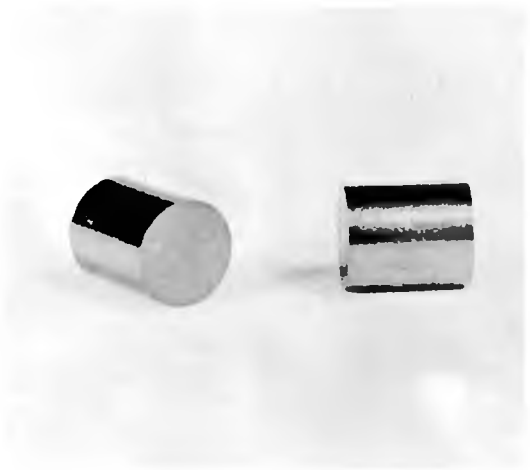


Fig. I-1. Enriched UO_2 Pellets (~2X)

Fig. I-2. Typical Specimen Tube End Closure (~2X)

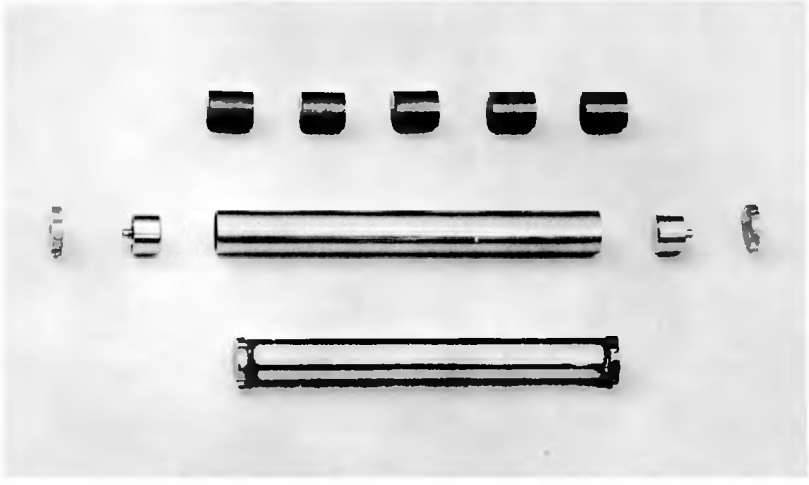


Fig. I-3. UO_2 Pellets, Specimen Tube Components Including End Plugs and Spacers

The outer capsule length and diameter are 5.5 inches and 0.525 inch, respectively. Each specimen tube, containing five oxide pellets, is approximately 2 inches long and has a wall thickness of 0.010 inch. The annular space between the specimen tube and inner capsule is filled with NaK.

Because of the use of unusually thin-walled tubing, difficulties were encountered in the initial attempts to effect the end closure of the specimen tubes in the inert atmosphere arc welding chamber. After several experiments were performed to investigate the welding parameters, conditions were found under which a sound end plug weld could be obtained in at least a 90% helium atmosphere. A photograph of such an end closure is presented in Fig. I-2.

The ten groups of enriched pellets tentatively set aside for irradiation testing (see Table I-2) were then sealed in their respective tubes. The components involved in this step are illustrated in Fig. I-3. The spacer discs shown were not attached, however, until after the end plug welds had been tested for defects.

All tubes were found to be free of leaks detectable by a gross leak checking technique and by mass spectrograph helium leak detection.

The ten specimen tubes were also subjected to radiographic examination to assure the soundness of the welds. A preliminary exposure revealed the presence of a large inclusion, probably tungsten, in one of the welds, which was cause for rejection. The oxide pellets were recovered from the rejected tube and resealed.

After several trials to establish the proper final conditions for radiographing the weld areas, the ten specimen tubes were exposed to 110 kv X-radiation for two minutes at a target to film distance of 36 inches. These conditions were sufficiently sensitive to show a 0.005-inch penetrameter hole as a reference in the developed film. All resulting radiographs were inspected and no defects could be found in weld areas.

At this point in the program, the six pellet groups to be further encapsulated for the actual irradiation were selected. The corresponding specimen tubes, the assigned irradiation capsule for each, and pertinent data on the pellets are listed in Table I-3.

Flux monitors, in the form of 1/2-inch loops of 0.030-inch diameter aluminum wire containing 0.15% cobalt, were inserted in the wells of the end plugs of the six specimen tubes. The spacers which were then tack-welded to the end plugs served to hold these dosimeters in place.

The specimen tubes, each with a 1-1/2-inch long aluminum-cobalt wire alongside, were then placed in the inner capsules which had been filled previously with NaK (22% Na). The excess NaK was decanted and the inner capsules were welded shut. All of this work was conducted in the helium atmosphere of the welding chamber.

TABLE I-3. DATA ON IRRADIATION CAPSULES

Capsule No.	Planned Burnup MWD/T	Estimated WTR Cycles	Specimen Tube No.	Geometric Pellet Density g/cm^3	Geometric Pellet Density T.D.%	Initial Diametral Clearance in.	Sintering Temp. °C
1	10,000	5	1	10.43	95.1	0.002	1300
			7	10.75	98.1	0.006	1200
2	20,000	11	2	10.44	95.3	0.002	1300
			3	10.55	96.3	0.004	1550*
3	20,000	11	6	10.66	97.3	0.004	1000
			8	10.73	97.9	0.006	1200

*Hydrogen-sintered.

No leaks could be found in the three inner capsules and no defects were detected in the weld area by radiographic techniques.

The final encapsulation step was completed by shrink-fitting the inner capsules in the outer tubes. The outer jacket end closures were then accomplished by arc welding in a helium atmosphere. The size relationship between the specimen tubes, inner capsule and outer capsule is illustrated in Fig. I-4.

No defects were found as a result of leak checking and radiographing the end closures of the outer capsules. Upon completion of these tests, spacer lugs were welded at both ends for the purpose of centering in the test reactor location. The three fully assembled irradiation capsules are shown in Fig. I-5.

In addition to weld examination, radiography was employed to establish the internal arrangement of the specimens and the location of the NaK. As a result of this work, it was found that centrifuging was required to assure that all the NaK was in the annular space between the specimen tubes and inner capsule.

The three capsule experiments were accepted by the Westinghouse Testing Reactor and irradiation was begun on June 1.

3. Pre-irradiation Testing

a. O/U Ratio Determinations

In addition to the routine dimensional measurements and density calculations usually performed on pellets, the pre-irradiation testing phase of the program included a set of final O/U ratio determinations to verify that the oxide had reverted to stoichiometric composition. The importance of the latter data was recently emphasized by Robertson[1] in his report which summarized information confirming that excess oxygen is undesirable in UO_2 fuel. The major reasons given were that non-stoichiometric material exhibits larger diametral expansion and greater release of fission-product gases than does stoichiometric UO_2 under similar conditions. Of greater significance is the estimate that the gas release requirements of an oxide-fueled reactor dictate a maximum O/U ratio of 2.01. It was important, therefore, to establish the reliability of the sampling and analytical procedures for this determination.

The analytical method is based on the weight gain accompanying oxidation to U_3O_8. For each O/U ratio determination, a representative pellet from a sintering run is crushed and two samples, each weighing approximately one gram, are withdrawn, introduced into ceramic crucibles, and heated at

(1) J. A. L. Robertson, "Concerning the Effects of Excess Oxygen in UO_2," CRFD-973, October 1960.

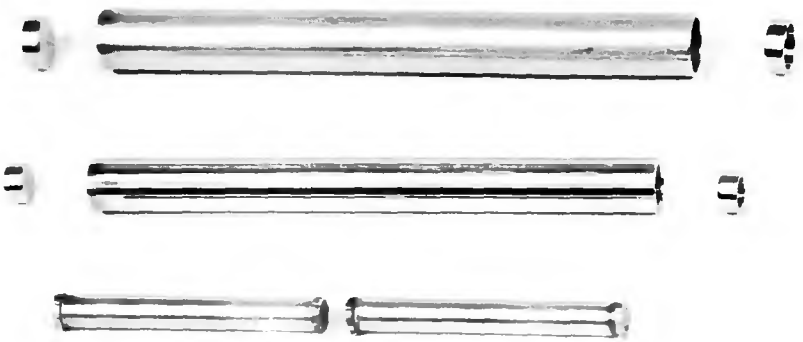


Fig. I-4. Assembled Specimen Tubes, Inner Capsule and Outer Capsule Components

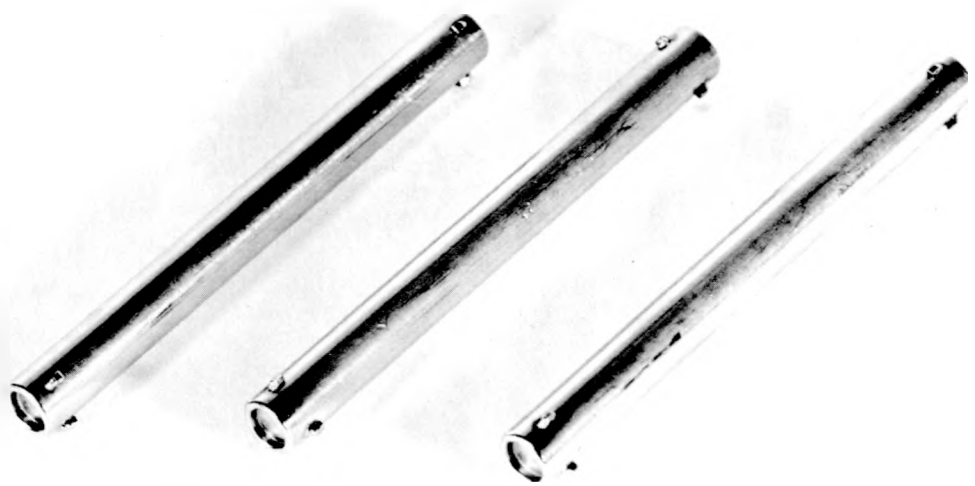


Fig. I-5. Fully Assembled Irradiation Capsules

700°C in a muffle-type furnace. After a four-hour period at temperature, the crucibles are removed from the furnace and cooled to room temperature in a desiccator preparatory to weighing. The O/U ratio of the representative pellet is obtained by calculation based on averaging the results from the two observed weight gains. The resulting value is reported as the O/U ratio of all the pellets sintered in the particular run.

A total of three such O/U ratio determinations were performed on UO_2 specimens representative of enriched pellets selected for irradiation testing. The results of the initial set of determinations have already been presented in Table I-2. These are compared in Table I-4 with the O/U ratio values obtained in the subsequent sets of determinations. The precision found for the method, in terms of average error, agrees fairly well with that reported by Canadian workers(2) who found that the ratio can be determined to within 0.005 by this technique. It is worth noting that the first and third sets of determinations were run by the same technician, whereas the second set was performed by another technician who has less experience with the analysis. The results, therefore, also reflect error probably introduced by this personal factor.

TABLE I-4. PRECISION OF PELLET O/U RATIO DETERMINATION

Sinter Code No.	Sintering Process	Sintering Temp., °C	Pellet O/U Ratio				
			1st Set	2nd Set	3rd Set	Mean	Avg.Error
38P91	Nitrogen	1300	2.003	2.004	2.002	2.003	± 0.001
39P05	"	1200	2.001	2.013	2.000	2.005	± 0.005
39P09	"	1000	1.996	2.012	2.000	2.003	± 0.006
40P02	Hydrogen	1550	2.003	2.024	2.005	2.011	± 0.009

b. Initial Grain Size of UO_2 Specimens

One of the objectives of the irradiation program is to learn whether the initial grain size is a critical factor in the performance of UO_2 as a nuclear fuel. Comparatively little is known about the role of this property in the radiation behavior, especially fission gas release, of UO_2 prepared either by high temperature hydrogen sintering or by low

(2) N. F. H. Bright, et al., "The Determination of Oxygen-Uranium Atomic Ratio in Non-stoichiometric Uranium Dioxide and Other Oxide of Uranium," Mines Branch Report No. MD-207, Department of Mines and Technical Surveys (Canada), July 5, 1956.

temperature nitrogen sintering. Pre-irradiation micrographic examination was performed, therefore, on representative pellets from the groups selected for testing, to measure grain size for subsequent correlation with the results of the irradiation test.

The average grain size of the specimens was measured by the Intercept Method, as described in ASTM Standards 1958, Part 3, Metals Test Methods. The resulting values are reported in Table I-5, along with sintering conditions and pellet densities.

TABLE I-5. AVERAGE GRAIN SIZE OBSERVED IN REPRESENTATIVE ENRICHED (4.95%) UO_2 PELLET SPECIMENS

Pellet Code No.	Sintering Schedule Temp. °C	Time, hr. N_2	Time, hr. H_2	Pellet Density % Theoretical	Avg. Grain Size, Microns After Sintering	Avg. Grain Size, Microns After Annealing*
38P96-20	1300	1	1	95.3	10	13
39P05-13	1200	1	1	98.1	9	12
39P09-18	1000	1	3	97.3	5	13
40P02-18	1550	0	4	96.3	8	13
40P04-37	1550	0	4	97.9	9	15

*Annealed for 144 hours in nitrogen at 1300°C.

It is noteworthy that (1) the average grain size obtained after sintering in hydrogen at 1550°C is essentially the same as that obtained after sintering in nitrogen at 1200°C and 1300°C, and (2) the average grain size of pellets sintered at 1000°C is approximately one-half of that resulting from nitrogen sintering at 1200°C and 1300°C.

c. Effect of Annealing

The planned irradiation conditions are expected to produce central fuel temperatures in the 1500°C to 1600°C range. Since this is considerably higher than the temperature employed in fabrication by nitrogen sintering, an experiment was conducted to determine how the oxide grain size is affected by exposure to an environment in which the fuel temperature is equal to or exceeds the sintering temperature. For this work, representative pellets were annealed at 1300°C in nitrogen for 144 hours. The average grain sizes measured by the Intercept Method after this treatment are presented in Table I-5.

The data show no significant difference in final grain size whether the pellets were prepared by nitrogen sintering or by hydrogen sintering. Although the pellet sintered at

1000°C exhibited the most grain growth, its final grain size was essentially the same as the others. The latter specimen was the only one which increased in density, going from 97.3% T.D. to 98.4% T.D. during the annealing treatment.

C. Micrographic Studies

In addition to the above grain size characterization of the enriched oxide pellets, a systematic micrographic investigation was conducted on several depleted oxide pellets with the objective of determining the influence of the following factors on oxide microstructure: (1) nitrogen sintering temperature, (2) soaking time, (3) raw oxide pretreatment, (4) sintering process (low temperature vs. high temperature), and (5) prolonged annealing after sintering. Again, of primary concern was the magnitude of the grain size obtained and the grain growth behavior of the sintered oxide.

All but one of the pellets selected for this work were produced from the same raw material, Davison Lot 3, and all specimens were prepared for examination by the following procedure which was also used in the work on the enriched oxide.

1. Grinding: Each specimen was first hand-ground perpendicular to the major pellet axis on wet silicon carbide papers progressing through the grit series 200, 320, 400 and 600. After each grinding operation, the oxide surface was cleaned ultrasonically in an alcohol bath, followed by a warm water rinse.

2. Mounting and Polishing: The ground pellets were then mounted and polished. Rough and final polishing were performed on microcloth-covered wheels revolving at approximately 1000 and 200 rpm, respectively, using 0.1 micron γ -Al_2O_3 suspended in 2% chromic acid.

3. Etching: The polished specimens were etched with a solution containing 9 parts H_2O_2 (30%) and 1 part H_2SO_4 by volume.

The results of grain size measurements, by the Intercept Method, involving the effects of the first four factors are presented in Table I-6. Data on the effect of a prolonged annealing treatment are summarized in Table I-7.

An increase in average grain size of at least twofold was observed as the nitrogen sintering temperature was increased from 1000°C to 1300°C. Photomicrographs of the pellets which were examined for this effect are presented in Fig. I-6 to permit comparison of microstructure. It should be noted that, despite a considerable effort to delineate microstructure by repeated polishing and etching, the 1000°C sintered pellet exhibited amorphous regions as well as regions where grain boundaries were comparatively well defined. Because the average grain size of 5 μ reported was the result of measurements on one of the latter areas, the value should be considered as an upper bound. The photomicrograph of this material (Pellet No. 1) illustrates an area where both the amorphous characteristics can be seen and where grain boundaries are clearly discernible.

TABLE I-6. GRAIN SIZE DATA ON OXIDES SINTERED BY TWO-STAGE NITROGEN AND HIGH TEMPERATURE HYDROGEN SINTERING PROCESSES

Sample No.	Method of Oxide Treatment	Sintering Schedule Temp. °C	Time, Hr. N_2	Time, Hr. H_2	Average Grain Size Microns	Geometric‡ Density g/cm³
Two-Stage Sintering Schedule						
Grain growth vs. sintering temperature						
1	Davison Lot 3, ox.-red., 1 cycle, roasted 16 hours at 160°C	1000	1	1	5	10.41
2		1100	1	1	8	10.55
3		1200	1	1	10	10.64
4*		1300	1	1	12	10.72
Grain growth vs. soaking time						
5	Davison Lot 3, ox.-red., 1 cycle, roasted 16 hours at 160°C	1200	1	1/4	8	10.69
6		1200	1	1	10	10.64
7		1200	1	3	15	10.56
Grain growth vs. oxidation-reduction cycling conditions						
8	Davison Lot 3, roasted 16 hours at 160°C	1300	2	1	12	10.02
9* (1 cycle)	Ox.-red., Davison Lot 3, roasted 16 hours at 160°C	1300	1	1	12	10.72
10 (3 cycles)		1300	1	1	16	10.63
11 (7 cycles)		1300	1	1	16	10.56
High Temperature Sintering Schedule						
12	Davison Lot 3, as received	1650	0	6	38	10.33
13	Davison Lot 3, ox.-red.	1650	0	6	37	10.65
14	Davison Lot 3, ox.-red.	1500	0	2	18	10.54
15	MCW Lot 3, as received	1650	0	6	9	10.05

* Oxide was oxidized 16 hours instead of the standard 1-1/2 hours in the activation treatment.

‡Theoretical density of stoichiometric UO_2 - 10.97 g/cm³.

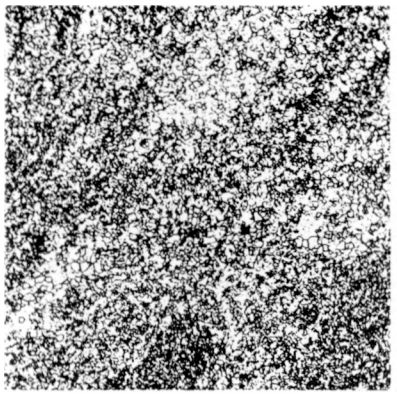
TABLE I-7. EFFECT OF ANNEALING AT 1300°C ON THE GRAIN GROWTH OF SINTERED ACTIVATED DAVISON LOT 3 DEPLETED UO_2

Sample No.	Sintering Schedule Temp. °C	Time, Hr. N_2	Time, Hr. H_2	Annealing Period, Hr.	Average Grain Size, Microns Before	Average Grain Size, Microns After
16*	1200	1	0	-	11	-
17*	1200	1	0	97	-	17
18**	1300	1	1	-	12	-
19	1300	1	1	144	-	17

* Non-stoichiometric pellets: O/U - 2.19.

** Oxide was oxidized 16 hours instead of the standard 1-1/2 hours in the activation treatment.

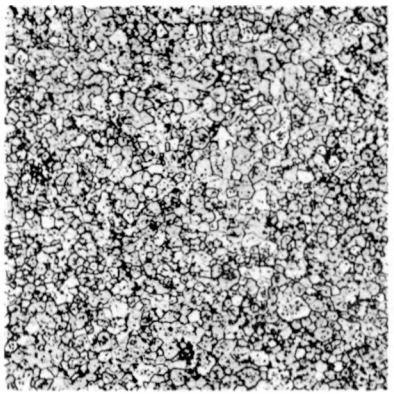
FIG. I-6 - UO_2 PELLETS FROM DAVISON LOT 3 SINTERED BY TWO-STAGE PROCESS - GRAIN SIZE AS FUNCTION OF SINTERING TEMPERATURE



Pellet No. 1

1000°C - 2 hr
Average Grain Size - 5 μ
94.9% T.D.

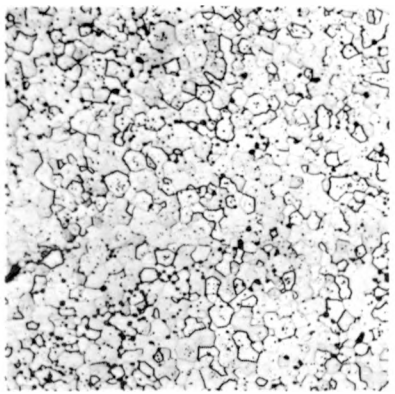
250X



Pellet No. 2

1100°C - 2 hr
Average Grain Size - 8 μ
96.2% T.D.

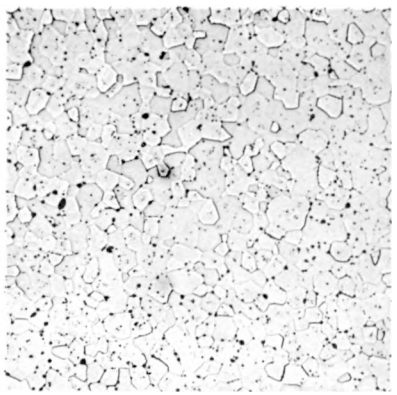
250X



Pellet No. 3

1200°C - 2 hr
Average Grain Size - 10 μ
96.9% T.D.

250X



Pellet No. 4

1300°C - 2 hr
Average Grain Size - 12 μ
97.7% T.D.

250X

Although pellet density apparently did not increase with additional hydrogen soaking time, the average grain size of the oxide showed a definite increasing trend. Photomicrographs of the pellets demonstrating the effect of increasing soaking time on grain growth appear in Fig. I-7.

Varying the oxidation-reduction cycling conditions did not significantly affect microstructure as is evident from the data shown for Pellets No. 8 to 11 in Table I-6.

From the limited information on pellets sintered by the high temperature process presented in Table I-6, it appears that the average grain size is a function of sintering temperature and, perhaps, soaking time. The grain size difference between the Davison Lot 3 pellets sintered at 1650°C and those sintered at 1500°C is believed to reflect the difference in sintering temperature. The considerably smaller grain size of the MCW Lot 3 oxide, sintered at 1650°C, is attributed to a difference in raw material characteristics. This material did not sinter as rapidly as the Davison oxide and extensive porosity probably inhibited grain growth. The photomicrographs of these pellets illustrated in Fig. I-8 clearly show these microstructure variations.

The results of the prolonged annealing treatment of sintered non-stoichiometric and stoichiometric pellets shown in Table I-7 appear to suggest that the presence of excess oxygen did not affect the grain growth behavior of the former material. It was found subsequently, however, that the non-stoichiometric pellet had reverted to $UO_{2.00}$ during the test, so that no valid conclusion concerning the role of excess oxygen could be drawn. In any case, pellets representing both categories each exhibited a final average grain size of 17 microns after a long term anneal at 1300°C in a static nitrogen atmosphere. This value is less than half of that obtained from sintering in hydrogen at 1650°C.

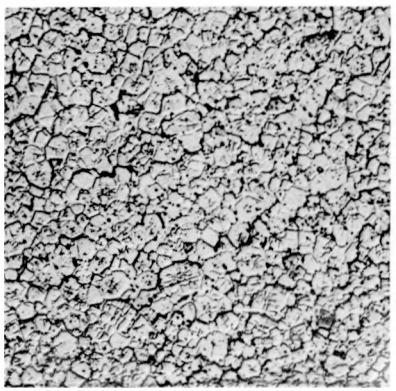
D. Process Development Studies

1. Sinterability of "Superactive" UO_2

Although the process development phase of the project was essentially completed prior to the fabrication of enriched pellets for irradiation testing, it was considered of interest to investigate the properties and low temperature sinterability of a recently received lot of Mallinckrodt "Superactive" ceramic grade UO_2. This material is reported by the supplier to be considerably more active than normally produced ceramic grade oxide.

The as-received bulk density of this lot was found to be 1.02 g/cm^3, which is far below the value of 3 g/cm^3 exhibited by the MCW "dense" oxides, such as the 4.95% enriched UO_2. It is also the lowest bulk density observed among all as-received oxides previously investigated on the project.

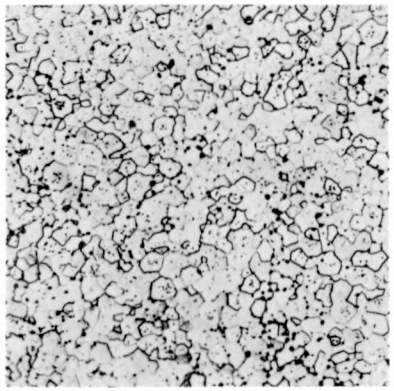
FIG. I-7. UO_2 PELLETS FROM DAVISON LOT 3 SINTERED BY TWO-STAGE PROCESS - GRAIN SIZE AS FUNCTION OF SOAKING TIME



Pellet No. 5

1200°C - 1-1/4 hr Total
Average Grain Size - 8 μ
97.4% T.D.

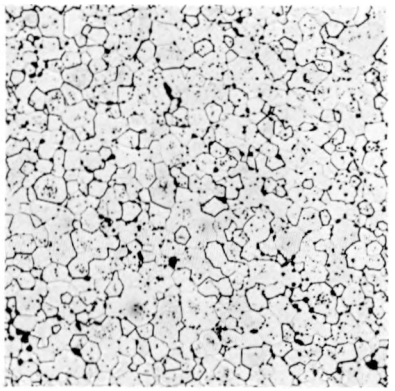
250X



Pellet No. 6

1200°C - 2 hr Total
Average Grain Size - 10 μ
96.9% T.D.

250X

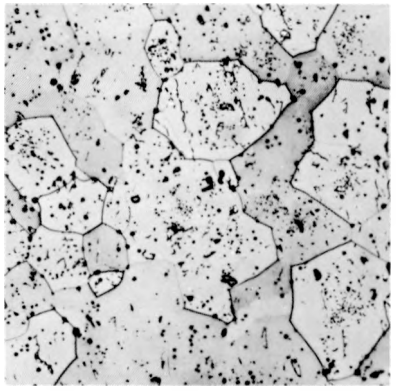


Pellet No. 7

1200°C - 4 hr Total
Average Grain Size - 15 μ
96.3% T.D.

250X

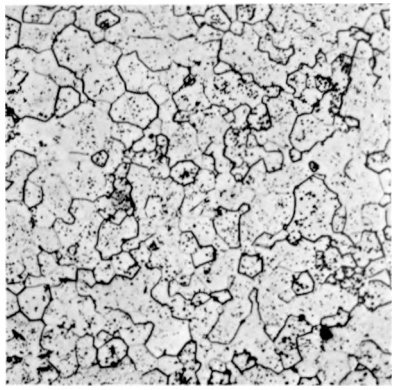
FIG. I-8. HIGH TEMPERATURE HYDROGEN-SINTERED UO_2 PELLETS



Pellet No. 13

Dav. Lot 3 - 1650°C for 6 hr
Average Grain Size - 37 μ
97.1% T.D.

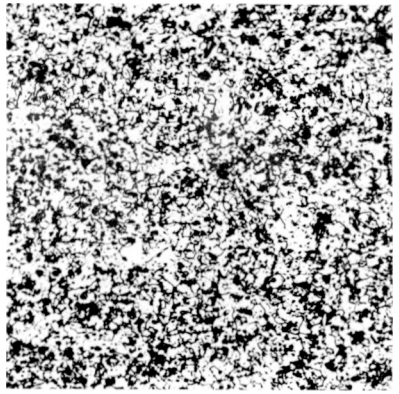
250X



Pellet No. 14

Dav. Lot 3 - 1500°C for 2 hr
Average Grain Size - 18 μ
96.1% T.D.

250X



Pellet No. 15

MCW Lot 3 - 1650°C for 6 hr
Average Grain Size - 9 μ
91.6% T.D.

250X

The results of the sieve analyses are as follows:

Dry Sieve Analysis	%
+20 mesh	0
20/40	4.1
40/60	13.6
60/100	16.5
100/200	11.9
200/325	32.5
-325	21.4
Wet Sieve Analysis	
% remaining on 200 mesh	29.9

Sintering experiments were conducted on two batches of this oxide. One batch consisted of as-received material air-roasted for 16 hours at 160°C. The other batch was first subjected to a standard oxidation-reduction cycle before being air-roasted under the same conditions. The former roasted non-uniformly, whereas the latter behaved well during this pretreatment. Green compacts were prepared from the two batches using the normal procedure with a forming pressure of 20 tsi. The densities obtained after sintering at 1300°C for one hour in nitrogen, followed by one hour in hydrogen, are as follows:

Batch	O/U Ratio After Roasting	Sintered Geometric Density, % T.D.
As received	2.493	97.0
Oxidized-reduced	2.367	97.6

While the high O/U ratio of the batch which was roasted only has probably contributed to sinterability, the major factor leading to the high density obtained is believed to be the inherent activity of the raw material. It is worth noting that the fluorine content of the "Superactive" oxide lot was found to be less than 20 ppm. Inasmuch as our previous work[3] has shown that fluorine is a very effective sintering inhibitor, its absence undoubtedly contributed to the observed activity of this oxide.

(3) "Quarterly Progress Report for January 1 to March 31, 1961," NYO-2692, May 17, 1961.

2. Effect of Fluoride Impurity on UO_2 Sinterability

Several UO_2 powders and sintered pellet samples were analyzed for fluorine to obtain a better understanding of the role of oxidation-reduction cycling in removing fluoride impurity and to determine whether additional fluorine is removed during the two-stage sintering operation. The results obtained are reported in Tables I-8 and I-9, respectively. Data previously developed on as-received and fluoridated powders are included in the former table for comparison. The fluorine content values reported represent an average of two determinations.

As noted in the Quarterly Progress Report for January 1 to March 31, 1961 (NYO-2692), previous work had shown that (1) fluorine introduced by a treatment of the oxide with aqueous HF leads to a deterioration of sinterability, (2) oxidation-reduction cycling at 500°C to 530°C removes a substantial amount of the fluorine as well as restores sinterability, and (3) heating the fluoridated oxide at the same temperature in dry nitrogen is not as effective in removing this impurity or improving sintering behavior. The analytical data on which this review is based is presented in Table I-8 under Oxide Lot O.

Since it is of greater significance to determine the response of an oxide containing high fluorine contamination in the as-received condition, representative samples of Davison Lot 5 oxide powder, at various stages of processing, were subjected to fluorine analysis. This oxide when nitrogen-sintered, without prior oxidation-reduction cycling, yielded a maximum pellet density of 86.5% T.D. After the activation treatment, pellet densities exceeding 95% of theoretical were obtained under similar sintering conditions. The analytical results in Table I-8 show that over 90% of the fluorine had been removed during the oxidation-reduction cycle, as was observed with fluoridated Lot O. Moreover, it was found, quite unexpectedly, that the hydrogen reduction treatment at 510°C and the air roasting operation at 160°C removed large amounts of fluorine from the Lot 5 powder.

At this point, consideration was given to characterizing the form in which fluorine contaminates the fluoridated and as-received oxides. In both cases, the major fluorine compound present is most likely uranyl fluoride (UO_2F_2). A recent paper[4] on the decomposition of UO_2F_2 indicates that this compound is stable in a dry atmosphere below 700°C. Furthermore, from earlier Manhattan Project work,[5] it is reported that superheated steam removes fluorine from UO_2F_2 leaving a residue of UO_3 at 450°C. Thus, a significant reduction in fluorine level

(4) L. M. Ferris and F. G. Baird, "Decomposition of Uranyl Fluoride between 700° and 950°C," J. Electrochem. Soc., Vol. 107, No. 4, p. 305 (April 1960).

(5) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," p. 570, McGraw-Hill Book Company, New York (1951).

TABLE I-8. FLUORINE ANALYSES OF DAVISON OXIDE POWDERS

Code No.	Oxide Lot No.	Oxide Treatment	Fluorine ppm
23P49-1	0	None	190
33P14-1	0	Fluoridated by addition of HF	2450
33P26	0	Fluoridated, oxidized-reduced, 1 standard cycle	170
33P36-1	0	Fluoridated, heated in dry N_2 at 530°C for 2-1/2 hours	1750
23P49-3	5	None	2200
40P14-3	5	Oxidized-reduced, 1 standard cycle	170
24P88	5	Hydrogen reduced at 510°C for 1 hour	375
28P98	5	Roasted at 160°C for 16 hours	625
40P27	5	Heated in wet nitrogen (3 v/o H_2O) at 500°C for 1-1/2 hours	40

TABLE I-9. FLUORINE ANALYSES OF DAVISON OXIDE SINTERED PELLETS

Code No.	Oxide Lot No.	Oxide Treatment	Fluorine in Powder ppm	Sintering Schedule Temp. °C	Time, hr. N_2	Time, hr. H_2	Geo. Den. g/cm^3	Fluorine in Pellet ppm
24P94-7	5	H_2 reduced at 500°C, no binder	375[a]	1300	2	1	7.90	160
24P100-3	5	H_2 reduced at 500°C, no binder	375[a]	1300	2	0	8.98	70
26P66-7	4	Roasted	850[b]	1300	2	1	9.66	70
31P12-1	5	Roasted	625[a]	1100	1	1	8.27	65
33P24-1	0	Fluoridated, roasted	2450[a]	1300	2	1	8.10	30
26P200-8	4	Oxidized-reduced	850[b]	1300	2	1	10.55	20

[a] After treatment.

[b] As-received.

could not be expected from heat treatment of the oxide below 700°C unless moisture were present. An examination of the oxide treatment conditions listed in Table I-8 and the fluorine contents resulting revealed that, where substantial fluorine reductions were obtained, the furnace atmosphere probably contained moisture. This was the case for air roasting at 160°C and air oxidation at 500°C, since no attempt was made to dry the air used in these operations. It was also true for the hydrogen reduction of non-stoichiometric oxide which produces water.

To show conclusively that water was the agent primarily responsible for the removal of fluorine from Davison Lot 5, an oxide heat treating experiment was conducted at 500°C for 1-1/2 hours in nitrogen previously passed through a water bubbler at room temperature to introduce approximately 3 v/o H_2O. The residual fluorine content obtained of 40 ppm is the lowest value found after any oxide treatment and is in sharp contrast with the 1750 ppm remaining in fluoridated Lot O after a treatment in dry nitrogen under more rigorous heating conditions (see Table I-8).

Fluorine analyses on pellets produced from various Davison oxides are reported in Table I-9 and show that most of the fluorine originally present in the powder or introduced by the fluoridation treatment is removed by the end of the sintering operation.

Relatively low densities were obtained with all of these materials except oxidized-reduced Lot 4, which, it should be noted, produced the pellet having the least residual fluorine. Since untreated Lot O normally sintered to high density, the adverse effect of fluorine on pellet density is demonstrated clearly in the case of the fluoridated Lot O, from which a pellet of only 74% T.D. was produced.

E. Conclusions

Repeated O/U ratio determinations on nitrogen-sintered enriched UO_2 pellets representative of those selected for irradiation testing confirm that the residual excess oxygen has been reduced to levels considered satisfactory for fuel performance.

The results of the annealing treatment of the sintered enriched oxide pellets suggest that, as far as the thermal effect is concerned, the test specimens under irradiation will exhibit similar grain growth behavior regardless of the variation in sintering conditions employed in their fabrication.

Probably the most significant finding of the micrographic investigation was that the oxide grain size resulting from sintering apparently is influenced more by the sintering temperature than by the sintering method per se.

Fluorine analyses on low temperature sintered pellets demonstrate that substantially all the fluorine present in the raw material is removed during pellet fabrication.

F. Work Plan for the Next Quarter

Except for preparing a summary report covering the process development phase of the project and following the status of the irradiation test, no significant work is planned until the post-irradiation examination is performed on Capsule No. 1 scheduled for removal from the WTR on or about November 1.

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 experimental variables affecting the carbon analyses in the propane reaction were delineated and reported in the previous Quarterly Reports, NYO-2691 and NYO-2692. In the range of carburizing temperatures from 500°C to 650°C and time at reaction temperature from one-quarter hour to three hours, an optimum time-temperature relationship of one-half hour at 600°C was selected for obtaining 4.8 w/o carbon uranium carbide. These conditions were based on carburizing data obtained in the Inconel retort using a charge of 600 grams uranium metal hydrided at 250°C, and carburized with propane flowing at the rate of 2.0 liters per minute.

The objective of work on the propane reaction during this report period was to determine the reproducibility of the total carbon content under experimental conditions that could be duplicated in the laboratory.

In the arc melting and casting of uranium carbide a series of castings weighing approximately 500 grams was prepared by melting uranium carbide of approximately 4.6 w/o carbon. This melting stock was made by the carbon reduction of the oxide. The purpose of work during this period was to evaluate the castings in terms of chemical composition and casting defects.

B. Uranium Monocarbide by the Propane Reaction

In the previous experiments, as much as eighty per cent of the desired carburization was obtained in the period of time that the retort was heated from the hydriding (250°C) to the carburizing (600°C) temperature. Although the rate at which the retort attained carburizing temperature appeared to be extremely important in determining the extent of carburization, insufficient data were tabulated to establish with certainty the optimum thermal cycle. In addition, the data showed that the carbon content, as well as the carburizing rate, increase with increasing temperatures.

A series of twelve carburizing runs were made to determine the effect of a copper insert and the reproducibility of the carbon content. Six runs were processed with a copper insert in the retort and six without the use of the insert. The formation of flake pyrolytic carbon was decreased when the uranium was supported on copper during reaction with propane. The runs were scheduled for one-half hour at 600°C reaction temperature with propane flowing through the retort at the rate of two liters per minute. The charge consisted of 600 grams uranium; identical runs were made with both derby and extruded uranium rod.

The data reported in Table II-1 indicated that the use of either extruded rod or derby uranium and a copper insert for the retort had little effect on the total carbon content of the carbide. However, the use of a copper insert was desirable to eliminate the formation of carbon flakes in the product. The average carbon content of the series of twelve runs was 4.6 w/o. The free carbon content was erratic, and varied from 0.1 to 0.8 w/o. The free

TABLE II-1. CARBON CONTENT OF URANIUM CARBIDE CARBURIZED FOR ONE-HALF HOUR AT 600°C IN PROPANE

Run No.	Experimental Conditions			Composition, w/o	
	Charge Material	Retort Insert	Time to Attain 600°C, Min.	Total Carbon	Free Carbon
7K-364251	Rod	Copper	120	4.6	0.7
7K-364253	Rod	Copper	100	4.8	0.4
7K-364254	Rod	Copper	124	4.9	0.2
7K-364255	Derby	Copper	106	4.8	0.3
7K-364257	Derby	Copper	60	4.7	0.1
7K-364258	Derby	Copper	71	4.0	0.1
7K-364259	Rod	None	57	4.6	0.2
7K-364261	Rod	None	67	4.7	0.2
7K-364262	Rod	None	47	4.4	0.1
7K-364263	Derby	None	55	4.4	0.1
7K-364264	Derby	None	57	4.5	0.8
7K-364265	Derby	None	47	4.4	0.1

carbon content of powder sieved through a minus 325 mesh screen had no effect on the structure of carbide powders sintered for three hours at 1800°C. However, prior to screening the powder, flake pyrolytic carbon remained as discreet particles in the sintered structure.

The thermal data from these twelve runs showed that the thermal cycle was not necessarily duplicated. This, in part, was due to the endothermic reaction related to the decomposition of uranium hydride occurring at about 400°C. During the carburizing cycle, the introduction of propane decreases the retort temperature, after which it increases to the hydride decomposition, then further increases at a different rate to the reaction temperature. Even-though the specific time required for the retort to reach temperature may not be significant in itself, these data are included in Table II-1 to indicate difference in the thermal cycle in the series of twelve runs.

Further experimental work was completed in which the time required to heat the retort to reaction temperature was held to a minimum, and the total time of the carburizing cycle held constant. A summary of results is shown in Table II-2. The thermal history of each run was accurately recorded, and runs with a deviation from a prescribed thermal cycle were not included in determining the reproducibility of the carburizing reaction. The heating rate of the retort from the hydriding to the carburizing temperature was governed by the power input to the furnace.

The carbon content of the carbide powder from this series of runs is shown in Table II-2. The data indicated that the propane reaction was reproducible to within 0.1 w/o carbon. The average analysis was 4.70 w/o carbon, with maximum and minimum values of 4.80 w/o carbon and 4.62 w/o carbon respectively.

C. Sintering of Uranium Carbide Powder

The effect of die lubricant on the density of sintered uranium carbide was investigated. Previous work indicated that cetyl alcohol and camphor were satisfactory lubricating compounds. Propane produced uranium carbide containing 4.0 w/o, 4.4 w/o and 4.8 w/o carbon was selected for this work. The lubricant was dissolved in petroleum ether; the solvent was evaporated from the powder in the press dry box under an argon atmosphere. When dry, the powders were cold compacted into rectangular bars approximately 3/8-in. x 1/2-in. x 2-1/2-in. The bars were supported on cast uranium carbide discs and vacuum sintered in a graphite boat for three hours at 1800°C. The specimens were analyzed for carbon after sintering. The analyses and densities are shown in Table II-3.

The data in Table II-3 showed no correlation between the sintered densities and the lubricant used in cold pressing the compact. Metallographic examination of the sintered specimens showed free uranium in the structure of compacts made from 4.0 w/o and 4.4 w/o carbon powders. Platelets of uranium dicarbide were observed in the structure of specimens prepared from 4.8 w/o carbon powder.

Figure II-1 shows the structure of a specimen containing an average of 4.3 w/o carbon. The structure consists of free uranium surrounding uranium monocarbide grains, and uranium spheroids within the monocarbide grains. The structure of this material showed no porosity. The small dark areas in

TABLE II-2. SUMMARY OF RESULTS OF CARBURIZING EXPERIMENTS

Test No.	Carburizing Temperature,* Deg. C	Time of Carburizing Cycle, Min.	Total Carbon Content, w/o
7K-364270	593	130	4.7
7K-364273	632	130	4.6
7K-364282	627	130	4.8
7K-364287	629	130	4.7
7K-364297	616	130	4.6
9K-487801	632	130	4.8

*Controller setting was constant in each experiment. The temperature recorded in this Table is approximate steady-state temperature.

TABLE II-3. EFFECT OF LUBRICANT ON THE DENSITY OF URANIUM CARBIDE SINTERING FOR THREE HOURS AT 1800°C

Carbon Content, w/o		Sintered Density, g/cm^3	Lubricant
Powder	Sintered Compact		
4.0	4.3	13.1	1% cetyl alcohol
4.0	4.1	13.9	1/2% camphor
4.0	4.3	13.9	None
4.4	4.4	12.3	1% cytyl alcohol
4.4	4.9	11.3	1/2% camphor
4.4	4.7	11.8	None
4.8	4.8	12.0	1% cetyl alcohol
4.8	4.9	11.8	1/2% camphor
4.8	4.9	12.1	None

the photomicrograph result from spheroids of uranium being dislodged from the monocarbide grains during polishing. Grain growth occurred during sintering.

In contrast to the structure shown in Figure II-1, porosity was observed in specimens containing 4.4 w/o and 4.7 w/o carbon. The latter structures are shown in Figures II-2 and II-3 respectively. The structures shown in Figures II-1, II-2 and II-3 are not equilibrium structures because uranium was continuously vaporized from the specimen at the sintering temperature. The structures shown in these micrographs are typical structures obtained near the center of the specimens. Specimens containing appreciable quantities of free uranium, that is analyzing about 4.0 w/o carbon prior to sintering, varied from a hypo-stoichiometric structure, similar to that shown in Figure II-1, to a hyper-stoichiometric structure at the extreme surface. Figure II-4 shows dicarbide platelets precipitated at the surface of another specimen which contained 4.1 w/o carbon prior to sintering.

The effect of compacting pressure on green density of propane produced uranium carbide powders is shown in Table II-4. The green densities increased directly as the compacting pressure. Compacts from Sample A powder were sintered for three hours at 1800°C. The sintered densities as a function of compacting pressures are shown in the following tabulation.

Compacting Pressure, tsi	Sintered Density, g/cm^3
40	13.7
50	13.1
60	13.7
70	13.4
80	13.4
90	13.7

The sintered densities showed that the compacting pressure had no significant effect on the sintered densities of uranium carbide powder containing 4.1 w/o carbon. The optimum pressure used for compacting should be selected to minimize warpage and reduce shrinkage, and of such force to form a satisfactory shape without excessive die wear. Satisfactory pressures are from 30 to 50 tons per square inch.

Further experimental work was carried out on the sinterability of propane produced uranium carbide containing 4.2 w/o, 4.4 w/o and 4.7 w/o carbon. These materials were compacted under argon in the press dry box at 40 tons per square inch pressure using 0.5 w/o camphor for die lubrication. The compacts weighed between 70 and 75 grams, and were approximately 0.5-in. in cross-section by 2.5-in. long. The bars were sintered in a covered graphite boat 0.75-in. inside diameter by 2.75-in. long, resting on cast uranium carbide discs.

The 4.2 w/o carbon material was sintered for one and three hours at 1200°C and 1400°C. Free uranium segregated at the lower end of the compact in each sintering experiment, forming globular excretions on the surface of the bars. Eventhough densities above 13 g/cm^3 were obtained on sintering this material, the free uranium content in 4.2 w/o carbon material was too high for sintering at these temperatures without some segregation of the uncombined uranium in the specimen.

442461-6

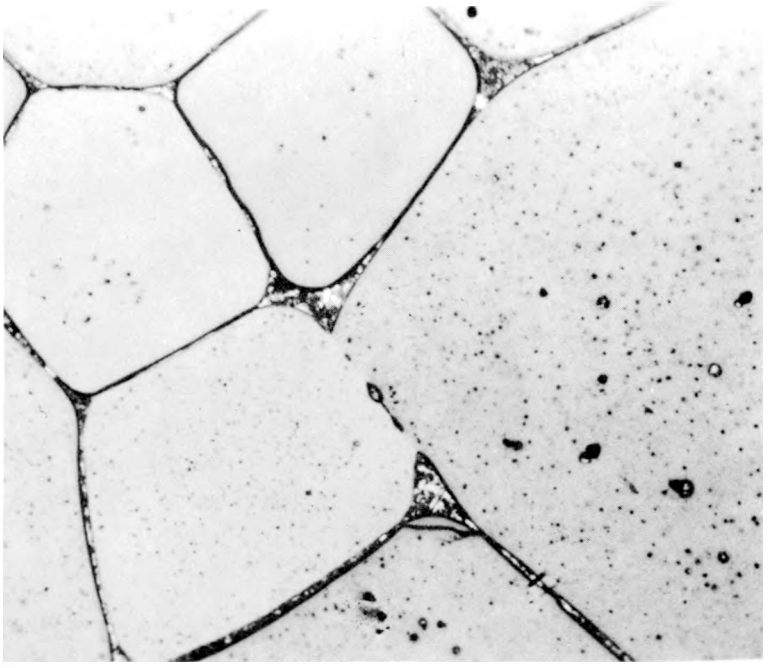


Fig. II-1. Structure of uranium carbide containing 4.3 w/o carbon sintered for three hours at 1800°C. The powder contained 4.0 w/o carbon prior to sintering. Structure near center of specimen. Density: 13.9 g/cm^3. Magnification: 500 diameters.

441261-2

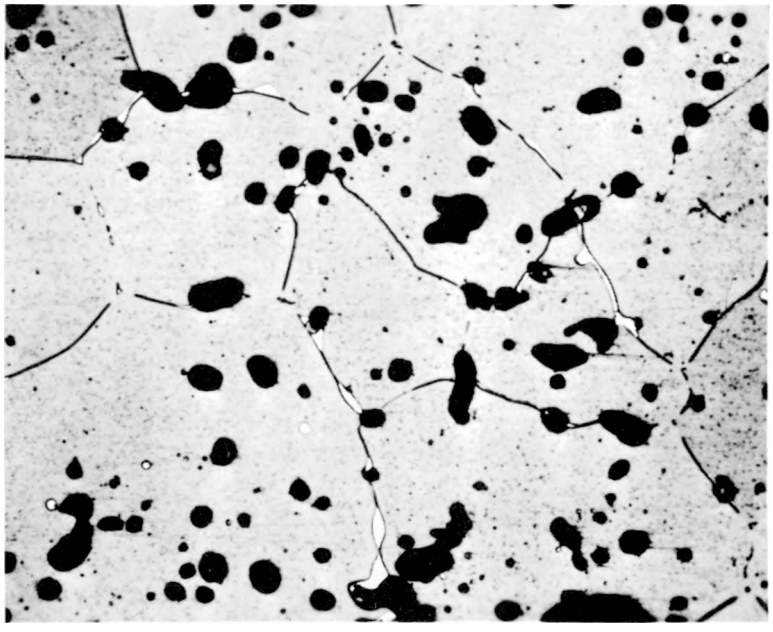


Fig. II-2. Structure near center of specimen of uranium carbide containing 4.4 w/o carbon. The specimen was sintered for three hours at 1800°C and contained 4.4 w/o carbon before sintering. Density: 13.1 g/cm^3. Magnification: 500 diameters.

441261-3

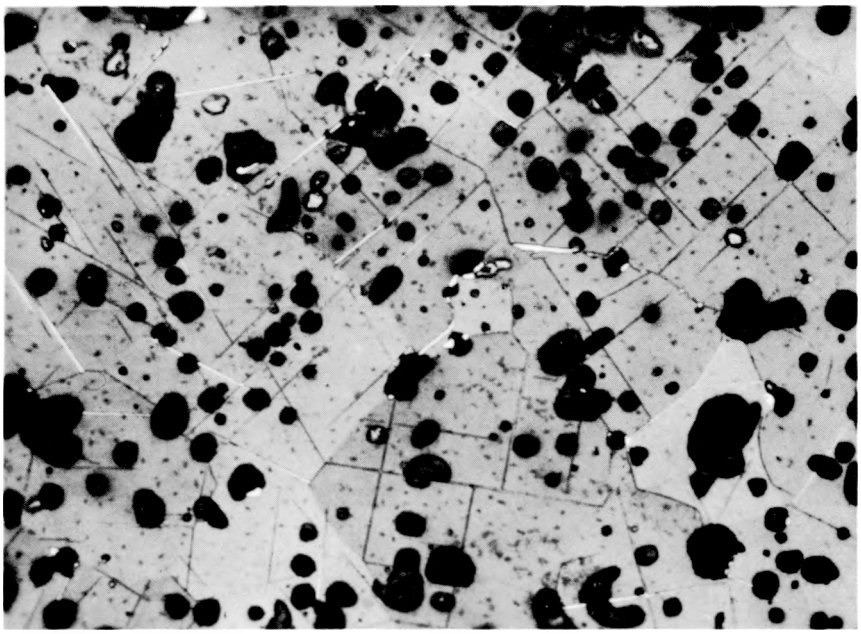


Fig. II-3. Structure of uranium carbide containing 4.8 w/o carbon. The specimen was sintered for three hours at 1800°C and contained 4.7 w/o carbon before sintering. Density: 11.9 g/cm^3. Magnification: 500 diameters.

452461-1

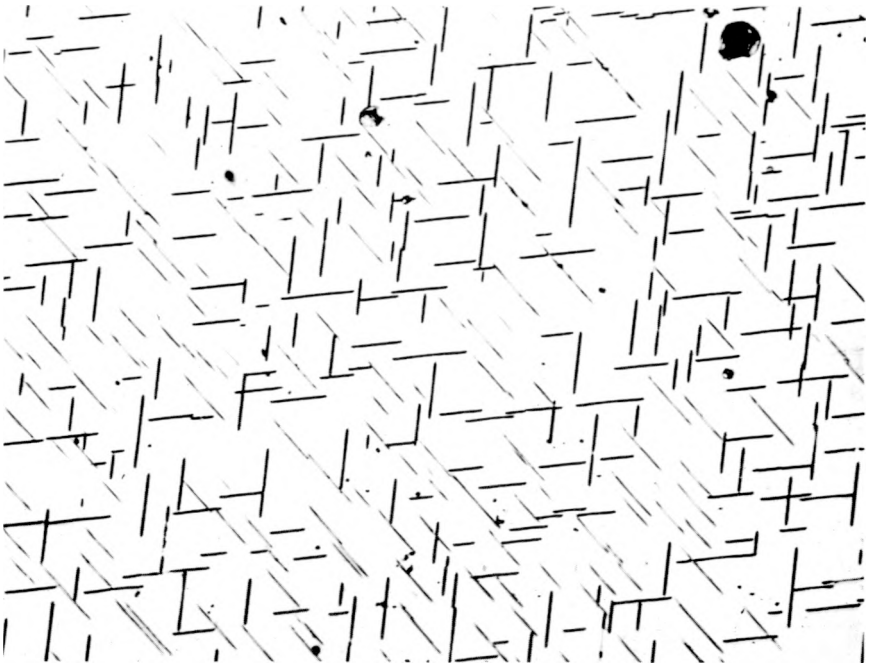


Fig. II-4. Dicarbide platelets at the surface of hypo-stoichiometric uranium carbide sintered in vaccum for three hours at 1800°C. The powder before sintering analyzed 4.1 w/o carbon. Magnification: 500 diameters.

TABLE II-4. EFFECT OF COMPACTING PRESSURE ON THE GREEN DENSITY OF URANIUM CARBIDE

Compacting Pressure, tsi	Green Densities, g/cm^3		
	Sample A	Sample B	Sample C
30	7.6	7.5	7.4
40	8.0	7.8	7.9
50	8.3	8.0	8.0
60	8.5	8.2	8.4
70	9.0	-	-
80	9.1	-	-
90	9.6	-	-

Sample A - 4.1 w/o carbon, 0/5 w/o free carbon
Sample B - 4.1 w/o carbon, 0.7 w/o free carbon
Sample C - 4.7 w/o carbon, 0.3 w/o free carbon

The 4.4 w/o carbon material was sintered for one and three hours at 1200°C. After sintering for one hour, the density of the bar was 12.5 g/cm^3, equivalent to 90% theoretical density. The density was increased to 13.2 g/cm^3 (95% of theoretical) by increasing the sintering time to three hours. The weight loss during sintering was 0.7%, and the shrinkage was 14.5%.

The 4.7 w/o carbon material was sintered for one and three hours at 1800°C, and for three hours at 1900°C. The sintered density was 12.3 g/cm^3, equivalent to 90.5% theoretical density. Increasing the sintering time from one to three hours at 1800°C, and the observed sintering temperature from 1800°C to 1900°C did not result in increasing the density. Weight loss during sintering was 1.7%, and the shrinkage was 14.1%.

D. Arc Melting and Casting Uranium Carbide

A series of fifteen 7/16-in. diameter by 6-in. long castings were made to study variables in the skull arc melting method for consolidating uranium carbide. The operation of the skull furnace was described in a previous report (Refer to NYO-2689). A blended mixture of uranium dioxide and graphite was briquetted, and reacted in vacuum for two hours at 1700°C to provide the charge material. Assuming complete reaction, the calculated carbon content of the charge was 4.66 w/o.

The effect of mold temperature on the casting surface was one of the variables studied during this report period. The average casting weight was 500 grams. An average loss of 52 grams (14%) was noted between the charge and casting weights; 90% of this loss was recoverable. The compound was cast into machined graphite molds having 1/16-in. wall thickness. The molds were outgassed by resistance heating. The mold assembly is shown in Figure II-5. A platinum-platinum 13% rhodium thermocouple was attached to the center section of the mold through a hole in the alumina support. The thermocouple was brought out of the furnace through a vacuum seal to a recorder-controller which actuated a DC power supply for heating the molds. All molds were outgassed at 1000°C whether or not they were heated to a determined temperature to receive the casting.

To establish a basis for comparison, three castings were made in molds at ambient temperature; the remaining castings were made in molds heated at temperatures selected from 200°C up to 1100°C.

The experimental data are recorded in Table II-5. Each casting was analyzed for total carbon. In addition to carbon content, four of the castings were analyzed for oxygen and nine for nitrogen. The average oxygen and nitrogen content was about 400 ppm and less than 100 ppm respectively. The carbon content increased by about 0.5 w/o during the melting operation. A carbon pick-up of this magnitude was not considered to be out of line for an arc skull melting operation.

The incident of fracture in the mold of castings of this size was eight out of fifteen. In addition, four castings were cracked. Ten castings were piped, and eight showed some degree of porosity. The extent of flowlines and presence of cold shuts on the casting surface was not related to the mold temperature. Mold pre-heat temperatures above 700°C resulted in noticeable reaction between the mold and uranium carbide surface. A photograph of castings made in molds

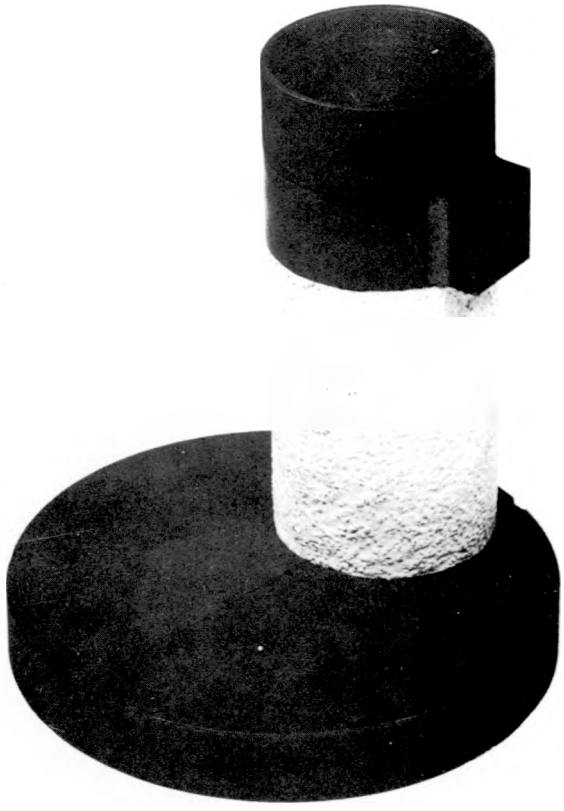


Fig. II-5. General view of mold assembly.

TABLE II-5. EXAMINATION OF FIFTEEN 7/16-IN. DIAMETER URANIUM CARBIDE CASTINGS

Casting No.	Composition, w/o Carbon		Mold Finish	Mold Temp., Deg. C	Remarks
	Charge	Casting			
14D-525-3SM46	4.5	4.7	Reamed	100	Fractured; shrinkage porosity
14D-527-3SM48	4.7	5.0	Reamed	100	Shallow pipe; cracked
14D-548-3SM58	4.8	5.3	Polished	100	Porosity; pipe
14D-549-3SM59	4.7	5.3	Reamed	200/300	Cracked; pipe
14D-544-3SM56	4.6	5.1	Reamed	700	Pipe; fractured; cracked
15D-506-3SM65	4.6	5.3	Reamed	700	Fractured; shrinkage
15D-510-3SM69	4.9	5.4	Polished	700	Fractured; cracked; shrinkage; porosity; pipe
15D-508-3SM67	4.6	5.3	Reamed	900	Cracked
15D-509-3SM68	4.8	5.3	Reamed	900	Fractured; shrinkage
14D-528-3SM49	4.7	5.0	Polished	1000	Porosity; pipe
14D-533-3SM53	4.8	5.0	Reamed	1000	Fractured; porosity; pipe
14D-535-3SM55	5.6	5.2	Reamed	1000	Fractured; porosity; pipe
14D-529-3SM50	4.7	5.0	Polished	1100	Fractured; porosity; pipe
14D-531-3SM52	5.3	5.2	Polished	1100	Fractured; porosity; pipe
15D-507-3SM66	4.6	5.4	Polished	1100	Pipe

heated to various temperatures is shown in Figure II-6. In the mildest cases this was evident as dull patches on the casting; at 1100°C, the casting adhered to the mold along most of its length. As long as a thin walled graphite mold was used, the surface quality of the castings was not improved through the use of a heated mold.

Six castings were ground to clean-up the surface imperfections. The initial diameter was 0.425-in. Three of the six castings cleaned-up after grinding to 0.400-in. diameter. Of the three remaining castings: one cleaned-up at 0.390-in. diameter; one at 0.380-in. diameter; while the other showed a longitudinal crack after grinding to 0.380-in. diameter. The results of this work indicate that a 7/16-in. diameter mold was suitable for preparing 0.375-in. diameter specimens for irradiation studies.

Experimental work with 3/4-in. diameter and 7/16-in. diameter castings indicated the desirability of maintaining constant conditions with regard to charge size, net change of skull before and after melting and melt cycle, in order to keep the casting composition constant. When going from 3/4-in. diameter castings to 7/16-in. diameter castings this uniformity might be preserved by making three castings in one pour. Three 7/16-in. diameter castings were equivalent in weight to one 3/4-in. diameter casting.

A three-mold assembly was fabricated and several three-casting clusters were made. The casting weights were of the order of one kilogram. The as-cast surfaces of these castings were in general typical of as-cast surface for single castings. One cluster prepared from unreacted charge material (700 grams of UO_2-graphite and 200 grams of carbide striker), was analyzed for total carbon at top and bottom locations of each casting. The range of carbon content was uniform and varied from 4.60 to 4.66 w/o. The cluster mold will be used for the preparation of irradiation test specimens.

Three attempts were made to coat a graphite electrode with uranium carbide as a method for reducing the carbon picked up from the graphite electrode during melting. It was found, however, that a coating could not be formed on the graphite electrode by vacuum melting. Further work was discontinued.

To provide some indication of the extent of carbon transferred from the graphite electrode to the melt during melting, weights of electrodes were taken prior to and subsequent to melts made during this period. This was, in a sense, a continuation of similar determinations made with electrodes of varying geometry during the last period. Two different grades of graphite were used for the electrode material during the current melts - AUC and AGOT. Both grades are produced by National Carbon; the former has a density of 1.68 g/cm^3, the latter 1.71 g/cm^3. The average ash content of AUC is 0.03, while that for AGOT is 0.075 w/o. Weight losses determined for eight melts are shown in Table II-6.

Since some deposition of uranium carbide occurs on the electrode during melting, the true weight loss cannot be determined. The data in Table II-6, however, do not indicate any clear trend, either in regard to graphite grade or successive melts on the carbon loss.

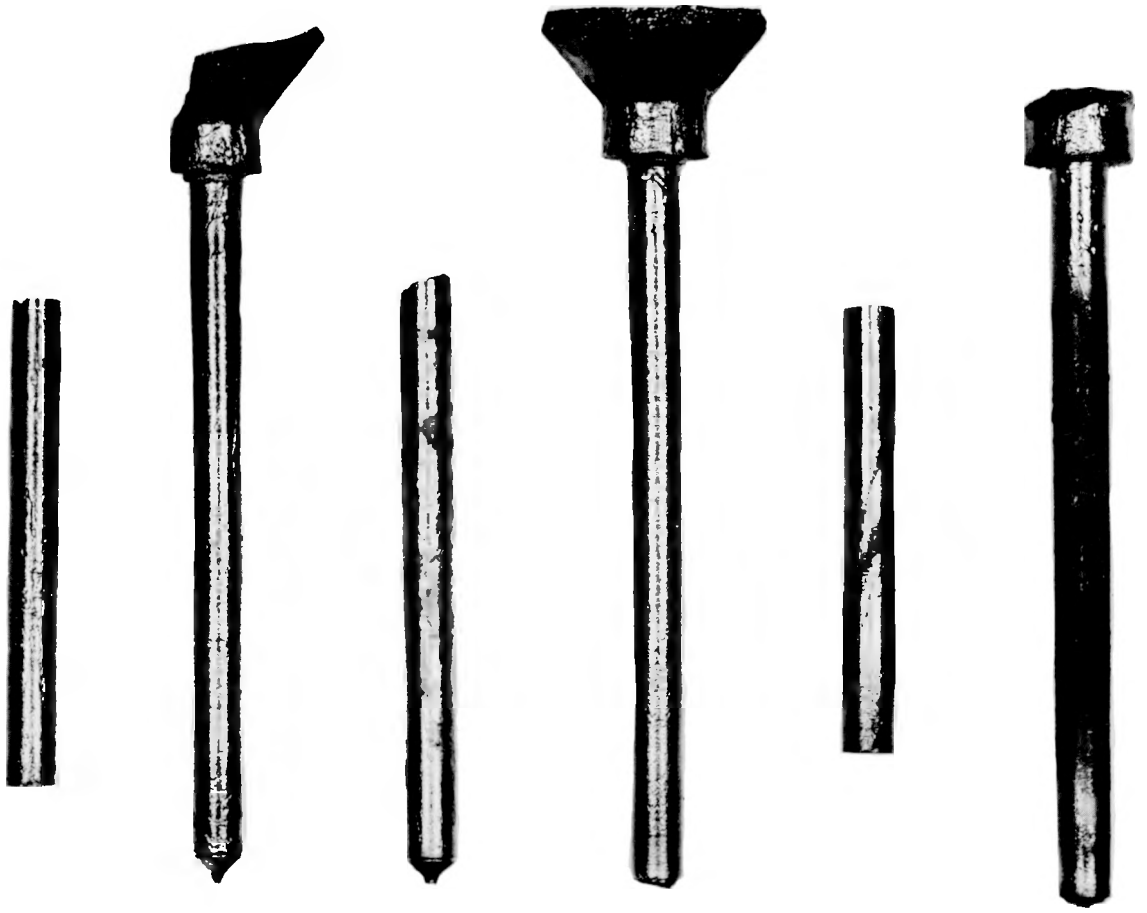


Fig. II-6. Surface of carbide castings made in molds heated from ambient to a temperature of 1100°C.

TABLE II-6. LOSS IN WEIGHT OF AUC AND AGOT GRAPHITE ELECTRODES

Number of Melts After Machining	Weight Loss, grams	
	AUC Electrode	AGOT Electrode
1	5, 5	2
2	4, 5	4
3	2	
4	2	

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