Report No. UNC-3001
UC-25 Metallurgy and Ceramics
(TID-4500, 15th Ed.)
Special Distribution

NUCLEAR FUEL RESEARCH
FUEL CYCLE DEVELOPMENT PROGRAM
QUARTERLY PROGRESS REPORT
OCTOBER 1 TO DECEMBER 31, 1961

Date of Issuance: February 1, 1962

Nuclear Fuel Research Laboratory
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Contract AT(30-1)-2374

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SUMMARY

This report presents the progress made by United Nuclear Corporation, Fuels Division, under Contract No. AT(30-1)-2374 during the period October 1 to December 31, 1961.

Under Task I, the irradiation testing program involving the three capsules containing enriched UO_2 pellets fabricated by low temperature sintering was continued. Two of these are still under irradiation in the Westinghouse Testing Reactor, while the third, or pilot capsule, has been undergoing hot cell examination at the Vallecitos Atomic Laboratory. Preliminary results of this work have been made available.

Flux monitor data indicate an average burnup level in the capsule of 5800 MWD/T, which is considerably less than the 9100 MWD/T calculated from reactor operating data. The burnup analysis on one of the two specimen tubes in the capsule is in good agreement with the flux data, whereas the burnup level appears to be somewhat higher in the second tube. The latter also contained approximately 100 times more released Kr-85 fission gas than the former; however, the fractional release, 0.2% of that theoretically generated, is relatively low for the irradiation conditions.

Under Task II of this program, five different high purity uranium carbide irradiation test specimens were prepared of 12% enrichment. The propane reaction was used as a route for preparing powder metallurgy specimens of two compositions, viz., 4.4 ± 0.1 w/o and 4.8 ± 0.1 w/o carbon. Skull melting and casting was used for preparing three compositions, containing 4.4 ± 0.1 w/o, 4.8 ± 0.1 w/o and 5.2 ± 0.1 w/o carbon. The charges for the arc furnace were made by reducing uranium dioxide with graphite.

Carburization of 12% enriched uranium metal was carried out in four carburizing runs to yield powder containing 4.51 w/o, 5.15 w/o, 4.50 w/o and 2.68 w/o carbon. In the fabrication of specimens containing 4.8 ± 0.1 w/o carbon by powder metallurgy, the uranium carbide powder containing 4.51 w/o carbon was compacted at 60 tsi pressure and vacuum sintered for three hours at 1800°C . The irradiation test specimens machined from the sintered compacts contained 4.86 w/o carbon and had a density of 12.59 g/cm^3 , equivalent to 92.3% of the theoretical density. The nitrogen content was less than 0.01 w/o, and the oxygen content 0.080 w/o. Uranium volatilization accounted for the increase observed in carbon content of the compacted powder during sintering. The hypostoichiometric composition was processed by blending a powder containing 4.50 w/o carbon with one containing 2.68 w/o carbon to yield a composition containing 4.31 w/o carbon. The specific carbon content was critical for obtaining a high density sintered product. The powder was compacted at 60 tsi pressure and vacuum sintered for three hours at 1200°C . The irradiation test specimens machined from the sintered compacts contained 4.31 w/o carbon and had a density of 13.77 g/cm^3 , equivalent to 98.0% theoretical density. The nitrogen content was less than 0.01 w/o, and the oxygen content 0.039 w/o.

The initial step for the conversion of 12% enriched uranium dioxide to

uranium carbide by skull melting was the preparation of a 7 kg skull for the arc furnace. For the carbothermic reduction, uranium dioxide was mixed with graphite, briquetted, then reacted for two hours at 1700°C. The reaction product was arc melted to form the skull, which analyzed 4.43 w/o carbon. The composition of the skull was varied from one composition range to another by remelting the entire skull with calculated amounts of either graphite or enriched uranium dioxide.

The molten carbide compositions were cast into thin wall, three-cluster, 7/16-in. diameter by 6 in. long, degassed graphite molds. The cast rods contained the normal amount and extent of porosity, pipe and thermal cracks previously reported in cast depleted uranium carbide.

Irradiation test specimens were machined from the cast rods. The hypo-stoichiometric composition contained 4.45 w/o carbon, less than 0.01 w/o nitrogen, and 0.018 w/o oxygen. The specimens had a density of 13.90 g/cm³, equivalent to 99.6% theoretical density. The stoichiometric composition contained 4.72 w/o carbon, less than 0.01 w/o nitrogen, and 0.003 w/o oxygen. The specimens had a density of 13.63 g/cm³, equivalent to 99.3% of theoretical density. The hyperstoichiometric composition contained 5.19 w/o carbon, less than 0.01 w/o nitrogen, and 0.031 w/o oxygen. The specimens had a density of 13.36 g/cm³, equivalent to 99.1% of the theoretical density.

The irradiation test specimens were shipped to Battelle Memorial Institute for encapsulation. Two capsules, each containing five specimens, are scheduled for insertion in the ETR on February 19, 1962, and the third for insertion on March 19, 1962. Sodium will be used in the first two capsules for the heat transfer media, while the specimens are to be canned under helium in the third capsule.

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

Work on the irradiation testing phase of the project was continued during this reporting period. Two capsules containing stoichiometric UO_2 pellets prepared by low temperature inert atmosphere sintering remained under irradiation in the Westinghouse Testing Reactor. The third capsule involved in the program, designated as No. 1, was removed from the WTR at the end of the previous quarter and transferred to the General Electric Vallecitos Atomic Laboratory for hot cell examination (see NYO-2695).

During this quarter, further data on the progress of the WTR irradiation was received and preliminary results on the post-irradiation examination of the pilot capsule were obtained.

B. Irradiation Testing Program

1. Status of WTR Irradiations

Three irradiation test capsules, each holding two specimen tubes containing sintered enriched UO_2 pellets, were initially introduced into the WTR on May 25, 1961. A detailed description of these experiments was published in a previous quarterly progress report, NYO-2693. After the completion of four cycles on September 30, 1961, irradiation of the pilot capsule (No. 1) was terminated because it had been irradiated close to its originally planned burnup level of 10,000 MWD/T on a calculated basis.

The irradiation of the two remaining capsule experiments in the WTR is proceeding essentially on schedule with the completion of the seventh cycle on December 31. A summary of the Irradiation Units (1 I.U. = 10^{20} nvt cubic inches) supplied to date in the program is presented in Table I-1.

Table I-1. Summary of Irradiation Units Supplied by WTR^a

Capsule No.	WTR Cycle							Total I.U.
	14	15	16	17	18	19	20	
1 ^b	7.16	6.73	6.56	8.26	-	-	-	28.71
2	7.27	6.84	6.76	8.43	7.36	9.11	7.40	53.17
3	6.73	6.25	6.10	7.76	6.88	8.86	7.40	49.98

a. 1 Irradiation Unit = 10^{20} nvt cubic inches.

b. Capsule No. 1 was removed for hot cell examination at the end of Cycle 17.

To have achieved the planned burnup rate and heat generation conditions in these experiments, 7.5 I.U. were calculated to have been required per cycle. The data in the table indicate that the irradiation conditions are somewhat, but not significantly, less severe than originally planned.

2. Hot Cell Examination of Pilot Capsule

Capsule No. 1, containing Specimen Tubes No. 1 and 7, was opened by General Electric personnel at the Vallecitos Atomic Laboratory on October 27. Pertinent pre-irradiation data, reported previously, concerning the contents of these stainless steel tubes are as follows:

<u>Specimen Tube</u>	<u>Pellet Density % of Theo.</u>	<u>Initial Diametral Clearance in.</u>	<u>Sintering Temp. °C</u>
1	95.1	0.002	1300
7	98.1	0.006	1200

Each tube was approximately 2 inches long, had a wall thickness of 0.010 inch and contained five enriched (4.95%) oxide pellets having a nominal diameter of 0.250 inch.

In the post-irradiation inspection, the tube diameters were measured at several points and compared with pre-irradiation values. No significant differences were found.

At this point, the fission gas was collected from each tube and submitted for analysis. The tubes were then cut open. All the oxide pellets were found to be cracked and there were no signs of central melting. Photographs of the tubes' contents at this stage of the examination are shown in Figures I-1 and I-2. It was not possible to remove the fuel fragments in a manner which would permit dimensional and weight measurements on a reconstructed pellet.

The three aluminum-cobalt flux monitors associated with each specimen tube were analyzed for Co^{60} . The following table shows the integrated thermal neutron exposure indicated by each.

<u>Specimen Tube</u>	<u>Location of Monitor</u>	<u>Exposure 1020 nvt</u>
1	Top	3.42
	Full length	3.09
	Bottom	3.06
7	Top	3.59
	Full length	3.12
	Bottom	3.42

Section of Pellet No. 3
Taken for
Micrographic
Examination

Pellet No. 4
Taken for
Burnup
Analysis

Section of Pellet No. 5
Taken for
Micrographic
Examination

Figure I-1. Post-Irradiation Appearance of Pellets in Specimen Tube 1

Figure I-2. Post-Irradiation Appearance of Pellets in Specimen Tube 7

A computed exposure based on the Irradiation Units reported by WTR yields a value of 5.6×10^{20} nvt. This is calculated by applying the factor of 1.8 supplied by WTR for the ratio of reported unperturbed flux to effective flux for this particular capsule design. On the basis of the flux monitor data, it would appear that either the factor of 1.8 or the represented flux is in error. The burnup level in the pilot capsule calculated from the flux monitor data is approximately 5800 MWD/T instead of the 9100 MWD/T using quoted reactor conditions.

As indicated in Figure I-1 and Figure I-2, one pellet was taken from each tube for burnup analysis and two pellets were selected for micrographic examination. Preliminary results on the burnup analysis are presented in Table I-2. The burnup level was determined by dissolving a whole pellet and analyzing for the ratios of Cs-137-to-uranium and Ce-144-to-uranium.

Table I-2. Burnup Levels, MWD/T

<u>Sample</u>	<u>Cs/U</u>	<u>Ce/U</u>
Tube 1	5,670	5,950
Tube 7	8,210	7,740

The burnup data on Tube 1 is in good agreement with the flux monitor data. The burnup in Tube 7, on the other hand, is 30% to 40% higher than that calculated from such data. Although this inconsistency has not yet been fully resolved, the fact that the pellet selected for analysis was taken from the end of the tube, rather than from nearer the center as in the case of Tube 1, may have contributed to this difference. (Flux suppression is more pronounced at the center of a tube of pellets than it is at the ends.)

Tentative fission gas release data have also been obtained which are the result of measuring the krypton-85 activity of the gas collected from each specimen tube. The total number of Kr-85 atoms found in each tube and the corresponding percent of that generated during irradiation, based on the average measured burnup level, are as follows:

<u>Specimen Tube</u>	<u>Atoms Kr-85</u>	<u>% Fission Gas Release</u>
1	$<9.9 \times 10^{12}$	<0.002
7	1.4×10^{15}	0.2

These data suggest that the fuel in Tube 7 may have been operated at a higher temperature than that in Tube 1. Although the fuel in Tube 7 is more dense than that in Tube 1 (98.1% vs. 95.1%), this hypothesis is consistent with the higher measured

burnup, the slightly higher flux and the larger initial diametral clearance (0.006 in. vs. 0.002 in.) associated with the former. It is worth noting that preliminary micrographic examination has found some grain growth in the oxide pellets from Tube 7, while none has been observed in those from Tube 1. This tends to support the higher fuel temperature hypothesis.

3. Irradiation of Fuel Rods in VBWR

Enriched (5%) oxide raw material has been received from GE/APED for the fabrication of pellets which are to be produced by the low temperature sintering process and placed in full-scale fuel rods of VBWR design for irradiation. At the end of the quarter, the fuel tube components had not yet been received from GE/APED so that the completion of this work may be delayed.

C. Work Plan for the Next Quarter

Post-irradiation examination of the pilot irradiation capsule will be completed and the data will be analyzed to arrive at estimates of actual in-pile thermal conditions. A decision based on these results will be reached concerning the programing of the remaining two capsules in the WTR with a view toward possibly attaining an actual burnup of 20,000 MWD/T as originally planned. Work on the fabrication of fuel rods for the irradiation in the VBWR will also be completed.

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

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

A. Introduction

The objective of the work this quarter was the conversion of 12% enriched uranium metal and uranium dioxide into high purity uranium carbide, and the fabrication of specimens for the irradiation program. Five different uranium carbide materials will be irradiated; two prepared by powder metallurgy and three by skull melting procedure. The high purity uranium carbide was prepared to three specific carbon contents as follows: 4.4 ± 0.1 w/o, 4.8 ± 0.1 w/o and 5.2 ± 0.1 w/o. The first two compositions were fabricated by both the powder metallurgy and casting procedure, and the latter composition by casting. The material was fabricated to as high density as technically feasible for a given carbon content. The physical dimensions of the specimens were 0.375 ± 0.001 -in. diameter by 0.750 ± 0.005 -in. long.

B. Preparation of Enriched Uranium Carbide Powder

The 12% enriched derby, received from the Chemical Division, United Nuclear Corporation, analyzed 99.96% uranium and weighed 1.988 kilograms. The derby was cut for the preparation of four retort charges, weighing 612.2, 610.4, 608.8 and 125.0 grams, respectively.

Uranium carbide was prepared from each charge. The charges were pickled in 50 v/o nitric acid, rinsed with water, dried with alcohol and reweighed. After loading, the retort was purged with argon having a dewpoint of less than minus 60°C. Hydriding was performed with hydrogen of a similar dewpoint for 18 hours at 200°C. The carburizing cycle was carried-out with chemically pure tank propane flowing through the retort at 2.0 liters per minute. The dewpoint of the propane was better than minus 30°C. The carburizing data are shown in Table II-1.

The carbon content of the powders prepared in runs E-1-488377, E-3-488392 and E-4-488397 were within the desired composition range. The carbon content, however, of the enriched uranium carbide powder in run No. E-2-488381 exceeded the desired carbon content by about 0.2 w/o, although the experimental conditions established for carburizing depleted uranium were duplicated in this experimental work. In terms of enriched derby analyses, the carbon and chromium contents were 290 ppm, respectively, compared to 50 ppm and 10 ppm, in depleted derby. Other impurities, such as nickel, iron, aluminum and silicon were lower in the enriched material. There were no observed anomalies either in the experimental conditions or chemical analyses of the charge material to account for the apparent increased carburization rate of the enriched derby in that one run. Powder from the high carbon content run was not used, however, to prepare irradiation specimens.

TABLE II-1. CARBURIZATION OF 12% ENRICHED URANIUM BY THE PROPANE REACTION

<u>Run No.</u>	<u>Charge Weight, grams</u>	<u>Carburizing Time, Minutes</u>		<u>Carburizing Temperature, °C</u>	<u>Product Weight, grams</u>	<u>Carbon Content, w/o</u>
		<u>To Attain Temperature</u>	<u>Time at Temperature</u>			
E-1-488377	612.2	88	30	601	635.9	4.51
E-2-488381	610.4	114	40	624	620.6	5.15
E-3-488392	608.8	76	20	601	629.3	4.50
E-4-488397	125.0	53	Not Held	500	128.1	2.68

C. Sintering 12% Enriched Uranium Carbide Powder

The enriched uranium carbide powder batches were processed under an argon atmosphere having a dewpoint of less than minus 40°C. Three 95-gram lots of powder from run No. E-1-488377 were weighed out and blended with 19 cc of a 2.5% camphor-petroleum ether solution. After blending and drying the powder for 45 minutes, rectangular compacts were formed at 60 tsi pressure. The compacting data are shown in Table II-2.

The compacts were transferred to the sintering furnace under an argon atmosphere. The first three bars shown in Table II-2 were sintered in a degassed graphite boat for three hours at 1200°C at a maximum pressure of 0.3 micron. The shrinkage was 11.7%. The loss in weight was 0.62%. The sintering boat gained 0.3 gram in weight, accounting for the difference in camphor content (0.5%) and weight loss during sintering. The average sintered density was 11.93 g/cm³, as determined by mercury immersion.

In as much as a low average density was obtained on sintering the first series of three compacts for three hours at 1200°C, showing that powder E-1-488377 contained insufficient metallic uranium for liquid phase sintering, the second series of three compacts shown in Table II-2 was sintered for three hours at 1800°C at a maximum pressure of 0.3 micron. The sintered compacts were cooled from the sintering temperature to 1200°C in one hour. Linear shrinkage was 12.7%. The loss in weight was 0.75%. The sintering boat gained 0.7 grams, corresponding to the difference between the camphor content (0.5%) and the total weight loss during sintering of this series of compacts. The average sintered density was 12.39 g/cm³, as determined by mercury immersion.

The first group of compacts, sintered for three hours at 1200°C, was re-sintered for three hours at 1800°C. The sintered compacts were cooled from the sintering temperature to 1200°C in one hour. On re-sintering, shrinkage occurred only in the length, and amounted to 0.84% in linear dimension. The sintering boat gained 1.0 gram, and the total weight loss of the bars was 1.1 grams. The average density on re-sintering was 12.42 g/cm³, as determined by mercury immersion.

The carbon content was 4.79 w/o and 4.86 w/o, respectively, on compacted bars from the first and second series of compacts. The singly sintered compacts were selected for the preparation of irradiation test specimens. The nitrogen content in these specimens was less than 0.01 w/o, and the oxygen content 0.080 w/o. The density of the sintered bars was 12.4 g/cm³, corresponding to 91.2% of the theoretical density for stoichiometric uranium carbide.

There was no difference detected in the metallographic structure of the two groups of sintered compacts. The microstructure was essentially stoichiometric uranium carbide, with scattered porosity within and at the grain boundaries. Uranium dicarbide platelets were observed near the surface of the compacts in scattered locations, resulting from uranium evaporation from the surface during sintering. The metallographic structures are shown in Figures II-1 and II-2.

TABLE II-2. COMPACTS FROM ENRICHED POWDER E-1-488377

<u>Bar No.</u>	<u>Compact Weight, grams</u>	<u>Compact Dimension, inches</u>	<u>Green Density, g/cm³</u>
E-1-1	92.2	0.507 x 0.532 x 2.539	8.2
E-1-2	92.5	0.512 x 0.532 x 2.537	8.2
E-1-3	91.0	0.502 x 0.532 x 2.536	8.2
E-1-4	92.2	0.505 x 0.532 x 2.540	8.2
E-1-5	93.3	0.515 x 0.532 x 2.538	8.2
E-1-6	92.5	0.510 x 0.534 x 2.540	8.2

Fig. II-1. Representative microstructure of stoichiometric (4.86 w/o carbon) uranium carbide irradiation test specimens prepared by powder metallurgy.

Magnification 500

Fig. II-2. Microstructure near the surface of sintered compact E-1-5. Uranium evaporation resulted in precipitation of uranium dicarbide in the monocarbide matrix.

Magnification 500

In the preparation of hypostoichiometric uranium carbide, the carbon content of powder E-3-488392 was reduced from 4.50 w/o to 4.44 w/o by adding a calculated amount of powder E-4-488397. In the blended composition, 6.6 grams of powder E-4-488397 was mixed with 93.4 grams of powder E-3-488392 under argon in a rotating container for 15 minutes. The blended composition was screened through a 325 mesh screen, and transferred in a sealed bottle to the press dry box. It was then blended with 19 cc of a 2.5% camphor-petroleum ether solution. After drying, the mixture was compacted into a rectangular bar at 60 tsi. The compact weighed 95.5 grams and had a green density of 8.26 g/cm³. The compact (designated E-5-1) was vacuum sintered for three hours at 1200°C. The linear shrinkage was 14.4%. The sintered density, as determined by mercury immersion, was 13.13 g/cm³.

A second composition was prepared to increase the free uranium still further and thus promote sintering and to further increase the sintered density. In the new composition, 11.0 grams of powder E-4-488397 was blended with 89.0 grams of powder E-3-488392 to yield a composition containing 4.31 w/o carbon. The powder mixture was blended in a sealed polyethylene bottle for two hours on an inclined rotating blender. As in the previous composition, one-half percent camphor was added for die lubrication, and the powder compacted at 60 tsi. The compact weighed 95.7 grams and had a green density of 8.42 g/cm³. The bar (designated E-6-1) was vacuum sintered for three hours at 1200°C. The linear shrinkage was 14.6%. The density of the sintered compact, as determined by immersion in carbon tetrachloride, was 13.62 g/cm³.

The effect in decreasing the carbon content within specification range of 4.4 ± 0.1 w/o carbon for hypostoichiometric uranium carbide is shown as follows:

<u>Carbon Content, w/o</u>	<u>Sintered Density, g/cm³</u>
4.50	12.10
4.44	13.13
4.31	13.62

Because of the significantly higher sintered density, the 4.31 w/o carbon composition was selected for the preparation of the irradiation test specimens.

The 4.31 w/o carbon composition for the irradiation test specimens was then prepared by blending 33.0 grams of uranium carbide powder E-4-488396 with 267.0 grams of uranium carbide powder E-3-488392. After blending for two hours in an inclined rotating mill, three rectangular compacts were formed at 60 tsi pressure using 0.5% camphor-petroleum ether for die lubrication. The compacting data are shown in Table II-3.

The compacts were transferred under argon to the induction furnace and sintered for three hours at 1200°C at a pressure of less than 0.3 micron. The shrinkage was 14.9%. The weight loss was 0.79%. The density of the sintered compacts was 13.69 g/cm³, as determined by immersion in carbon tetrachloride.

TABLE II-3. COMPACTS FROM BLEND OF ENRICHED POWDERS E-3-488392 AND E-4-488392

<u>Bar No.</u>	<u>Compact Weight, grams</u>	<u>Compact Dimension, inches</u>	<u>Green Density, g/cm³</u>
E-6-2	96.7	0.521 x 0.533 x 2.535	8.4
E-6-3	95.9	0.517 x 0.532 x 2.535	8.4
E-6-4	96.8	0.522 x 0.532 x 2.536	8.4

The carbon content of the sintered bars was 4.31 w/o. The nitrogen was less than 0.01 w/o, and the oxygen was 0.039 w/o.

The metallographic structure was uniform throughout the cross-section, consisting of uranium monocarbide surrounded by a network of free uranium. Scattered porosity was observed in the microstructure. The typical metallographic structure is shown in Figure II-3.

D. Skull Melting and Casting

The initial step for processing 12% enriched uranium carbide irradiation test specimens was the preparation of a 7-kg. skull for the arc melting furnace. The skull was prepared by reacting 12% enriched uranium dioxide, Lot No. K02LU, received from the Chemicals Division, United Nuclear Corporation, containing 87.9% uranium, with Grade 48 graphite, obtained from the National Carbon Division, and melting the product in the skull furnace. The particle size of the 12% enriched oxide was less than 325 mesh and the graphite was 98% through 200 mesh.

In the preparation of the skull, seven UO_2 -graphite charges were used. Each charge was comprised of 1,000 grams of uranium dioxide and 128.5 grams of graphite which had been blended for two hours and compacted, without die lubricant, at 30 tsi pressure in a one-half inch diameter die. This oxide-to-graphite ratio was calculated to yield 4.3 w/o carbon after reaction, in accordance with the reaction: $\text{UO}_2 + 3\text{C} \rightleftharpoons \text{UC} + 2\text{CO}$. Each pellet weighed approximately 5 grams. The pelletized charges were then reacted separately in an induction furnace for two hours at 1700°C under reduced pressure (5- to 15-in. Hg absolute). The reacted charges were unloaded from the induction furnace, weighed and transferred to the skull furnace under argon. Melting of the seven charges, homogenizing of the skull and formation of a skull cavity were performed in seven melting cycles.

The charges for making castings to prepare irradiation test specimens of 4.4 ± 0.1 , 4.8 ± 0.1 and 5.2 ± 0.1 w/o carbon consisted of 900 grams of uranium oxide blended with 115.6, 118.8 and 121.7 grams of carbon calculated to yield, respectively, 4.3, 4.7 and 5.0 w/o carbon after reaction.

Each charge was placed in the skull cavity and given a standard five-minute melt. The pour was then made into a three-mold cluster, yielding three 7/16-in. diameter by 6-in. long castings. The compositions of the castings are shown in Table II-4.

Changes of the skull carbon content required to prepare the different casting compositions were made by additions of uranium dioxide or graphite, as required. Homogenizing melts incorporating the required additive into the skull were made to insure homogeneity of the skull prior to melting a given charge.

This series of melts clearly established that a given casting carbon content could be achieved by the skull casting method within the limits of one-tenth weight percent carbon provided the charge and skull compositions were properly chosen and controlled.

Fig. II-3. Representative microstructure of hypostoichiometric uranium carbide (4.31 w/o carbon) irradiation test specimens prepared by powder metallurgy.

Magnification 500

TABLE II-4. COMPOSITION OF 12% ENRICHED IRRADIATION TEST SPECIMENS

<u>*Specimen No.</u>	<u>Description of Uranium Carbide Material</u>	<u>Composition, w/o</u>			
		<u>Total Carbon</u>	<u>Free Carbon</u>	<u>Nitrogen</u>	<u>Oxygen</u>
E-6-Series	Hypostoichiometric - Powder Metallurgy	4.31	None	<0.01	0.039
E-1-Series	Stoichiometric - Powder Metallurgy	4.86	None	<0.01	0.080
19D-728-Series	Hypostoichiometric - Cast	4.45	None	<0.01	0.018
19D-709-Series	Stoichiometric - Cast	4.72	None	<0.01	0.003
19D-715-Series	Hyperstoichiometric - Cast	5.19	None	<0.01	0.031

*Refer also to Table II-5

Metallographic structures of specimens representing the three compositions, 4.45, 4.72 and 5.19 w/o carbon are shown in Figures II-4, 5, 6 and 7. Evidence of uranium segregation in 4.4 w/o carbon cast material can be seen by comparing Figure II-4 with II-5; the latter figure shows appreciably more free uranium present at the center of the casting than was observed at the surface of the specimen.

E. Irradiation Test Specimens

The sintered bars and cast rods as described in the preceeding sections were ground to form right cylinders for irradiation testing. The material was ground with medium-soft bonded 60 mesh silicon carbide grinding wheels using Sunicut 1B mineral oil coolant. The specimen dimensions were 0.375 ± 0.001 -in. diameter by 0.750 ± 0.005 -in. long. A total of twenty specimens were required; three from each series for encapsulation and one for control purpose.

The specimens were within the chemical and physical specifications established for the irradiation program. The compositions are summarized in Table II-4, and the physical measurements are recorded in Table II-5. Photographs of the five series of specimens are shown in Figures II-8 to II-12 inclusive.

The densities of the test specimens showed reasonable agreement between geometric and Archimedes' measurements. The specimens containing 4.86 w/o carbon and prepared by powder metallurgy had the lowest density - 92.3% of the theoretical value. The average density of 12.59 g/cm^3 , however, was relatively high for stoichiometric material processed by powder metallurgy. The density of hypostoichiometric uranium carbide (4.31 w/o carbon) processed from powder was 98.0% theoretical. As anticipated, the average densities of the cast specimens were somewhat higher, ranging from 99.1% to 99.6% of the theoretical values for the specific composition.

F. Irradiation Program at Battelle Memorial Institute

The objective of the irradiation program is to investigate the effects of compositional and fabrication variables on the radiation stability of uranium monocarbide at high irradiation temperatures and high fission heat production rates. Three capsules are to be irradiated, each containing one of the five series of uranium carbide materials described in Tables II-4 and II-5.

Fabrication of the component parts of the capsules, as described in BMI-1534, has been completed. A longitudinal cross section of the capsule design is shown in Figure II-13.

The compatibility relationships between niobium, uranium carbide and sodium were questioned in reference to the materials system in the capsule design. The possible reactions which were considered in these studies were sodium corrosion of uranium carbide, and carburization of the niobium fuel containers. The compatibility studies were performed with specimens identical to those to be used in the irradiation capsules.

Fig. II-4. Representative microstructure of cast hypostoichiometric (4.45 w/o carbon) uranium carbide irradiation test specimens.

Magnification 500

Fig. II-5. Segregation of free uranium near the center of cast hypostoichiometric (4.45 w/o carbon) uranium carbide irradiation test specimens.

Magnification 500

TABLE II-5. DESCRIPTION OF 12% ENRICHED IRRADIATION TEST SPECIMENS

Specimen No.	Weight, grams	Dimensions, in.		Density, g/cm ³	
		Diameter	Length	Archimedes ^{1*}	Geometric
E-6-2B	18.7712	0.3758	0.7538	13.76	13.70
E-6-3	18.7326	0.3755	0.7540	13.77	13.69
E-6-4A	18.7450	0.3756	0.7540	13.77	13.69
E-6-4B	18.7102	0.3753	0.7534	13.77	13.70
E-1-4A	17.2127	0.3750	0.7540	12.51	12.61
E-1-4B	17.3514	0.3750	0.7540	12.68	12.48
E-1-5	17.2186	0.3750	0.7490	12.57	12.69
E-1-6	17.3321	0.3760	0.7530	12.61	12.65
19D-728-4SM38-1A	18.7854	0.3754	0.7540	13.90	13.80
19D-728-4SM38-1B	18.8816	0.3753	0.7535	13.94	13.80
19D-728-4SM38-2B	18.7940	0.3756	0.7530	13.84	13.74
19D-728-4SM38-3A	18.5951	0.3749	0.7475	13.92	13.73
19D-709-4SM18-1C	18.5081	0.3756	0.7517	13.68	13.55
19D-709-4SM18-2A	18.4821	0.3751	0.7535	13.64	13.54
19D-709-4SM18-2B	18.4402	0.3759	0.7515	13.58	13.49
19D-709-4SM18-2C	18.4179	0.3756	0.7497	13.61	13.52
19D-715-4SM24-1A	18.0044	0.3743	0.7510	13.36	13.30
19D-715-4SM24-2A	17.9161	0.3751	0.7460	13.32	13.26
19D-715-4SM24-2B	18.2162	0.3755	0.7535	13.36	13.34
19D-715-4SM24-3A	18.0239	0.3748	0.7480	13.40	13.33

*Archimedes' densities measured by immersion in carbon tetrachloride, except E-1 series (4.86 w/o carbon processed by powder metallurgy) which were measured by immersion in mercury.

Fig. II-6. Representative microstructure of cast stoichiometric (4.72 w/o carbon) uranium carbide irradiation test specimens.

Magnification 500

Fig. II-7. Representative microstructure of cast hyperstoichiometric (5.19 w/o carbon) uranium carbide irradiation test specimens.

Magnification 500

Fig. II-8. Series of hypostoichiometric uranium carbide specimens prepared by powder metallurgy.

Fig. II-9. Series of stoichiometric uranium carbide specimens prepared by powder metallurgy.

Fig. II-10. Series of hypostoichiometric uranium carbide specimens prepared by skull melting.

Fig. II-11. Series of stoichiometric uranium carbide specimens prepared by skull melting.

Fig. II-12. Series of hyperstoichiometric uranium carbide specimens prepared by skull melting.

Fig. II-13.

Cross section showing the component parts of the irradiation test capsules. Helium will replace sodium in one of the three capsules.

The containers were fabricated with 0.030-in. thick niobium with a 0.020-in. gap between the cladding and the prototype fuel sample. The gap between the uranium carbide and cladding was filled with sodium which acted as a heat transfer medium. The specimens were centered in the cladding with 0.015-in. diameter molybdenum wire which was reported to be compatible with both sodium and uranium carbide at the temperatures of these experiments^{1,2}. The fuel and sodium were loaded in the specimens under a helium atmosphere in a dry box and the end caps were welded by Heliarc techniques.

Two such specimens, one containing uranium-4.4 w/o carbon alloy and one containing uranium-5.2 w/o carbon alloy, were heat treated in a vacuum furnace for 260 hours at 1500°F. A 260-hour test was selected because the results could be obtained prior to encapsulation of the irradiation specimens and it was believed that the initial stages of any reactions should be apparent after this length of time. A temperature of 1500°F was selected to approximate the intended specimen surface temperature during irradiation. After completion of the tests, the containers were cut open and the sodium was reacted in butyl alcohol.

The microstructure of the uranium-4.4 w/o carbon alloy prior to the compatibility test was that of a uranium monocarbide matrix with metallic uranium randomly dispersed in the grain boundaries, as shown in Figure II-14. Some porosity was detected in the matrix, as would be expected for a sintered material.

After the compatibility test, the microstructure was unchanged except for a slight attack on the uranium in the grain boundaries at the specimen surface, as shown in Figure II-15. The characteristic dull grey appearance of UO_2 was observed in the grain boundaries in place of the metallic uranium which had originally been present, as noted in Figures II-16 and II-17. By examining these areas under polarized light, it was found that the reaction product polarized, at UO_2 should, while the remainder of the specimen did not.

The maximum depth of penetration of the reaction into the specimen was found to be about 0.001-in. Apparently, there was sufficient oxygen in the sodium to oxidize the uranium in the grain boundaries to UO_2 . It is suspected that the source of oxygen may have been the oxygen impurity in the helium used in the dry box during loading of the specimens which reacted with the sodium. The sodium used in these specimens had been gettered in zirconium chips for five days at 1600°F, which should have lowered its oxygen content to less than 5 ppm³. This small amount of oxygen would not be expected to result in the observed amount of UO_2 .

Metallographic examination of the uranium-5.2 w/o carbon alloy prior to testing showed a uniform structure of uranium monocarbide with platelets of uranium dicarbide. The surface of this specimen was not perfectly smooth prior to testing, but at high magnification showed an irregular jagged edge. After the compatibility test, the microstructure appeared to be unaffected. However, some surface cracking was observed, as seen in Figure II-18, which appeared quite similar to the type of cracking observed as a result of oxidation in moist air² or in NaK containing oxygen⁴.

Fig. II-14. Surface microstructure of sintered 4.4 ± 0.1 w/o carbon uranium carbide prior to the compatibility study.

Magnification 100

Fig. II-15. Surface microstructure of specimen shown in Fig. II-14 after 260 hours at 1500°F in sodium contained by niobium-1 w/o zirconium alloy. Note the slight attack of uranium in the surface grain boundaries.

Magnification 100

Fig. II-16. View showing reaction of free uranium in the surface grain boundaries after testing.

Magnification 250

Fig. II-17. High magnification view of surface grain boundaries. Reaction product is believed to be uranium dioxide.

Magnification 750

Fig. II-18. View of surface of 5.2 w/o carbon uranium carbide after 260 hours at 1500°F in sodium contained in niobium-1 w/o zirconium alloy capsules.

Magnification 100

Fig. II-19. Reaction layer on the inner surface of the niobium-1 w/o zirconium container after compatibility tests.

Magnification 500

It is interesting to note that no evidence of rapid carbon diffusion was detected in these tests. Such an occurrence would have been evidenced by an increase in the amount of free uranium in grain boundaries or by a decrease in the amount of uranium dicarbide in the grains.

Metallographic examination of the niobium-1 w/o zirconium cladding, in which the uranium-5.2 w/o carbon alloy was contained, showed the presence of a thin reaction layer on the inner surface of the niobium, as shown in Figure II-19. This reaction layer was less than 0.0001-in. thick. Identification of this layer was not definite. It could be either Nb_2C , from a carbon diffusion or a niobium oxide or nitride. However, if this layer is a carbide layer, its effect during the irradiation would not be expected to be severe, since the rate of reaction is a linear function of the square root of time at temperature. No reaction layer was detected on the inner surface of the cladding on the uranium-4.4 w/o carbon alloy.

The results of these compatibility tests showed that hyperstoichiometric uranium carbide was decarburized and that free uranium in hypostoichiometric uranium carbide was oxidized by sodium in this material system. There was apparently sufficient residual oxygen left in the sodium to result in oxidation of the free uranium at the grain boundaries in the hypostoichiometric uranium carbide, producing uranium dioxide. Although these tests indicated the attack was of minor significance, the program was revised to insure that the best data are obtained by including one capsule which will be fabricated to contain the series of five specimens separately canned under a helium cover. The other two capsules will be fabricated as originally planned; that is, with sodium as the heat transfer media.

The assembly of the capsules is progressing at a rate which will permit two of the capsules to be inserted in the test reactor on February 19, 1962, and the third on March 19, 1962.

REFERENCES

1. Liquid Metals Handbook, June, 1952, 2nd Edition.
2. Rough, F. A., Chubb, W., "An Evaluation of Data on Nuclear Carbides," BMI-1441, May 31, 1960.
3. Hinze, R. B., "Control of Oxygen Concentration in Large Sodium Systems," NAA-SR-3638, December 1, 1959.
4. Rough, F. A., Chubb, W., "Progress on the Development of Uranium Carbide-Type Fuels," BMI-1488, December 27, 1960.