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LOS ALAMOS of the NEW MEXICO
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SOLID SOLUTION CARBIDES
OF URANIUM AND ZIRCONIUM

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LOS ALAMOS ██████████ of the ██████████ NEW MEXICO
University of California

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**SOLID SOLUTION CARBIDES
OF URANIUM AND ZIRCONIUM**

by

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ABSTRACT

This report includes a summary of various chemical reaction techniques used for the production of $(\text{UC})_x(\text{ZrC})_y$ powder, and the processes used to prepare intermediate raw materials used in certain of these techniques. Also reported are the results of analytical evaluations of the quality of the product prepared by each technique. A detailed account is given of the arc-melting of elemental constituents and of the subsequent thermal treatments used to remove extraneous phases. Analytical results are reported for the powders produced from arc-melted buttons, showing the reproducibility attainable by this procedure.

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CHAPTER I

INTRODUCTION

Carbides formed by low temperature reactions, high temperature reactions, low temperature plus high temperature reactions, and bomb (exothermic) reactions yielded products that varied greatly from desired stoichiometry. In no case was the reaction time at temperature of sufficient duration to permit complete solution of the alloy mixture.

Carbides of uranium and zirconium in solid solution having various uranium contents are of interest as a nuclear material capable of functioning at extremely high temperatures. Sub-solidus transformations, such as phase changes or precipitations, impose limitations on the practical applications of these materials. For reasons of compatibility, stoichiometric UC-ZrC solid solutions are essential; i.e., vestigial segregates such as free carbon and secondary phases such as U_2C_3 or UC_2 cannot be tolerated.

The combination of arc-melting and homogenization thermal treatment provides a means for producing high purity (UC)(ZrC) of desired stoichiometry. The feasibility of making solid solution (UC)(ZrC) that is free of extraneous phases has been fully demonstrated. This technique may be applicable to other compounds where high purity and close control of stoichiometry is desired.

CHAPTER II

RAW MATERIALS

A. Uranium Metal:

The starting material for U^{235} and U^{238} was 0.020 in. and 0.080 in. sheet, respectively. A typical analysis of each material follows:

	<u>Li</u>	<u>Be</u>	<u>B</u>	<u>Na</u>	<u>Mg</u>	<u>Al</u>	<u>Si</u>	<u>Ca</u>	<u>V</u>	<u>Cr</u>	<u>Mn</u>
U^{235}	20	0.1	0.2	1	4	1	70	2	20	1	2
U^{238}	0.1	0.1	0.2	3	1	7	150	2	20	1	2
	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Mo</u>	<u>Sn</u>	<u>Pb</u>	<u>C</u>	<u>O₂</u>	<u>N₂</u>	
U^{235}	15	5	20	2	30	1	1	100	40	20	
U^{238}	70	5	10	10	25	1	50	200	25	30	

All values reported as parts per million (ppm).

B. Uranium Hydride (UH_3):

The uranium sheet was electropolished and subsequently given an HNO_3 etch prior to subsequent processing. The metal strips were immediately loaded into a 2 in. I.D. pyrex furnace tube. The system was evacuated to 10^{-5} torr, outgassed at 400-450°C, then cooled to 260°C, at which point hydrogen gas at just under 1 atm pressure was admitted.

The hydrogen used was either the ultra high purity grade (Sigma 10 ppm impurities) or was tank hydrogen purified by passing the gas through a De Oxo unit, a BaO drying column, and a uranium metal chip purifying train at 600-700°C.

After hydriding, the powder was dehydrided under vacuum at 400°C and was subsequently rehydrided to form a loose powder. Upon completion of the rehydriding, the reaction tube was evacuated at room temperature and transferred to the air lock of the dry box.

A typical dry box train is shown in Fig. 1. As is evident in the photograph the two dry boxes are connected by a vacuum lock. Shown in Fig. 2 are some of the items used in the dry box for comminution and storage of powders. The material is loaded into the lock and the lock evacuated and back-purged with helium twice and sampled for oxygen before the material is transferred to the working area of the dry box. Utilization of this vacuum lock obviates the necessity of purging the dry box each time entry into it is made. The helium inlet and gas sampling tubes for oxygen determination were at the top of the dry box and vacuum lock. A Beckman model E-2 oxygen analyzer was used to determine the oxygen content of the helium atmosphere. This analyzer measures oxygen content in excess of that in the standard helium sample. The instrument was standardized against the helium being used to back-fill the dry box.

The contents were removed from the tube, hand-crushed with a WC mortar and pestle, screened through -325 mesh, sampled for analysis, and bottled in plastic containers for storage in the dry box. The analytical results of several runs follow:

<u>Powder Lot No.</u>	<u>U, %</u>	<u>O₂, ppm</u>	<u>N₂, ppm</u>
23	97.35	9,200	2,500
26	97.77	9,000	1,100
90	97.62	6,400	
104	98.24	10,100	700
124	98.00	7,200	
128	97.70	8,200	
129	97.20	12,000	
134	97.40	9,200	
155	98.10	16,500	
156	98.40	17,000	
158	97.50	18,000	

It is evident from the data that this technique or the equipment employed leaves much to be desired, in that the oxygen content was extremely high, varying from a minimum of 6,400 ppm to as high as 18,000 ppm. It is obvious that the UH_3 is an excellent getter for oxygen.

It was noted that the gas sampling tube was at the top of the dry box. Since helium is lighter than air it is possible that the sample removed would not be representative of the atmosphere at the bottom of the dry box. All crushing and screening operations were performed on the floor of the dry box and the powder could have picked up oxygen during the

Fig. 1. Dry box train used for powder processing.

Fig. 2. Items used in dry box train for comminution and storage of powders.

powder processing. All raw materials and chemically reacted carbide powders were processed using this equipment and procedure.

C. Uranium Powder:

Uranium powder was made by the same procedure as was the UH_3 , except that it was given a final dehydriding treatment in vacuum at 400°C . The resulting powder was crushed, screened, weighed, and sampled for analysis, and the balance was bottled for dry box storage.

Typical analysis of uranium powder follows:

<u>Powder Lot No.</u>	<u>U, %</u>	<u>O₂, ppm</u>	<u>C, ppm</u>
21	99.25	4,700	700
25	99.76	2,500	
38	99.90	2,400	
70	99.39	2,900	500

It appears evident that the final dehydriding treatment in vacuum lowers the oxygen content of the resulting uranium powder as compared with the amount of oxygen still present in the UH_3 discussed previously.

D. Uranium Carbide (UC):

Initially, the UC was made by the reaction of uranium and carbon powders. These powders were roll-blended for 4 hr in a glass jar fitted with aluminum tumble wires. The blended powders were poured into a plastisol bag, plugged, and removed from the helium atmosphere dry box. The loaded bag was then hydrostatically pressed at 30,000 psi to yield a rod 3/4-1 in. dia by 4-6 in. long. Oil was wiped off the surface of the bag and the bag and pressing were returned to the dry box. The pressed rod was removed from the bag, placed in a quartz reaction tube, removed from the dry box, and sealed into a glass vacuum system with a tube furnace for heating of the charge. The charge was heated to a temperature of $1150-1160^\circ\text{C}$ for a reaction time which ranged from 4-8 hr. Following reaction, the loaded quartz tube was returned to the dry box and the slug was processed to powder by hand-crushing with a WC mortar and pestle and subsequent ball-milling in a uranium-lined ball mill with uranium balls. The analytical results of several runs follow:

Powder Lot No.	U, %	Total C, %	Free C, ppm	N ₂ , ppm	O ₂ , ppm	Reaction	
						Temp, °C	Time hr
28	95.07	4.70		400	2,300	1160	8
30	94.76	4.71		1,100	4,600	1160	8
68	95.20	4.72	1,300		4,200	1160	4
84	94.98	4.74	900		2,800	1160	4
92	94.62	5.14	6,400		3,700	1150	4
93	94.62	4.96	5,400		6,700	1150	4
101	94.21	5.04	10,040	200	4,700	1160	8
102	94.45	4.86	7,100	200	4,400	1160	8
103	94.77	4.67	2,000	1,200	6,000	1160	8
147	94.00	5.07	900		8,300	1160	8

The results above show a wide range in stoichiometry as well as excessive amounts of free carbon and varying high oxygen content. In view of these results, it was decided to investigate arc-melting for making UC. Details of the arc-melting equipment are described in Section B of Chapter III.

Four 50 g charges were placed in a five cavity copper hearth of a button arc-melting furnace. Each charge consisted of the stoichiometric quantity of electropolished uranium sheet and spectrographic carbon rod. Zirconium metal was placed in the fifth cavity to be used as a getter button. A 2% thoriated tungsten tip was used as the cathode. Before melting, the furnace was evacuated and back-filled with argon to a pressure of 19 in. Hg absolute. The argon was purified by passing it through a BaO drying column and a zirconium sponge furnace which was operated at 800°C.

A high frequency arc starter was used to initiate the arc on the zirconium getter button. After the zirconium getter button was melted, the arc was directed from cavity to cavity until all charges had been melted. Melting on each charge was 1 min for each side of each button for a total of six melts. Magnetic stirring was not used for the first melt, but maximum stirring power (approximately 45 gauss) was used for all succeeding melts to promote homogenization of the button.

The arc-melted buttons were placed in a dry box system identical to that described previously. Entry into the box was through a vacuum lock which was double evacuated and back-filled with argon, and the oxygen content was determined before entry into the dry box proper.

A WC mortar and pestle were used to crush the arc-melted buttons to -20 mesh powder. The powder was screened through 140 mesh. The +140 mesh powder was ball-milled for 3 min in a uranium mill with uranium balls.

Milling and screening was repeated until all of the material passed through the 140 mesh screen.

The powder was then screened into two fractions, -140 +325 mesh and -325 mesh. Each fraction was solution-treated at 2000°C for 4 hr in vacuum (10^{-5} torr) to reduce the free carbon content and to further homogenize the UC. Typical analysis of UC powder prepared by this technique follows:

<u>UC Powder</u>	<u>U, %</u>	<u>Total C, %</u>	<u>Free C, ppm</u>	<u>O₂, ppm</u>
Nominal	95.2 ± 0.02	4.8 ± 0.03		
-140 +325 mesh	94.69	4.76	900	1,200
-325 mesh	94.74	4.85	500	1,200

It is evident from these analyses that the arc-melting technique is far superior to the previously discussed technique. The major constituents are more nearly stoichiometric and the interstitials are reduced to what is considered a reasonable level.

E. Zirconium Metal:

The zirconium metal (hafnium free) was purchased as iodide crystal bar through the AEC office in Pittsburgh. The bars, approximately 3/4 in. hexagonal x 4 ft. long, were broken into 3/4 in. lengths and acid cleaned in a HF + 5% HNO₃ solution to remove the oxide scale from the surface.

The material was button arc-melted into plates 2-1/4 in. x 3-1/4 in. x 1/2 in. Each plate was melted four times and was flipped over between melts. Magnetic stirring (15 gauss) was used to stabilize the arc. The plate was cold-rolled to 0.090 in. thick sheet, cleaned in acid, washed and dried with acetone, and sheared for charge material. A typical analysis of the cleaned sheet follows:

<u>Li</u>	<u>Be</u>	<u>B</u>	<u>Na</u>	<u>Mg</u>	<u>Al</u>	<u>Si</u>	<u>K</u>	<u>Ca</u>	<u>Ti</u>	<u>V</u>	<u>Cr</u>	<u>Mn</u>	<u>Fe</u>	<u>Co</u>
10	3	3	30	3	30	10	30	30	100	100	10	10	100	30
<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>Sr</u>	<u>Nb</u>	<u>Mo</u>	<u>Ag</u>	<u>Cd</u>	<u>Sn</u>	<u>Ba</u>	<u>Hf</u>	<u>Pb</u>	<u>Bi</u>		
30	10	100	30	1,000	100	3	3	30	10	200	100	30		

All values are reported as ppm.

F. Zirconium Hydride (ZrH_2):

The procedure for ZrH_2 was similar to that for UH_3 , except that the zirconium metal was double hydrided at 600-700°C.³ The powder was crushed, screened, and sampled for analysis, and the balance was bottled for dry box storage.

Analysis of several lots follows:

<u>Lot No.</u>	<u>Zr, %</u>	<u>O₂, ppm</u>	<u>N₂, ppm</u>	<u>H₂</u>
15	98.52	2,200		Balance
18	97.82	1,400		Balance
22	96.30	1,400	500	Balance
27	97.97	500	200	Balance

G. Zirconium Metal Powder:

Zirconium metal powder was made by the same procedure as the ZrH_2 , except that it was given a final dehydriding treatment in vacuum at 800°C. This product did not require crushing and was screened and bottled for dry box storage.

H. Zirconium Carbide (ZrC):

The ZrC used was commercial ZrC (Shieldalloy), the analysis of which follows:

<u>Lot No.</u>	<u>Zr, %</u>	<u>Total C</u>	<u>Free C, ppm</u>	<u>N₂, ppm</u>	<u>O₂, ppm</u>
50	87.79	11.35	1,200	80	6,700

I. Carbon:

The carbon used in the preparations was grade SP-1 special high purity spectrographic graphite obtained from National Carbon Co. This material was screened through 325 mesh with no crushing operation. Powder larger than 325 mesh was discarded.

CHAPTER III

EXPERIMENTAL PROCEDURES

A. Powder Preparation $(\text{UC})_x(\text{ZrC})_y$:

When considering the use of the various UC-ZrC mixtures, distinct limitations are immediately imposed. The final product must be radio-graphically sound, reproducible, and analytically correct. It must be as free of as many contaminants as is possible, and must be capable of being fabricated by a technique applicable to production runs.

A number of approaches were available for the making of UC-ZrC solid solution mixtures. To date, every possible combination of U, UH_3 , UC, C, Zr, ZrH_2 , and ZrC has been tried. These mixtures have been combined by low temperature reactions, high temperature reactions, low temperature plus high temperature reactions, and bomb (exothermic) reactions yielding $(\text{UC})_x(\text{ZrC})_y$, with widely varying degrees of success. The most notable problem in the various procedures used was lack of reproducibility. Successful runs, when repeated as closely as possible, failed to yield identical results.

1. Low Temperature Reactions:

Mixtures prepared by low temperature reactions were generally blended for 4 hr and hydrostatically pressed to a right cylinder at 30,000 psi. This compact was reacted at 1160°C for up to 8 hr duration in vacuum. The results of the various mixtures are presented in Table I.

2. High Temperature Reactions:

These mixtures were prepared in essentially the same way as the above, except that the reaction temperature was 1650 - 1750°C for 2 hr. This reaction was usually carried out in a vacuum hot-press apparatus with no pressure applied. The results are presented in Table II.

TABLE I
LOW TEMPERATURE REACTIONS TO FORM $(UC)_x(ZrC)_y$

Mole %	Lot No.	Reactants	U, %	Zr, %	Total C, %	Free C, ppm	N ₂ , ppm	O ₂ , ppm	Reaction Temp, °C	Reaction Time, hr	Remarks
$(U^{238}C)_{.50}(ZrC)_{.50}$	Nominal		67.38 ± 0.3	25.82 ± 0.3	6.80 ± 0.03						
	31	U + ZrH ₂ + C	64.13	28.60	6.78	11,700	400	6,000	1160	8	
	43	U + UC + ZrC	64.50	28.15	7.02	6,200		5,300	1160	8	
	40	U + ZrC + C	63.80	28.40	6.96	5,800		5,100	1160	8	
	56		63.80	28.10	6.98	2,400			1300	8	
	33	UH ₃ + ZrH ₂ + C	63.40	29.80	6.82	9,000	700	6,400	1160	8	
	34		63.40	27.30	6.64	13,800	800	5,200	1160	8	Ni added
	41	UH ₃ + ZrC + C	63.90	28.40	7.08	2,800	600	6,300	1160	8	
	55		63.80	28.30	6.92	6,200			1300	8	
	46	UC + ZrH ₂ + C	64.20	28.30	6.80	5,000		5,900	1160	8	
	54		64.70	28.10	6.93	6,800			1300	8	
	66		63.60	28.30	6.90		700	11,900	1160	8	
	67		63.20	28.50	7.10	19,400		7,300	1160	8	
	71		64.30	28.51	6.99	500		2,100	1160	8	
	71A		64.50	28.44	6.94	800		3,400	1160	8	
	77		64.00	28.73	6.91	500		4,000	1160	8	
	80		63.80	28.00	7.33	14,100			1160	8	
	91		64.20	27.90	7.26	4,000		5,300	1160	6	
	36	UC + ZrC	65.30	27.30	7.16	15,400	500	4,600	1160	8	
	37		63.10	27.10	6.83	8,400	600	4,600	1160	8	Ni added
$(U^{238}C)_{.30}(ZrC)_{.70}$	Nominal		48.47 ± 0.3	43.38 ± 0.3	8.15 ± 0.03						
	83	UC + ZrH ₂ + C	49.60	41.20	8.43	23,700		4,100	1200	8	
$(U^{235}C)_{.30}(ZrC)_{.70}$	Nominal		48.15 ± 0.3	43.65 ± 0.3	8.20 ± 0.03						
	110B	UH ₃ + ZrH ₂ + C	48.50	43.50	7.96	1,100		5,100	1100	8	
$(U^{238}C)_{.18}(ZrC)_{.82}$	Nominal		33.05 ± 0.3	57.70 ± 0.3	9.25 ± 0.03						
	164	UC + ZrC	31.50	57.70	8.40	6,500			1160	6	
$(U^{235}C)_{.18}(ZrC)_{.82}$	Nominal		32.78 ± 0.3	57.94 ± 0.3	9.28 ± 0.03						
	165	UC + ZrC	29.40	59.70	8.00	6,700			1160	6	

TABLE II

HIGH TEMPERATURE REACTIONS TO FORM $(UC)_x(ZrC)_y$

Mole %	Lot No.	Reactants	U, %	Zr, %	Total C, %	Free C, ppm	O ₂ , ppm	Reaction Temp, °C	Reaction Time, hr	Remarks
$(U^{238}C)_{.50}(ZrC)_{.50}$	Nominal		67.38 ± 0.3	25.82 ± 0.3	6.80 ± 0.03					
	89A	UC + ZrH ₂ + C	63.90	28.60	7.06	3,300	4,600	1600	2	Hot pressed
$(U^{238}C)_{.30}(ZrC)_{.70}$	Nominal		48.47 ± 0.3	43.38 ± 0.3	8.15 ± 0.03					
	94	U + ZrH ₂ + C	48.20	42.90	8.45	7,600	3,000	1750	2	Hot pressed
	137		48.00	43.30	8.05	1,900	4,600	1650	3	
	96	U + ZrC + C	48.00	43.80	8.29	3,200	3,000	1700	2	
	95	UH ₃ + ZrH ₂ + C	47.80	43.40	8.43	4,200	2,400	1750	2	Hot pressed
$(U^{235}C)_{.30}(ZrC)_{.70}$	Nominal		48.15 ± 0.3	43.65 ± 0.3	8.20 ± 0.03					
	97	U + ZrH ₂ + C	49.30	42.50	8.24	3,200	3,000	1700	2	Hot pressed
	105	UH ₃ + ZrH ₂ + C	47.40	43.70	8.24	2,700		1750	2	Hot pressed
	107A		47.40	43.60	8.26	2,700	4,600	1700	2	Hot pressed
	141		47.00	44.00	7.78	2,700	8,900	1650	2	Hot pressed
	111		47.70	42.60	8.21	600	5,300	1650	2	Hot pressed

3. Low Temperature Plus High Temperature Reactions:

The mixtures were blended and hydrostatically pressed as previously described. The compact was then sintered at 1160-1300°C for periods of 4-8 hr in vacuum. The compact was then transferred to the vacuum hot-press unit where it was heated to 1650-1850°C for times of 2-3 hr. The analytical results of material prepared by this technique are presented in Table III.

4. Bomb (Exothermic) Reactions:

Again the mixtures were blended and pressed as previously described. The pressed compact was loaded into a quartz tube furnace, sealed, evacuated, and heated slowly to 800°C. At 400°C there was a dwell time of 2 or more hours to dehydride the UH_3 and again at 800°C to decompose the ZrH_2 .

When dehydriding was essentially complete (8-12 hr) the reaction vessel was left under vacuum, cooled, removed from the vacuum line, and readmitted to the dry box by the same procedures previously described. The compact was then removed from the reaction tube and loaded into a clean tool steel bomb reaction chamber containing an Al_2O_3 or MgO crucible. The bomb was closed, sealed, and vacuum leak tested, after which an inert atmosphere (helium or argon) was admitted to the bomb. It was then sealed and removed from the dry box. The bomb was subsequently induction-heated within a protective shell to 800-900°C, at which point an exothermic reaction was initiated which was monitored by means of thermocouple and pressure readings.

Upon cooling, the bomb was readmitted to the dry box and the compact was removed. The compact was then crushed and screened and sampled for analysis, and the balance was bottled for dry box storage. The analytical results of material prepared in this fashion are shown in Table IV.

5. Discussion:

The conclusions derived from Tables I through IV are listed as follows:

- 1) All of the techniques described resulted in stoichiometry which varied over a wide range and far beyond acceptable standard deviations.
- 2) In nearly all cases the interstitials (free carbon and oxygen) were excessive. This is a carry-over from the production of the various raw powders used in making the $(\text{UC})_x(\text{ZrC})_y$ combinations.
- 3) Countless numbers of steps were involved in obtaining the final product, any of which could have been responsible for oxygen pickup.

TABLE III

LOW TEMPERATURE PLUS HIGH TEMPERATURE REACTIONS TO FORM $(UC)_x(ZrC)_y$

Mole %	Lot No.	Reactants	U, %	Zr, %	Total C, %	Free C, ppm	O ₂ , ppm	Reaction Temp, °C	Reaction Time, hr	Remarks
$(U^{238}C)_{.50}(ZrC)_{.50}$	Nominal		67.38 ± 0.3	25.82 ± 0.3	6.80 ± 0.03					
	115	UC + ZrC	66.30	25.20	6.50	500		1160	8	
$(U^{238}C)_{.30}(ZrC)_{.70}$	Nominal		48.47 ± 0.3	43.38 ± 0.3	8.15 ± 0.03					
	138	U + ZrC + C	48.10	42.20	8.19	8,200	5,200	1100	4	
	120B	UH ₃ + ZrH ₂ + C	48.10	43.40	7.97	3,100	5,200	1700	2	Hot pressed
								1100	0.5	
	130		48.40	43.50	7.78	500	2,200	1650	2	
								1100	4	
	133		41.60	50.10	7.22	500	7,000	1850	3	
								1100	4	
								1875	3	
	127	UH ₃ + ZrC + C	48.00	42.90	7.85	4,200	2,400	1100	4	
								1700	3	
$(U^{235}C)_{.30}(ZrC)_{.70}$	83A	UC + ZrH ₂ + C	49.60	41.50	8.46	7,700	5,000	1200	8	
	87A		48.20	43.00	8.01	8,000	2,700	1650	2	Hot pressed
								1300	4	
								1750	2	Hot pressed
$(U^{235}C)_{.30}(ZrC)_{.70}$	Nominal	48.15 ± 0.3	43.65 ± 0.3	8.20 ± 0.03						
	125	UC + ZrC	47.60	42.50	8.06	4,200	5,900	1100	8	
								1700	3	
	131	UH ₃ + ZrH ₂ + C	47.90	43.80	7.80	700	2,500	1100	4	
								1850	3	
$(U^{235}C)_{.30}(ZrC)_{.70}$	126	UC + Zr + C	47.60	43.70	7.97	1,600	3,500	1160	4	
								1675	3	

TABLE IV

BOMB (EXOTHERMIC) REACTIONS TO FORM $(UC)_x(ZrC)_y$

<u>Mole %</u>	<u>Lot No.</u>	<u>Reactants</u>	<u>U, %</u>	<u>Zr, %</u>	<u>Total C, %</u>	<u>Free C, ppm</u>	<u>O₂, ppm</u>	<u>Reaction Temp, °C</u>	<u>Solution Treatment</u>	
									<u>Temp, °C</u>	<u>Time, hr</u>
$(U^{238}C)_{.30}(ZrC)_{.70}$	Nominal		48.47 ± 0.3	43.38 ± 0.03	8.15 ± 0.03					
	149	U + ZrH ₂ + C	48.00	43.30	8.23	1,900	3,800	800		
$(U^{238}C)_{.18}(ZrC)_{.82}$	Nominal		33.05 ± 0.3	57.70 ± 0.3	9.25 ± 0.03					
	1109-P1	UF ₃ + ZrH ₂ + C	38.90	50.40	10.35	13,500	2,000	900		
	1109-P2A		37.30	52.00	10.63	14,200		850		
	1109-P2B		36.60	52.40	10.50	14,500		850		
	1109-P2C		37.10	52.10	10.29	15,500		850	2000°C	24
	1109-P3A		37.40	51.80	10.54	15,400		850		
	1109-P3B		36.80	52.50	10.34	17,000		850	2000°C	24

- 4) All dry box operations were performed in a helium atmosphere. However, the atmosphere sampling port was at the top of the dry box and it is quite possible that the atmosphere on the bed of the box was not represented by the sample analysis. This would, in part, account for some oxygen pickup.
- 5) In no case was the reaction time at temperature of sufficient duration to permit complete solution of the alloy mixture. It is possible that prolonged solution treatment at higher temperatures would have improved this situation.
- 6) It is quite obvious that the low temperature reactions were of too short a duration to permit complete alloying.
- 7) The stoichiometry of the high temperature and the low temperature plus high temperature reactions is markedly improved over that of the low temperature reaction, as indicated by the lower free carbon content. However, the time at temperature was of insufficient duration to permit complete solution of the mixtures.
- 8) An apparent error in calculating the charge of the bomb-reacted product is shown by the abnormally high total carbon content. However, the pressure, temperature, and reaction times were insufficient to permit complete alloying. Those lots which were solution-treated at 2000°C for 24 hr in vacuum resulted in no measurable improvement in stoichiometry.
- 9) In nearly all cases, microscopic examination showed the resulting powders to contain varying amounts of UC_2 , U_2C_3 , and free carbon. For reasons of compatibility, such extraneous phases cannot be tolerated.

It was apparent that solid solution carbide powders free of extraneous phases were difficult to prepare. After careful consideration it was decided that the powders would be made by arc-melting the elemental materials of uranium, zirconium, and carbon into button form and solution-treating the melted button to eliminate the cored structure which is typical of a cast material.

B. Arc-Melting UC-ZrC Solid Solution:

1. Arc-Melting Procedure:

The development of the arc-melting technique was not without its problems. A mass effect was evidenced in arc-melting 100 g buttons due to the very high melting point of the alloy and the quantity of material involved. This problem was eliminated by going to a smaller charge of 25 g.

The buttons were produced by arc-melting the elemental constituents. The charge consisted of stoichiometric quantities except for carbon which was 5% in excess to compensate for carbon loss by vaporization during melting. Actual melting procedure for these charges was six 5 min melts. The buttons were turned over after each melt and maximum magnetic stirring power (45 gauss) was used at all times to improve homogeneity. Figures 3 and 4 show closed and open views of the button arc-melting furnace used for this work. The charges were placed in the cavity and the furnace closed and evacuated to less than 1 μ . Zirconium metal was placed in one of the cavities and was used to strike the arc as well as act as a getter. Actual melting was performed in a purified argon atmosphere at a pressure of 19 in. Hg absolute. Barium oxide was used for moisture removal, and zirconium sponge at a temperature of 800°C was used to remove gaseous impurities from the argon gas.

2. Metallography of Arc-Melted $(\text{UC})_x(\text{ZrC})_y$:

As was previously stated, the first attempts at arc-melting UC-ZrC solid solution was not without its problems. Initial attempts were made to melt 100 g buttons. Figure 5 shows a cross-section of one of the buttons at approximately 2X magnification. Microscopic examination of this button showed four distinct areas, indicating the mass effect of this high melting material.

Figure 5a shows a region of the button which is essentially single phase UC-ZrC as well as regions of isolated areas of UC/UC₂ in a UC-ZrC matrix.

Figure 5b shows a UC-ZrC region with an excessive amount of free uranium in the grain boundaries. Figure 5c shows a single phase region containing free carbon and some UC/UC₂.

Figure 5d shows single phase matrix with a grain boundary phase of UC/UC₂.

The above was typical of all 100 g buttons examined. In addition, it was noted that the last area to solidify exhibited a single phase UC-ZrC cored structure. In light of these considerations it was decided to reduce the charge weight to 25 g. Immediately a marked improvement was noted in the arc-cast material. Figure 6a shows a cross section of a typical 25 g button at approximately 2X magnification. Microscopic examination showed essentially a single phase cored structure typical of a cast material, with less than 1.0% second phase present, as compared with as high as 10% or more in the 100 g buttons.

Figure 6b shows a single phase region typical of the last portion of the button to solidify. Figure 6c shows an area representative of the cored structure. It was estimated, as stated above, that there was less than 1.0% second phase (UC/UC₂, UC₃) in the button.

Fig. 3. View of the arc-melting furnace in the closed position.

Fig. 4. View of the arc-melting furnace in the open position.

Fig. 5. Photomacrograph of an arc-cast 100 g $(\text{UC})_x(\text{ZrC})_y$ button and photomicrographs of four distinct areas showing the mass effect of this high melting material.

Fig. 6. Photomacrograph of an arc-cast 25 g $(UC)_x(ZrC)_y$ button and photomicrographs showing a single phase region and a cored structure representative of this size button.

While there was no metallographic evidence of free carbon, analytical results showed that considerable free carbon was still present, as will be discussed later. Following solution treatment of the arc-cast button (25 g) both metallography and X-ray diffraction showed a single phase UC·ZrC solid solution. However, complete solution of the free carbon did not occur during this 2000°C, 24 hr vacuum treatment. Analytical results showed that, while free carbon content was reduced, considerable free carbon was still present. The benefits of homogenization are fully evident in the solution-treated button. However, the material was crushed through 20 mesh and further solution-treated at 2000°C for 24 hr in vacuum. Analytical results of the solution-treated powder showed less than 500 ppm free carbon present, which is the lower limit of the analytical technique used.

Figure 7 is a typical microstructure of a solution-treated button showing a single phase equiaxed structure free of any extraneous phases. Figure 8 shows a typical structure of the solution-treated powder.

It was stated that there were isolated areas in these buttons containing a second phase. Figure 9 shows typical areas from three arc-cast buttons in the as-cast and button solution-treated condition. Note the generation of voids in the solution-treated buttons where the second phase was present originally. Figure 9f shows that all of the second phase was not removed during solution-treatment of the button; however, the quantity remaining was estimated to be less than 0.1%.

In order to develop a more practical thermal treatment, an attempt was made to eliminate the button solution-treatment. Figure 10 shows the microstructure of powder in the as-cast and solution-treated condition. Figure 10a shows the presence of second phase in the as-cast crushed condition. Figure 10b shows essentially a single phase material with voids where the second phase was originally. While the feasibility of a single solution-treatment was demonstrated, it was felt that in the interest of reproducibility and homogeneity the duplex treatment would be more reliable.

3. Evaluation of Arc-Melted $(\text{UC})_x(\text{ZrC})_y$:

Table V contains the results obtained on individual control buttons selected from the respective powder lots in the arc-cast condition. It becomes immediately apparent that a wide variation in chemistry exists. This wide spread is attributed to a sampling condition since a portion of the button was cut off for metallography and the remainder crushed and submitted for chemical analysis and X-ray diffraction phase identification. Perhaps more significant is the wide variation in free carbon in the as-cast button. Metallography of these buttons showed solid solution $(\text{UC})_{.18}(\text{ZrC})_{.82}$ plus 1-8% extraneous phases. These second

Fig. 7. Photomicrograph of an arc-cast 25 g $(UC)_x(ZrC)_y$ button following solution-treatment at $2000^{\circ}C$ for 24 hr in vacuum. ~100X

Fig. 8. Photomicrograph of the above button following crushing through 20 mesh and further solution-treatment at $2000^{\circ}C$ for 24 hr in vacuum. ~500X

(a)

(d)

(b)

(e)

(c)

Arc-Cast

(f)

Solution Treated

Fig. 9. Photomicrographs of three buttons in the arc-cast and solution-treated conditions. ~ 500X

(a) Arc-cast and crushed through 20 mesh.

(b) Solution treated at 2000°C for 24 hr in vacuum.

Fig. 10. Photomicrographs of powder in the as-cast and solution-treated conditions. ~ 500X

TABLE V
ANALYTICAL RESULTS OF ARC-MELTED $(UC)_x(ZrC)_y$
Arc-Cast Condition

Powder Lot	Arc-Cast Button Size, g	U, %	Zr, %	Total C, %	Free C, ppm	Metallographic Phase Identification ^a
$(U^{235}C)_{.18}(ZrC)_{.82}$	Nominal	32.78 ± 0.03	57.94 ± 0.03	9.28 ± 0.03		
1112-2-8	25	31.5	58.6	9.31	800	SS + 2-4% EP
18	25	30.8	59.5	8.92	3,700	SS + 2-4% EP
28	25	35.5	55.2	8.77	2,800	SS + 2-3% EP
38	25	36.7	59.3	9.42	1,700	SS + 3-5% EP
48	25	33.1	56.3	10.03	10,600	SS + 2-4% EP
58	25	30.0	58.6	9.79	1,700	SS + 1-2% EP
68	25	29.5	58.8	8.69	1,000	SS + 4-6% EP
78	25	31.3	57.5	9.32	< 500	SS + 4-5% EP
88	25	33.9	55.9	7.78	< 500	SS + 6-8% EP
98	25	31.8	57.8	9.50	1,600	SS + 3-5% EP
108	25	32.9	56.0	8.70	< 500	SS + 1% EP
1114-78	25	33.1	58.5	8.70	< 500	
98	25	32.3	57.9	9.80	1,500	
$(U^{238}C)_{.18}(ZrC)_{.82}$	Nominal	33.05 ± 0.03	57.70 ± 0.03	9.25 ± 0.03		
1111-6	50	30.7	58.2	9.53	< 500	SS + 2-4% EP
16	50	32.0	57.9	8.70	< 500	SS + 0.1-0.2% EP
26	50	32.7	57.5	8.98	< 500	SS + approx. 1% EP
36	50	31.2	58.9	9.33	< 500	SS + 3-4% EP
46	50	32.9	56.8	9.50	1,500	SS + 1-2% EP

^aSS - solid solution $(UC)_x(ZrC)_y$. EP - extraneous phases, which generally consisted of approximately 90% grey phase (presumably carbon) and 10% yellow brown phase (presumably UC/UC_2).

phases generally consisted of approximately 90% grey phase (presumably carbon) and 10% yellow brown phase (presumably UC/UC₂).

In view of the above, it became necessary to impose a homogenization thermal treatment. This treatment consisted of solution-treating the buttons in vacuum at 2000°C for 24 hr. The solution-treated buttons were crushed through 20 mesh, blended, and sampled for chemistry, X-ray diffraction, and metallography. A marked improvement as a result of solution-treatment is apparent as is shown in Table VI; however, free carbon is still quite high and some extraneous phases are still present.

All (UC)_x(ZrC)_y arc-melted buttons were crushed in the dry box system previously described. An argon atmosphere was used because of the difficulties discussed earlier regarding the use of helium relative to the location of the gas sampling tube. A WC mortar and pestle were used to crush the arc-melted buttons to -20 mesh powder. After solution-treatment the powder was screened through 200 mesh. All +200 mesh powder was ball-milled in a uranium mill with uranium balls. Milling and screening was repeated on the +200 mesh material until all of it passed through the 200 mesh screen.

Treatment for 24 hr at 2000°C in vacuum was arbitrarily chosen, and the results show that neither temperature nor time were sufficient for complete homogenization. X-ray diffraction showed the material to be single phase, solid solution, face-centered cubic, with lattice dimensions corresponding to those of a (UZr)C solid solution phase. The diffuseness of the high-angle diffraction lines in the diffraction photographs suggests some compositional variation on a micro scale.

A second thermal treatment consisting of 2000°C for 24 hr in vacuum was imposed on the crushed powder in an attempt to further homogenize the powder and eliminate the extraneous phases. The advantages of such a treatment become immediately apparent upon examining the data in Table VII. The chemistry of the major constituents is approaching the desired stoichiometry, free carbon has been greatly reduced, and in all cases metallography and X-ray diffraction show the material to be single phase -- the X-ray diffraction showed sharp high angle diffraction lines. It should be pointed out that 500 ppm carbon is the minimum quantity which can be accurately determined by present analytical techniques. The interstitial content (oxygen) is quite low in comparison to solid solution (UC)_x(ZrC)_y made by various other techniques. The feasibility of making solid solution (UC)_x(ZrC)_y free of extraneous phases has been fully demonstrated.

TABLE VI

ANALYTICAL RESULTS OF ARC-MELTED $(\text{UC})_x(\text{ZrC})_y$
Arc-Cast and Sol.-Treated 24 hr at 2000°C in Vac.

Powder Lot	Arc-Cast Button Size, g	U, %	Zr, %	Total C, %	Free C, ppm	O ₂ , ppm	X-ray diff. ^a	Metallographic Phase Identification ^b
$(\text{U}^{235}\text{C})_{.18}(\text{ZrC})_{.82}$	Nominal	32.78 ± 0.03	57.94 ± 0.03	9.28 ± 0.03				
1107 - P1	60-95	32.8	57.7	8.61	< 500		SPSS	SS + < 0.5% EP
1112 - P1	25	32.5	57.9	9.23	1,800		SPSS	SS + approx. 1% EP
P2	25	31.8	57.8	9.20	4,700		SPSS	
P3	25	32.4	57.6	9.41			SPSS	SS + 1-2% EP
114	25	31.6	59.4	9.30	1,100			SS + 0.1 to 0.5 EP
115	25	31.3	58.9	9.82	5,300			SS + 1-2% EP
1114-2-1	25	32.5	57.8	9.25				
2	25	32.5	58.0	9.37				
3	25	32.6	57.7	9.40				
$(\text{U}^{238}\text{C})_{.18}(\text{ZrC})_{.82}$	Nominal	33.05 ± 0.03	57.70 ± 0.03	9.25 ± 0.03				
1111 - P1	25	32.6	57.5	9.30	1,700		SPSS	SS + 1-2% EP
1113 - P1	50	32.1	58.1	9.44	6,600	500	SPSS	SS + > 2% EP
1115 - P1	25	32.8	58.1	9.30	1,800			
1116 - P1	25	33.0	57.9	9.31	1,300		SPSS	SS + < 1% EP
- P2	25	32.9	57.8	9.17	900		SPSS	SS + < 1% EP

^aSPSS - single phase solid solution $(\text{UC})_x(\text{ZrC})_y$.

^bSS - solid solution $(\text{UC})_x(\text{ZrC})_y$. EP - extraneous phases, which generally consisted of approximately 90% grey phase (presumably carbon) and 10% yellow brown phase (presumably UC/UC₂).

TABLE VII

ANALYTICAL RESULTS OF ARC-MELTED $(\text{UC})_x(\text{ZrC})_y$

Arc-Cast and Sol.-Treated as Button 24 hr at 2000°C in Vac. + Crushed and Sol.-Treated as Powder 24 hr at 2000°C in Vac.

Powder Lot	Arc-Cast Button Size, g	U, %	Zr, %	Total C, %	Free C, ppm	O ₂ , ppm	X-ray ^a Diff.	Metallographic Phase Identification ^a
$(\text{U}^{235})_{.18}(\text{ZrC})_{.82}$	Nominal	32.78 ± 0.03	57.94 ± 0.03	9.28 ± 0.03				
1112 - FLC	25	32.8	57.8	9.24	< 500		SPSS	SPSS
P3B	25	32.9	57.4	9.24	600		SPSS	SPSS
1114-3-1	25	31.9	58.2	9.24	680		SPSS	SPSS
2	25	32.0	57.8	9.28	< 500		SPSS	SPSS
3	25	32.6	57.1	9.32	680		SPSS	SPSS
4	25	32.4	56.6	9.34	820		SPSS	SPSS
FLB	25	32.3	57.5	9.26	< 500	700	SPSS	SPSS
$(\text{U}^{238}\text{C})_{.18}(\text{ZrC})_{.82}$	Nominal	33.05 ± 0.03	57.70 ± 0.03	9.25 ± 0.03				
1111 - FLB	25	33.3	57.0	9.20	< 500		SPSS	SPSS
1115 - 1	25	33.3	57.5	9.21	540		SPSS	SPSS
2	25	33.6	57.3	9.15	< 500		SPSS	SPSS
3	25	33.5	57.1	9.22	< 500		SPSS	SPSS
L	25	33.3	57.3	9.24	< 500		SPSS	SPSS
FLB	25	33.6	57.2	9.18	520	1,120	SPSS	SPSS
1116 - FLB	25	32.8	57.7	9.19	< 500		SPSS	SPSS

^aSPSS - single phase solid solution $(\text{UC})_x(\text{ZrC})_y$.