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CORRELATION OF COMPOSITION AND
HEAT-TREATMENT WITH THE MICROSTRUCTURES
OF URANIUM CARBIDES

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OAK RIDGE NATIONAL LABORATORY
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CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

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ABSTRACT

Optical photomicrographs, at magnifications of 250X and 1000X, of 78 different arc-cast and heat-treated uranium carbide specimens are presented. Specimens with total-C/U atom ratios ranging from 0.4 to 2.4 (2 to 11 wt % carbon) are included; however, the major emphasis is on the monocarbide-dicarbide, monocarbide-sesquicarbide, and sesquicarbide-dicarbide regions of the phase diagram. The phases present were identified by X-ray diffraction analysis of the specimens at room temperature and, in many instances, were further confirmed by determining the products of hydrolysis. The specimens were analyzed for uranium, total carbon, free carbon, oxygen, nitrogen, and tungsten to provide as complete a characterization as possible.

1. INTRODUCTION

Interest has developed in the use of uranium carbides as fuels for nuclear reactors because these compounds exhibit stability at high temperatures, favorable heat-transfer characteristics, high burnup potential, high uranium density, and good thermionic emission properties for the direct conversion of fission heat to electricity. Uranium monocarbide elements have been proposed for the Sodium/Graphite,¹ the Heavy-Water-Moderated Organic-Cooled,²⁻⁴ and the Organique Eau Lourde⁵ reactors, while mixed Pu-U monocarbide is under consideration for the Liquid Metal Cooled Fast Breeder Reactor.⁶ The fuel for the Peach Bottom reactor⁷ consists of pyrolytic carbon-coated Th-U dicarbide particles in a graphite matrix. Pure uranium sesquicarbide has not yet been proposed for use as a fuel; however, hyperstoichiometric uranium monocarbide fuels probably will contain a little sesquicarbide since the excess carbon, which is initially present as dicarbide, will react to form sesquicarbide when the fuel is heated in the range of 1765 to 1275°C⁸ (and probably at even lower temperatures).

Microstructural examination is a useful method for analyzing carbides. It provides information concerning the physical state (grain size, presence of cracks or voids, etc.) and, by comparison with standards, can often yield a good estimate of the chemical composition. It is probably the most effective technique available for analyzing coated-particle fuels in which quantitative chemical or mechanical separation of the coating from the kernel is virtually impossible. However, a good reference collection of uranium carbide photomicrographs for analytical purposes is not available. Although photomicrographs are scattered throughout the available literature on uranium carbides, the exact compositions of the specimens pictured are usually not given. In addition, many of the photomicrographs were reduced during printing to sizes that bear little relationship to the conventional microscope magnifications. Some of the most interesting papers on carbide microstructure are those by Mallett et al.,⁹ Gray et al.,¹⁰ and Accary.¹¹

This report presents a collection of optical photomicrographs at magnifications of 250X and 1000X, and occasionally 2000X, of 78 different arc-cast and heat-treated uranium carbide specimens with compositions ranging from $UC_{0.4}$ to $UC_{2.4}$ (2 to 11 wt % carbon). The carbide specimens were carefully analyzed for uranium, total carbon, free carbon, oxygen, nitrogen, and tungsten. Phases that were present were identified by X-ray diffraction analysis. Samples of many of these specimens were used in extensive studies of their hydrolytic properties,¹²⁻¹⁶ which served as additional criteria of their composition. A partial constitutional diagram for the uranium-carbon system from $UC_{1.0}$ to $UC_{2.4}$ based on the results of these studies has been described elsewhere,^{8,17} but only a few photomicrographs could be included in those papers.

Throughout this report, the formulas UC , U_2C_3 , and UC_2 are used to denote the monocarbide, sesquicarbide, and dicarbide phases, respectively, regardless of the exact chemical composition of the phase. The nonmetal/metal atom ratio is used to indicate a specific composition. For example, $UC_{2.0}$ signifies a specimen containing 2.0 carbon atoms for each uranium atom, with the phases undefined; UC_2 , on the other hand, denotes the dicarbide phase with the exact composition undefined.

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2. URANIUM CARBIDE SPECIMENS

2.1 Preparation of the Uranium Carbide Specimens

The uranium carbides were prepared in the form of 100-g buttons by arc-melting weighed quantities (± 1 mg) of high-purity uranium metal (< 400 ppm total impurities) and spectroscopic-grade carbon, using nonconsumable tungsten electrodes.¹⁸ The buttons were melted until visual examination indicated that all the carbon had dissolved in the melt; then they were melted an additional eight times (2-min melts) to ensure complete reaction. Excellent composition control was obtained by this method (see Table 1). Tungsten contamination, from the electrodes, was 0.15 wt % (0.07 at. %) or less in specimens containing 2.0 to 8.0 wt % carbon, but was 0.12 to 0.39 wt % (0.05 to 0.14 at. % in specimens containing 8.8% or more carbon because of the longer melting times required (Table 3, p. 7). Buttons containing 6 to 6.6% carbon shattered when they were quenched from the melt. Each attempt to prepare uranium carbides with graphite electrodes resulted in an extensive reaction between the electrode and the melt. For example, in arc-melting specimen 75 (Table 3, p. 7) with graphite electrodes, the carbon concentration increased from 8.75% in the initial uranium metal--carbon mixture to 10.6% in the product carbide.

Table 1. Composition Control in Arc-Melting Uranium Carbides with Tungsten Electrodes

Specimen Code	Carbon (wt %)		W (wt %)
	Synthetic ^a U + C Mixture	Product Carbide	
7A	1.93	1.95	0.02
6B	4.00	4.01	0.03
2C	4.77	4.64	0.02
16	5.26	5.25	0.001
17	5.71	5.72	0.002
3B	6.00	6.06	0.09
4B	7.04	7.00	0.06
5B	8.00	8.03	0.09
UC ₂ -21	8.30	8.26	0.03
UC ₂ -7A	8.54	8.54	?
UC ₂ -16A	8.80	8.80	0.19
UC ₂ -16C	8.80	8.84	0.13
UC ₂ -4A	8.87	8.88	0.12
UC ₂ -5A	9.16	9.06	0.21
UC ₂ -6A	9.99	9.78	0.22

^aCalculated from weights of carbon and uranium used.

2.2 Heat-Treatment of the Carbides

Most of the buttons were heat-treated in graphite crucibles in a Brew High Vacuum Furnace, No. 424 B, which was routinely operated at pressures of 1×10^{-5} torr or less; four of the specimens, however, were treated under slightly different conditions: two were heated in a Burrell Tube Furnace, and two were heated in a beryllia crucible. Temperatures were measured with an accuracy of $\pm 20^\circ\text{C}$ with a Leeds and Northrup optical pyrometer that had been calibrated by using both a platinum--10% rhodium thermocouple and a micro-optical pyrometer, which, in turn, had been calibrated against a National Bureau of Standards heat lamp. Although the samples were not quenched after the heat-treatments, they were furnace-cooled to 1000°C in less than 5 min, and to 500°C within 10 min. Specimens with compositions from $\text{UC}_{1.0}$ to $\text{UC}_{1.2}$ were set on small disks of uranium monocarbide to prevent reaction with the graphite crucible. Under these conditions, no visible reaction of the specimens with the crucibles was noted except in the case of specimen 39 ($\text{UC}_{1.5}$ heated at 1720°C for 65 hr; Table 3), which stuck slightly to the crucible.* Heating in the Brew furnace at temperatures of 2000°C or lower caused no significant change in the elemental analyses of the specimens (Table 2). The specimens heated at 2130°C did pick up a small amount of carbon from the crucible; for example, the carbon content of specimen 19 (code series 8) increased from 5.96% after the 1600°C heat-treatment to 6.52% after the 2130°C treatment (Tables 2 and 3). The Burrell furnace had a small leak, which caused an increase in the oxygen and nitrogen concentrations of specimens 6 and 42 after heat-treatment (Table 3).

2.3 Elemental Chemical Analyses

The heat-treatment conditions, along with the results obtained by analyzing the specimens for uranium, total carbon, free carbon, oxygen, nitrogen, and tungsten, are given in Table 3. Each of the specimens, except 6 and 42, contained an average of

*The surface area in contact with the crucibles was always quite small because of the shape of the specimens (either a rounded button or an irregularly shaped piece broken from a button).

Table 2: Effect of Heat-Treatments^a on the Carbon Content of Uranium Carbide Specimens

Code Series	Carbon Content (wt %) of							
	Synthetic ^b U + C Mixture	As-Cast Specimen	Specimen After Heat-Treatment					
			At 1600°C, 65 hr	First at 1600°C, Then at				
				1820°C, 6 hr	1900°C, 6 hr	2000°C, 4 hr	2070°C, 2 hr	2130°C, 2 hr
16	5.26	5.25	5.25 ^c	5.25 ^c	5.26 ^c			
17	5.71	5.72	5.71 ^c	5.74 ^c	5.69 ^c	5.72 ^c	5.70	
8	6.00	?	5.96 ^d	6.10	6.14	6.16	5.98	6.52
11	6.60	?	6.55	6.63	6.62	6.64	6.67	
U ₂ C ₃ -3	7.04	?	6.93	6.96	7.02	7.08		7.30
12	7.47	?	7.44	7.55	7.56	7.54		
10	8.00	?	7.98	8.06	8.16	8.24		
UC ₂ -21	8.30	8.26	8.27	8.34	8.32			

^aSpecimens were heated in graphite crucibles in a Brew furnace.

^bCalculated from weights of carbon and uranium used.

^cSet on UC disks.

^dBeryllia crucible used.

Table 3. Composition of Uranium Carbide Specimens

Specimen No.	Code	Fig. No.	Heat-Treatment ^a (°C)		Elemental Analysis						Total-C/U Atom Ratio	Combined-C/U Atom Ratio	X-Ray Powder Pattern ^b			For Hydrolysis Studies, See Reference
			First	Second	U	Total C	Free C	W	O	N			UC	U ₂ C ₃	UC ₂	
1	7A	4	as-cast		98.0	1.95	0.02	0.02	0.03	59	0.39	0.39	pc	-	-	13
2	6B	5	as-cast		96.0	4.01	<0.05	0.03	0.06	65	0.83	0.83	pc	-	-	13
3	2C	6	as-cast		95.4	4.64	<0.01	0.02	0.11	105	0.96	0.96	P	-	-	12
4	2G ^d	7	2000	-	95.0	4.75	0.05	0.15	0.04	72	0.99	0.98	P	-	-	16
5	2H ^e	8	1600	-	95.0	4.70	<0.01	0.01	0.01	84	0.98	0.98	P	-	-	14
6	2If	9	1275	-	95.2	4.64	0.03	0.10	~0.39	879	0.99	0.98	ph	-	-	Table 4
7	16	10	as-cast		94.7	5.25	0.01	0.001	0.01	71	1.10	1.10	P	-	W	
8	16H ^d	11	1500	1900	94.7	5.26	0.01	See spec-	0.01	33	1.10	1.10	P	-	W	
9	16I ^d	12	1600	1820	94.7	5.25	<0.01	imen	0.01	24	1.10	1.10	P	-	W	
10	16K ^d	13	1765	-	94.7	5.25	<0.01	imen	0.03	75	1.10	1.10	P	W	-	
11	16A ^d	14	1600	-	94.7	5.25	0.01	16I	0.02	45	1.10	1.10	P	W	-	
12	17	15	as-cast		94.3	5.72	0.01	0.002	0.02	51	1.20	1.20	P	-	W	
13	17M ^d	16	1600	2070	94.3	5.70	0.01	See spec-	?	?	1.20	1.20	P	-	W	
14	17J ^d	17	1600	2000	94.3	5.69	<0.01	imen	0.01	51	1.20	1.20	P	-	W	
15	17H ^d	18	1600	1900	94.2	5.74	0.01	imen	0.03	29	1.21	1.20	P	-	W	
16	17I ^d	19	1600	1820	94.3	5.71	<0.01	17I	0.03	30	1.20	1.20	P	-	W	
17	17A ^d	20	1600	-	94.2	5.74	0.01		0.02	61	1.21	1.20	P	W	-	
18	3B	21	as-cast		94.0	6.06	0.12	0.09	0.09	65	1.28	1.25	P	-	W	13
19	8G	22a, 22b	1600	2130	93.5	6.52	0.02	See spec-	<0.01	18	1.38	1.38	P	-	W	16
20	8M	23	1600	2070	94.0	5.98	0.01	imen	?	?	1.26	1.26	P	-	W	
21	8J	24	1600	2000	93.8	6.16	0.03	imen	<0.01	22	1.30	1.30	P	-	W	16
22	8H	25	1600	1900	93.9	6.14	0.03	8A ⁱ	<0.01	21	1.30	1.29	P	-	W	16
23	8I	26	1600	1820	93.9	6.10	0.01		0.01	66	1.29	1.29	P	-	W	16
24	8A ^e	27	1600	-	94.0	5.96	0.03	0.02	0.01	31	1.26	1.25	P	P	-	14
25	11M	28	1600	2070	93.3	6.67	0.01	See spec-	?	?	1.42	1.41	P	-	P	
26	11J	29	1600	2000	93.4	6.64	0.01	imen	0.02	38	1.41	1.41	P	-	P	16
27	11H	30	1600	1900	93.4	6.62	0.01	imen	<0.01	28	1.40	1.40	P	-	P	16
28	11I	31	1600	1820	93.4	6.63	0.01	11A ⁱ	<0.01	33	1.41	1.41	P	-	P	16
29	11A	32	1600	-	93.4	6.55	0.02	0.04	0.01	52	1.39	1.39	P	P	-	14
30	4B	33	as-cast		93.1	7.00	0.05	0.06	0.10	65	1.49	1.48	P	-	P	13
31	U ₂ C ₃ -3	34	as-cast		(same original as-cast button as all U ₂ C ₃ -3 series specimens)								P	-	P	Table 6
32	U ₂ C ₃ -3G	35	1600	2130	92.7	7.30	0.05		<0.01	45	1.56	1.55	P	-	P	
33	U ₂ C ₃ -3(2)	36	2000	-	(same original as-cast button as all U ₂ C ₃ -3 series specimens)								P	-	P	16
34	U ₂ C ₃ -3J	37	1600	2000	92.9	7.08	0.01	See spec-	<0.01	15	1.51	1.51	P	-	P	16
35	U ₂ C ₃ -3H	38	1600	1900	93.0	7.02	0.04	imen	0.01	43	1.51	1.49	P	-	P	16
36	U ₂ C ₃ -3I	39	1600	1820	93.0	6.96	0.03	imen	<0.01	52	1.48	1.48	P	-	P	16
37	U ₂ C ₃ -3H-2	40 (1)	1600, (2) 1900, (3) 1765		93.0	6.96	<0.01	U ₂ C ₃ -3A ⁱ	0.02	10	1.48	1.48	Qi	P	Q ^k	Table 6
38	U ₂ C ₃ -3K	41	1600	1765	93.1	6.94	<0.01		0.02	23	1.48	1.48	P	P	T	Table 6
39	13A	42	1720	-	92.9	7.05	0.01	0.02	0.01	26	1.51	1.51	-	P	T	Table 6
40	U ₂ C ₃ -1A	43	1600 ⁱ	-	93.0	6.93	0.04	0.13	0.08	40	1.48	1.47	Qi	P	Q ^k	14
41	U ₂ C ₃ -3A	44	1600	-	93.0	6.93	0.06	0.12	0.03	26	1.48	1.46	Q	P	-	Table 6
42	9A ⁱ	45	1275	-	92.8	7.02	0.24	0.10	~0.39	787	1.50	1.49	Qi	ph	Q ^k	Table 6
43	12J	46	1600	2000	92.4	7.54	0.01	See spec-	0.02	37	1.62	1.62	P	-	P	16
44	12H	47	1600	1900	92.4	7.56	0.01	imen	0.02	19	1.62	1.62	P	-	P	16
45	12I	48	1600	1820	92.4	7.55	0.01	imen	<0.01	20	1.62	1.62	P	-	P	16
46	12K	49	1600	1765	92.5	7.51	0.01	12A ⁱ	0.02	12	1.61	1.61	P	W	P	
47	12A	50	1600	-	92.5	7.44	0.01		0.06	37	1.59	1.59	-	P	P	14

Table 3. Composition of Uranium Carbide Specimens (Continued)

Specimen		Fig. No.	Heat-Treatment ^a (°C)		Elemental Analysis					Total- C/U Atom Ratio	Combined- C/U Atom Ratio	X-Ray Powder Pattern ^b			For Hydrolysis Studies, See Reference	
					(wt %)				(ppm)			UC U ₂ C ₃ UC ₂				
No.	Code	No.	First	Second	U	Total C	Free C	W	O	N			UC	U ₂ C ₃	UC ₂	
48	5B	51	as-cast		92.0	8.03	0.08	0.09	0.15	57	1.73	1.71	W	-	P	13
49	10G	52	1600	2130	91.8	8.24	?	See specimen 10A ⁱ	<0.01	46	1.78	?	W	-	P	
50	10H	53	1600	1900	91.8	8.16	0.01		<0.01	38	1.76	1.76	W	-	P	16
51	10I	54	1600	1820	91.9	8.06	0.05		?	46	1.74	1.73	W	-	P	16
52	18K	55	1765	-	92.0	8.00	0.01	0.10	0.02	3	1.73	1.72	W	-	P	
53	18N	56	1700	-	91.9	8.09	0.01	0.10	0.02	8	1.75	1.74	W	P	P	
54	10A	57	1600	-	92.0	7.98	0.08	0.14	0.06	26	1.72	1.70	T ^m	P	P	14
55	UC ₂ -21	58	as-cast		91.7	8.26	0.02	0.03	0.02	40	1.79	1.78	W	-	P	Table 5
56	UC ₂ -21H	59	1600	1900	91.7	8.32	0.03	See spec- imen UC ₂ -21 ⁱ	0.03	22	1.80	1.79	W	-	P	
57	UC ₂ -21I	60	1600	1820	91.6	8.34	0.01		0.01	26	1.80	1.80	W	-	P	Table 5
58	UC ₂ -21K	61	1765	-	91.6	8.30	0.03		0.03	55	1.79	1.79	W	-	P	Table 5
59	UC ₂ -21N	62	1700	-	91.7	8.36	0.02	0.03	0.03	3	1.81	1.80	W	-	P	
60	UC ₂ -21A	63a, 63b	1600	-	91.7	8.27	0.01	0.01	0.01	32	1.79	1.79	W ^m	W ⁿ	P	Table 5
61	UC ₂ -21L	54	1450	-	91.7	8.28	0.03	0.01	0.01	37	1.79	1.78	T ^m	W	P	Table 5
62	UC ₂ -7A	65	as-cast		91.5	8.54	?	?	?	?	1.85	?	?	?	?	
63	UC ₂ -16A	66	as-cast		91.2	8.80	0.14	0.19	0.02	42	1.91	1.88	-	-	P	13
64	UC ₂ -16C	67	as-cast		91.2	8.84	0.07	0.13	0.03	36	1.92	1.90	-	-	P	Table 5
65	UC ₂ -16G	68	1450	2130	91.2	8.79	0.19	0.14	0.01	38	1.91	1.87	T ^o	-	P	
66	UC ₂ -16J	69	2000	-	91.1	8.81	0.22	See specimen UC ₂ -16C ⁱ	<0.01	36	1.92	1.87	T ^o	-	P	Table 5
67	UC ₂ -16L	70	1450	-	91.2	8.80	0.25		0.02	32	1.91	1.86	T ^o	-	P	Table 5
68	UC ₂ -4A	71	as-cast		91.2	8.88	0.30	0.12	0.04	37	1.93	1.86	Q	-	P	13
69	UC ₂ -5A	72	as-cast		91.0	9.06	0.62	0.21	0.04	50	1.97	1.84	T ^o	-	pp	13
70	UC ₂ -15A	73	2000	-	90.8	9.10	0.62	0.39	0.01	25	1.99	1.85	T ^o	-	pp	16
71	UC ₂ -17A	74	1600	-	90.8	9.14	0.64	0.23	0.02	<5	2.00	1.86	T ^o	-	pp	14
72	UC ₂ -18A	75	1450	-	90.8	9.12	0.70	0.16	0.01	39	1.99	1.84	T ^o	-	pp	Table 5
73	UC ₂ -3A	76	1260	-	90.8	9.14	0.81	0.29	0.05	82	1.99	1.83	Q	-	pp	Table 5
74	UC ₂ -6A	77	as-cast		90.3	9.78	1.40	0.22	0.03	40	2.15	1.84	T ^o	-	pp	13
75	UC ₂ -19A	78	as-cast		89.4	10.58	2.20	0.9	0.05	25	2.35	1.87	T ^o	-	pp	15
76	UC ₂ -19J	79	2000	-	89.0	10.93	2.55	0.9	0.01	58	2.43	1.87	T ^o	-	pp	Table 5
77	UC ₂ -19L	80	1450	-	89.1	10.80	2.50	0.9	0.02	21	2.40	1.85	T ^o	-	pp	Table 5
78	UC ₂ -20A	81	as-cast		83.8	8.62	0.62	6.20 ^r	0.04	30			-	-	ps	15

^a Heat-treatment times:

2130°C, 2070°C: 2 hr

2000°C: 4 hr

1900-1765°C: 6 hr

1720-1450°C: 65 hr

1275°C, 1260°C: 240 hr.

^b P, present; W, weak; T, probably present in trace quantities; Q, questionable.^c Uranium metal also detected in X-ray pattern.^d Set on UC disks during heat-treatment.^e Beryllia crucible used for heat-treatment.^f Burrell Tube Furnace used for heat-treatment.^g Varied with distance from oxidized surface.^h Trace of UO₂ also detected in X-ray pattern.ⁱ Assumed to be the same before and after heat-treatment.^j Based on relative intensity of common line with UC₂ at 2.48 Å.^k Based on faint line at 3.04 Å.^l Brief excursion to 1680°C.^m Based on relative intensities of lines which are common to U₂C₃ or UC₂.ⁿ U₂C₃ is stronger than UC.^o Based on very faint lines at 1.42 and 2.87 Å.^p Diffuse graphite lines also observed in X-ray pattern.^q Graphite electrode used to arc-melt specimen.^r Tungsten added intentionally.^s Tungsten metal and WUC₂ also detected in X-ray pattern.

0.02 wt % oxygen and 42 ppm of nitrogen. Specimens 6 and 42; which had been heat-treated in the Burrell tube furnace, contained an average of about 0.3% oxygen and 0.08% nitrogen. The centers of these two specimens were almost pure carbide (by chemical analysis), while their outside surfaces appeared to be completely oxidized (by visual examination). Tungsten content of the specimens averaged 0.06% for compositions $UC_{0.39}$ to $UC_{1.80}$ (2.0 to 8.3% carbon) and 0.21% for compositions $UC_{1.91}$ to $UC_{2.15}$ (8.8 to 9.8% carbon). Specimens in the UC_2 -19 series (Nos. 75-77) were prepared with graphite electrodes and thus contained no tungsten. Spectrographic analysis showed that the specimens contained about 40 ppm of nickel, 25 ppm of calcium, and 15 ppm of copper; the concentrations of all other metallic impurities were less than 5 ppm. The analytical procedures used are described in the Appendix.

In general, the specimens in Table 3 are arranged in order of increasing carbon concentration from 1.95 to 10.9%, and, for a given carbon composition, in order of decreasing temperature of the final heat-treatment (i.e., as-cast to 1260°C). In the specimen code, usually the number indicates the melt and the letter denotes the specific heat-treatment. For example, code 16A signifies melt 16, heat-treatment A. The 2 series (specimens 3-6) and the UC_2 -16 series (specimens 63-67) were exceptions to this convention. The 2 series was comprised of different buttons; however, these buttons were prepared "assembly line fashion" to the same specifications from the same batch of uranium metal and carbon by arc-melting four buttons each time the furnace was evacuated. The UC_2 -16 series of buttons was prepared similarly; however, specimens 64, 66, and 67 were taken from the same as-cast button. Although it is not obvious from the analyses, specimens 75-77 were taken from the same arc-cast button. The free carbon was not homogeneously distributed throughout this button, probably because it came from the graphite electrode during the arc-melting process.

2.4 Phases Identified by X-Ray Diffraction Analysis at Room Temperature

The major carbide phases in the specimens, as determined by X-ray diffraction analysis at room temperature, are tabulated in Table 3. The X-ray diffraction powder

patterns for uranium monocarbide and dicarbide were identical to those presented by Litz, Garrett, and Croxton;¹⁹ the diffraction pattern for the sesquicarbide was the same as that reported by Mallett, Gerds, and Vaughen.²⁰ No shifts occurred in the spacings of the lines in the monocarbide, sesquicarbide, or dicarbide powder patterns when either the carbon content or the heat treatment was varied; hence none of the specimens contained solid solutions at room temperature. Specimens having C/U atom ratios of less than 1.0 (4.8 wt % carbon) were two-phase mixtures of uranium metal and monocarbide. The $UC_{1.0}$ specimens were stable during short heat-treatments between 1275 and 2000°C; long heat-treatments were not made. Specimens that had combined-C/U atom ratios from 1.10 to 1.87 (5.3 to 8.6% carbon) and were in the as-cast condition or had been subjected to a final heat-treatment at 1820°C or higher were two-phase mixtures of the mono- and dicarbides (Fig. 1). Specimens of $UC_{1.5}$ (7.0% carbon) that had been heat-treated in the range of 1765 to 1275°C for several hours were composed mostly of sesquicarbide, with traces of a residual mono- and/or dicarbide impurity from the original as-cast mixture. Only sesqui- and monocarbides were present in $UC_{1.1}$ to $UC_{1.4}$ compositions (5.3 to 6.6% carbon) after heat-treatment at 1765 to 1600°C (Fig. 1). Sesquicarbide-dicarbide mixtures were found in the composition region between $UC_{1.5}$ (7.0% carbon) and $UC_{1.7}$ (8.0% carbon) at about 1760°C and in $UC_{1.80}$ (8.3% carbon) at about 1650°C (Fig. 1). All the strong monocarbide lines are common to lines in either the sesquicarbide or the dicarbide patterns. This means that low concentrations of monocarbide can be detected in mixtures of the three carbides only when the sesquicarbide and/or the dicarbide concentration is sufficiently low to permit the monocarbide to make a significant contribution to the intensities of these common lines. All specimens with combined-C/U atom ratios of 1.83 to 1.87 contained a trace of monocarbide in addition to the dicarbide. As-cast specimens 63 and 64, which had combined-C/U atom ratios of 1.88 and 1.90, respectively, were single-phase uranium dicarbide. Diffuse graphite lines were observed in all specimens containing 0.6% or more free carbon. Uranium dioxide was detected in specimens 6 and 42, which had been heat-treated in the Burrell furnace with the small leak.

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Fig. 1. Major Phases Detected by X-Ray Diffraction Analysis of Heat-Treated Uranium Carbides. Analysis done at room temperature. Specimen numbers refer to Table 3. The dashed curve shows the high-temperature monocarbide-dicarbide immiscible region.¹⁷

2.5 Hydrolysis of the Carbides

The three uranium carbides and uranium metal yield different gaseous products on reaction with water;^{12-14,16} therefore, hydrolysis of specimens was used as an aid in phase identification. Results of the hydrolysis studies were consistent with the X-ray diffraction analyses. While any temperature between 25 and 99°C may be used for the hydrolysis, it was convenient, experimentally, to conduct the reactions at 80°C to benefit from the higher reaction rates without encountering the difficulties of operating near the boiling point of water. The gas chromatographic analyses were accurate to about $\pm 10\%$ of the value reported for hydrogen, the least accurate analysis.

Hydrolysis of practically single-phase uranium monocarbide produced 93 ml (STP) of gas per gram of carbide. This gas was comprised mainly of methane (86 vol %) and hydrogen (11 vol %), but also contained a small amount (3 vol %) of C_2 - to C_8 -hydrocarbons.^{12,13} Methane is the expected product since there is no C-to-C bonding in the monocarbide crystal.²¹ Hydrolysis of uranium metal-monocarbide mixtures gave the products that would be expected from the monocarbide, in addition to two moles of hydrogen for each mole of free uranium metal present (Figs. 2 and 3).¹² With both monocarbide and metal-monocarbide mixtures, all the carbide carbon was found in the gaseous hydrolysis products (no waxes were formed). Hydrolysis of $UC_{1.0}$ compositions that had been heat-treated at temperatures from 1275 to 2000°C yielded the same gaseous hydrolysis products (see Appendix, Table 4). The volume of gas evolved from specimen 6 was low by about 3%, and 2 wt % of the original specimen was recovered as insoluble UO_2 after the hydrated uranium(IV) product from the carbide hydrolysis had been dissolved in 6 M HCl; however, this specimen, which had been heat-treated in the defective Burrell furnace, was known to contain UO_2 (by X-ray diffraction analysis) and 0.3 wt % oxygen (by chemical analysis).

Uranium dicarbide specimens with total-C/U atom ratios of 1.9 to 2.3 (combined-C/U ratios of 1.83 to 1.90; specimens 63-77) produced an average of 42 ml of gas per gram of carbide. This gas consisted of about 41 vol % hydrogen, 15 vol % methane, and 44 vol % C_2 - to C_8 -hydrocarbons (chiefly ethane, ethylene, butane, and butenes)

Fig. 2. Gaseous Products From the Reactions of Uranium Carbides with Water at 80°C. Circles represent as-cast specimens;¹³ squares, specimens heat-treated at 1600°C;¹⁴ and triangles, specimens heat-treated at 1820 to 2000°C.¹⁶

Fig. 3. Volume of Gas Evolved From the Reactions of Uranium Carbides with Water at 80°C.

(see Appendix, Table 5).^{13,14,16} The preponderance of hydrocarbons with an even number of carbon atoms is to be expected because the dicarbide crystal lattice contains discrete C_2 units.²¹⁻²⁴ A nonvolatile wax was also formed. The presence of methane and other hydrocarbons containing an odd number of carbon atoms indicates that these specimens also contained some single C units. Some of the single C units undoubtedly came from the monocarbide that was detected in most of the samples by X-ray diffraction analysis. It is also possible that in the tetragonal dicarbide itself, which appears to be carbon-deficient with a room-temperature composition of about $UC_{1.89}$,⁸ a few C units have replaced C_2 units in the lattice. Within the limits of experimental error ($\pm 10\%$), heat-treatment at 1450 to 2000°C produced no effect on the volume or the composition of the gas from specimens having total-C/U atom ratios of 1.9 to 2.3 (see Appendix, Sect. 5.3). Specimens prepared with graphite electrodes (specimens 75-77) gave essentially the same results as the ones made with tungsten electrodes.

The volume and the composition of the gas from the hydrolysis of uranium monocarbide--dicarbide mixtures varied with the type of mixture (i.e., as-cast, heat-treated, or physical) and, for a given type, varied systematically with the carbon concentration of the mixture (Figs. 2 and 3).¹⁶ Two reactions apparently competed for the C units in the monocarbide lattice during the hydrolysis of mixtures: the hydrogenation reaction to form methane, and the polymerization reaction with C_2 units from the dicarbide to form higher hydrocarbons. The extent of the C- C_2 reaction was proportional to the monocarbide-dicarbide interphasial area. No significant amount of C- C_2 reaction was observed when physical mixtures of monocarbide and dicarbide powders were hydrolyzed, whereas rather extensive polymerization occurred when as-cast mixtures (in which the phases were intimately mixed) were hydrolyzed. The volume of gas evolved per gram of carbide decreased from about 93 to 42 ml as the total-C/U atom ratio increased from 1.0 to 1.9 (Fig. 3). No further decrease in volume was observed as the total-C/U ratio increased from 1.9 to 2.2; also, the composition of the evolved gases¹³ did not change. These results indicate that the maximum combined-C/U atom ratio is approximately 1.9.

Uranium sesquicarbide (specimens 37-42) produced about 62 ml of gas per gram of carbide. This gas consisted of about 60 vol % hydrogen and 36 vol % C_2 - to C_8 -hydrocarbons (mainly ethane, ethylene, butane, and butenes)(see Appendix, Table 6).¹⁴ These specimens were unique among the uranium carbides in that hydrolysis yielded only a small amount of methane, which probably came from the trace of monocarbide phase rather than from the sesquicarbide itself. Again, the preponderance of C_2 - and multiples of C_2 -hydrocarbons in the hydrolysis products reflects the presence of C_2 units in the sesquicarbide crystal lattice.^{21,23} It should be noted that, although U_2C_3 is the common abbreviation for the sesquicarbide, both the neutron diffraction data^{21,23} and the hydrolysis studies show that the minimum formula is $U_4(C_2)_3$. The large amount of hydrogen resulted from the oxidation, by water, of the trivalent uranium in the sesquicarbide to a tetravalent, hydrated oxide.¹⁴ Some wax was also formed.¹⁴ Specimen 42, which, like specimen 6, had been heat-treated in the defective Burrell furnace, contained some UO_2 , which was recovered as a hydrochloric acid-insoluble solid after hydrolysis was complete and after the hydrated uranium(IV) oxide product had been dissolved. Heating the sesquicarbide to temperatures of 1820°C or higher to decompose it into the mono- and dicarbides caused a marked change in the gaseous hydrolysis products. For example, specimen 41, which was principally sesquicarbide, yielded a gas containing 5 vol % methane on hydrolysis; after heat-treatment of the specimen (as specimen 35) at 1900°C, the off-gas was comprised of 56 vol % methane (see Appendix, Table 6).

Both the volume and the composition of the gas produced by the hydrolysis of mixtures of uranium sesquicarbide and monocarbide or dicarbide showed a systematic dependence on the carbon concentration (Figs. 2 and 3).¹⁴

3. MICROSTRUCTURES OF THE URANIUM CARBIDES

Photomicrographs of as-cast and heat-treated uranium carbide specimens with total-C/U atom ratios varying from 0.4 to 2.4 (2 to 11 wt % carbon) are shown in Figs. 4-81. The phases detected by the X-ray diffraction analyses (Table 3) can be

readily identified in most of the photomicrographs made at a magnification of 1000X, except that uranium monocarbide cannot be differentiated from sesquicarbide or graphite platelets in specimens that are predominantly dicarbide (Figs. 48-49, 52-56, 59-64, and 68-70). Although examination at 250X is useful in determining the homogeneity of a specimen, small quantities of a second phase may be overlooked at this magnification (e.g., see Fig. 58). Also, it is difficult to differentiate between a sesquicarbide precipitate and a dicarbide precipitate in a monocarbide matrix (Figs. 16-20). The nitric acid--acetic acid--water solution etched the uranium monocarbide dark, and the uranium dicarbide light; the sesquicarbide etched light in monocarbide-sesquicarbide mixtures and dark in sesquicarbide-dicarbide mixtures. As viewed under the microscope, the sesquicarbide phase was generally dark blue or purple, while the monocarbide and dicarbide phases were varicolored; the graphite was black. Bright field illumination was used unless otherwise specified. The appearance of the monocarbide and dicarbide phases under polarized light resembled that under bright field illumination; however, in some specimens, the grain structure of the sesquicarbide could be observed under polarized light when it was not visible under bright field illumination (Figs. 27 and 50). Specimens containing < 0.1% free carbon were listed according to their combined-C/U atom ratios since the trace amounts of free carbon were not observed in the photomicrographs. The procedures for preparing the metallographic specimens and making the photomicrographs are described in the Appendix.

Specimens having C/U atom ratios of less than 1.0 (4.8 wt % carbon) were two-phase mixtures of uranium metal and monocarbide (Figs. 4 and 5). All $UC_{1.0}$ specimens contained trace amounts of metal and higher carbides heterogeneously dispersed throughout the monocarbide matrix (Figs. 6-9). Theoretically, the metal and the dicarbide should have combined to form monocarbide, but the diffusion rates are so low that complete reaction is difficult to achieve. Although single-phase uranium monocarbide was not prepared in this study, its room-temperature composition appears to be very close to the stoichiometric $UC_{1.00}$ (Figs. 5, 6, and 10). Specimens of $UC_{1.0}$ were stable during short heat-treatments between 1275 and 2000°C (Figs. 6-9).

As-cast specimens with compositions from $UC_{1.1}$ to $UC_{1.8}$ (5.2 to 8.3% carbon) consisted of a very fine Widmanstätten precipitate of the minor component in the major phase, indicating that at high temperatures a complete range of solid solution from cubic monocarbide to cubic dicarbide exists (Figs. 10, 15, 21, 33, 34, 51, 58, and 65). As-cast $UC_{1.25}$ (5.9% carbon) had a dicarbide-rich intergranular structure (Fig. 21) in contrast to $UC_{1.48}$ (7.0% carbon), which had a monocarbide-rich phase at the grain boundaries (Fig. 33). This reversal in the intergranular phase could result from a minimum in the melting-point curve between $UC_{1.25}$ and $UC_{1.48}$, or possibly from a nonequilibrium eutectoid decomposition during cooling. Since no eutectoid was observed, there is probably a minimum in the melting point curve, although melting point data are not available to confirm this. The blocky structure within the equiaxed grain structure of the dicarbide matrix is caused by the phase change, at about 1800°C, from the cubic crystal, which is the stable form at high temperatures, to the tetragonal crystal (Figs. 51, 58, and 65).

Heat-treated specimens with compositions from $UC_{1.1}$ to $UC_{1.8}$ (5.2 to 8.3% carbon) may be divided into five general groups according to their microstructures. The first type (Type I) consists of oriented platelets of monocarbide or dicarbide homogeneously dispersed throughout the entire specimen, and was obtained when specimens were heat-treated in a region where the monocarbide and dicarbide formed a solid solution¹⁷ (Figs. 1, 11, 12, 22, 28, 35-37, 46, 47, 52-55, and 59-62). This type of microstructure is similar to that observed by Takahashi *et al.*²⁵ for slow-cooled specimens; and, in general, the postulates of these authors concerning the morphologies of the precipitates are applicable here. The platelets are larger than in the as-cast specimens because the longer cooling time in the heat-treating furnace allowed more segregation to occur. In general, the monocarbide platelets do not cross the twinning boundary from the dicarbide phase transformation; this indicates that they precipitated from a tetragonal UC_{2-y} phase rather than from a cubic phase (Figs. 52-55 and 59-62). Upon cooling in the furnace, the $UC_{1.5}$ and $UC_{1.8}$ solid solutions apparently precipitated first into UC_{1+x} and UC_{2-y} phases, which, upon further cooling, separated into a monocarbide phase containing some fine dicarbide platelets and a dicarbide phase

containing some fine monocarbide platelets (Figs. 35-37 and 52). This substructure within the large platelets was best observed at a magnification of 2000X (Fig. 52), and probably would have been found in other Type I microstructures if they had been examined at this magnification.

A second type of microstructure was observed in some $UC_{1.2}$ to $UC_{1.6}$ specimens (5.7 to 7.6% carbon) that had been heat-treated in the temperature range from 1820 to 2070°C. This type of microstructure (Type II) consisted of large, irregularly shaped areas of monocarbide-rich and dicarbide-rich phases, which are indicative of immiscible phases at the heat-treating temperature¹⁷ (Figs. 1, 16-19, 23-26, 29-31, 38-39, and 48-49). The Type II microstructures also contained some oriented platelets, which suggested partial formation of a solid solution. In appearance the dicarbide-rich areas were similar to the $UC_{1.7}$ (8.0% carbon) specimens that had been heated in the single-phase region (Figs. 54 and 55), and always contained parallel platelets of monocarbide that did not cross the twinning boundaries. Because of a fine substructure (observed at 2000X; Figs. 38 and 39), the relative areas of monocarbide and dicarbide in the dicarbide-rich phase could not be estimated by point counting on a grid. The monocarbide-rich sections of the $UC_{1.2}$ and $UC_{1.3}$ specimens (5.7 and 6.0% carbon; Figs. 16-19 and 23-26) resembled the $UC_{1.1}$ specimens that had been heated in the single-phase region (Figs. 11 and 12), and contained parallel sets of dicarbide lamellae having as many as three different orientations. The composition of the monocarbide phase in equilibrium with excess dicarbide at 1820, 1900, 2000, and 2070°C was estimated to be close to $UC_{1.10}$ by point counting, on a 0.25-in., 187-point grid, the relative areas of the dicarbide platelets and the monocarbide matrix in the monocarbide-rich portions of these $UC_{1.20}$ specimens and then correcting for the densities of the mono- and dicarbides.

A third type of microstructure (Type III), consisting of irregularly shaped areas of monocarbide and sesquicarbide, was obtained when specimens of compositions $UC_{1.1}$ to $UC_{1.4}$ (5.2 to 6.5% carbon) were heat-treated at 1765 or 1600°C (Figs. 13, 14, 20, 27, and 32). There appeared to have been very little solid solubility at the heat-treating temperature, as would be expected since the monocarbide crystal is

face-centered cubic while the sesquicarbide is body-centered cubic.^{21,26} A trace of a needle-like precipitate was observed throughout the monocarbide phase, indicating that at 1600 to 1765°C the monocarbide phase probably contained slightly more than one carbon atom for each uranium atom; as the specimen cooled, traces of dicarbide then precipitated in fine needles (which were not detected by the X-ray diffraction analysis). At a magnification of 250X, the Type III microstructures were virtually identical to the Type II microstructure of corresponding carbon content; however, at 1000X the fine platelets throughout the light dicarbide phase of the Type II microstructure are readily apparent, while no precipitate is observed throughout the light sesquicarbide phase of a Type III microstructure (Figs. 26 and 27). At compositions of $UC_{1.26}$ and higher carbon contents, the Type II and Type III microstructures are distinctly different under polarized light, which develops the grain structure of the sesquicarbide (Figs. 26 vs 27, 31 vs 32).

Specimens of $UC_{1.5}$ (7.0% carbon) that had been heat-treated between 1765 and 1275°C were composed, primarily, of uranium sesquicarbide; some residual mono- and/or dicarbide impurity from the original arc-melting preparation was also present (Figs. 40-45). The grains of sesquicarbide were much larger in the specimens prepared at the higher temperatures, but the microstructures were similar otherwise.

The sesquicarbide phase could be readily identified in the microstructure of the $UC_{1.6}$ specimen that had been heat-treated at 1600°C (7.4% carbon; Fig. 50). But, the microstructures of $UC_{1.6}$ to $UC_{1.8}$ (7.5 to 8.2% carbon) specimens, which had been heat-treated at temperatures near the phase boundaries shown in Fig. 1 so that they consisted of a dicarbide matrix with a sesquicarbide precipitate, were nearly identical to the Type I or Type II microstructure of corresponding carbon content (Figs. 48 vs 49, 55 vs 56, 62 vs 63). The light matrix in all these specimens obviously must be the dicarbide phase; however, the monocarbide and the sesquicarbide precipitates appeared to be identical. In these cases, the precipitate had to be identified by an independent method such as X-ray diffraction analysis.

Arc-cast specimens with a total-C/U atom ratio of 1.90 to 1.92 (8.80 to 8.84% carbon) and a combined-C/U ratio of 1.88 to 1.90 were virtually single-phase uranium

dicarbide with only a trace of spherically shaped graphite particles (Figs. 66 and 67). After heat-treatment at 1450 to 2130°C, these specimens contained a number of parallel platelets (Figs. 68-70). The larger platelets are probably the graphite found in the chemical analysis since X-ray fluorescence microprobe analysis showed a slight increase in the carbon concentration whenever the probe crossed a large platelet. Presumably, the very fine platelets are the trace of monocarbide that was detected in the X-ray diffraction analysis; however, this could not be confirmed with the microprobe since the platelets were much smaller than the area covered by the microprobe. Note that the appearance of the graphite platelets is the same as that of the monocarbide and sesquicarbide platelets in the heat-treated $UC_{1.8}$ specimens (Figs. 59-64). Rod-shaped graphite was first observed in the as-cast $UC_{1.93}$ specimen (8.9% carbon); the amount increased with the increasing total-carbon concentration above 8.9% (Figs. 72-80). At 1000X a very fine precipitate was observed throughout the dicarbide phase of as-cast specimens having compositions from $UC_{2.0}$ to $UC_{2.4}$ (Figs. 72, 77, and 78). This is probably the trace of monocarbide that was detected in the X-ray diffraction analysis and may also include some free carbon. Heat-treating specimens of $UC_{2.0}$ to $UC_{2.4}$ (9.1 to 10.6% carbon) at 1260 to 2000°C had no significant effect on their chemical or X-ray diffraction analyses; however, it did affect the microstructures. The larger platelets observed in the heat-treated specimens (Figs. 73-76, 79, and 80), as compared with the as-cast specimens, probably represent the agglomeration of the very fine precipitate in the as-cast samples. More platelets appear to be present than can be accounted for solely by the trace of monocarbide found in the X-ray diffraction analysis. This indicates that some of the platelets are probably free carbon that at some time was soluble in the carbide phase and precipitated upon cooling.

The final microstructure (Fig. 81) shows uranium dicarbide with rod-shaped graphite and WUC_2 at the grain boundaries.

Fig. 4. As-Cast $UC_{0.39}$ (1.93% C; Specimen 1), Showing Uranium Monocarbide Grains (Dark Areas) and Uranium Metal.

Fig. 5. As-Cast $UC_{0.83}$ (4.01% C; Specimen 2), Showing Uranium Monocarbide with Uranium Metal at the Grain Boundaries (Light Areas) and as a Spheroidized Precipitate Within the Grains (Black and Light Dots at 1000X).

Fig. 6. As-Cast $UC_{0.96}$ (4.64% C; Specimen 3), Showing (Left) Areas of High-Purity Uranium Monocarbide with Traces of Uranium Dicarbide as a Precipitate of Fine Needles and Traces of Uranium Metal both at the Grain Boundaries and as a Spheroidized Precipitate Within the Grains; (Center) Uranium Metal in the Grain Boundaries at a Magnification of 1000X; and (Right) Area With Dicarbide Precipitate at 1000X. Other as-cast specimens with compositions from $UC_{0.97}$ to $UC_{0.99}$ had similar microstructures except that the metal and dicarbide impurities were not usually found in the same field.

Fig. 7. $UC_{0.98}$ Heat-Treated at $2000^{\circ}C$ (4.70% C; Specimen 4), Showing Uranium Monocarbide with Traces of Uranium Metal at the Grain Boundary and Within the Grains (White Dots) and Uranium Dicarbide (Needle-Like Precipitate Within the Grains).

Fig. 8. $UC_{0.98}$ Heat-Treated at $1600^{\circ}C$ (4.70% C; Specimen 5), Showing Uranium Monocarbide with Traces of Uranium Metal at the Grain Boundary. A needle-like precipitate (not pictured) of uranium dicarbide was found in other areas of this specimen.

Fig. 9. $UC_{0.93}$ Heat-Treated at $1275^{\circ}C$ (4.61% C; Specimen 6), Showing Uranium Monocarbide and Uranium Dioxide (the Gray Precipitate Found Along the Grain Boundary Near the Oxidized Surface of the Specimen), With Traces of What is Probably Sesquicarbide (Irregularly Shaped "Circles") and Dicarbide (Needle-Like Precipitate). Only monocarbide and dioxide were detected by X-ray diffraction analysis.

Y-57237

Y-57238

Fig 10. As-Cast $UC_{1.10}$ (5.24% C; Specimen 7), Showing Uranium Monocarbide Matrix (Dark) with Uranium Dicarbide (Light). The fine Widmanstätten platelets within the grains indicate the presence of a high-temperature solid solution of monocarbide and dicarbide that precipitated upon further cooling.

Fig. 11. $UC_{1.10}$ Heat-Treated First at 1600°C and Then at 1900°C (5.25% C; Specimen 8), Showing Uranium Monocarbide (Dark) with Dicarbide Platelets. The large white areas are dicarbide platelets in a horizontal orientation. The platelets are larger than in the original as-cast specimen (see Fig. 10) because the longer cooling time allowed more segregation to occur. The specimen appears to have been heated in a single-phase region.

Fig. 12. $UC_{1.10}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1820^{\circ}C$ (5.25% C; Specimen 9), Showing Uranium Monocarbide with Dicarbide Platelets (Light). The specimen appears to have been heated in a single-phase region. This microstructure is similar to that in Fig. 11.

Fig. 13. $UC_{1.10}$ Heat-Treated at $1765^{\circ}C$ (5.25% C; Specimen 10), Showing Uranium Sesquicarbide (Irregularly Shaped Light Areas) in the Monocarbide Matrix. Needles are probably a trace of dicarbide that was not detected by X-ray diffraction analysis.

Fig. 14. $UC_{1.10}$ Heat-Treated at $1600^{\circ}C$ (5.24% C; Specimen 11), Showing Uranium Sesquicarbide (Irregularly Shaped Light Areas) in the Monocarbide Matrix. Needles are probably a trace of dicarbide that was not detected by X-ray diffraction analysis. Left and center, bright field illumination; right, polarized light. This microstructure is similar to Fig. 13.

Fig. 15. As-Cast $UC_{1.20}$ (5.71% C; Specimen 12), Showing Uranium Monocarbide (Dark) with Fine Platelets of Uranium Dicarbide. Note the dicarbide-rich, intergranular structure.

Y-61016

Y-61017

Fig. 16. $UC_{1.20}$ Heat-Treated First at $1600^{\circ}C$ and Then at $2070^{\circ}C$ (5.70% C; Specimen 13), Showing Uranium Mono- and D'carbides. The specimen appears to have been heated in a two-phase region,¹⁷ with the UC_{1+x} phase precipitating, when cooled, into monocarbide (dark) with dicarbide platelets (light), and the UC_{2-y} phase precipitating into dicarbide (large, irregularly shaped, white areas) with monocarbide platelets (the dark lines faintly visible within the white areas). Note that at a magnification of 250X this structure might be confused with that of a monocarbide-sesquicarbide mixture, although at 1000X the structures are clearly different (see Fig. 20).

Fig. 17. $UC_{1.20}$ Heat-Treated First at $1600^{\circ}C$ and Then at $2000^{\circ}C$ (5.69% C; Specimen 14), Showing Uranium Monocrbide (Dark) and Dicarbide. The specimen appears to have been heated in a two-phase region. This microstructure is similar to the microstructures shown in Figs. 16, 18, and 19.

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Fig. 18. $UC_{1.20}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1900^{\circ}C$ (5.73% C; Specimen 15), Showing Uranium Monocarbide (Dark) and Dicarbide. The specimen appears to have been heated in a two-phase region. This microstructure is similar to the microstructures shown in Figs. 16, 17, and 19.

Fig. 19. $UC_{1.20}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1820^{\circ}C$ (5.71% C; Specimen 16), Showing Uranium Monocarbide (Dark) and Dicarbide. The specimen appears to have been heated in a two-phase region. This microstructure is similar to the microstructures shown in Figs. 16-18.

Fig. 20. $UC_{1.20}$ Heat-Treated at $1600^{\circ}C$ (5.73% C; Specimen 17), Showing Uranium Monocarbide (Dark) and Uranium Sesquicarbide (Light) Under Bright Field Illumination (Left and Center), and Under Polarized Light (Right). Needles are probably a trace of dicarbide that was not detected by X-ray diffraction analysis. Note that at a magnification of 250X this structure might be confused with that of a monocarbide-dicarbide mixture, although at 1000X the structures are clearly different (see Figs. 16-19).

Fig. 21. As-Cast $UC_{1.25}$ (5.94% C; Specimen 18), Showing Uranium Dicarbide (Light) in Uranium Monocarbide (Dark). Note the dicarbide-rich, intergranular structure.

Fig. 22a. Specimen 19 After Heat-Treatment First at 1600°C and Then at 2130°C, Showing the Low-Carbon Portion of the Specimen (About $UC_{1.3}$). The specimen appears to have been heated in a region where the monocarbide and dicarbide form a solid solution. The "zebra" pattern is caused by a different orientation of the platelets.

Fig. 22b. Specimen 19 After Heat-Treatment First at 1600°C and Then at 2130°C, Showing the High-Carbon Portion of the Specimen (About $UC_{1.7}$). This portion had reacted with the graphite crucible during heat-treatment. All the specimens with carbon contents ranging from about $UC_{1.3}$ to $UC_{1.7}$ appeared to have been heated in a region where the monocarbide and dicarbide form a solid solution. Note the substructure, at 2000X, within the monocarbide platelets (dark). This indicates that, first, at UC_{1+x} phase precipitated from the solid solution and, then, upon further cooling, the UC_{1+x} phase separated into monocarbide and dicarbide. In general, the monocarbide platelets precipitated from the UC_{2-y} phase after the dicarbide had transformed from the cubic to the tetragonal phase, as indicated by the fact that the platelets do not cross the dicarbide twinning boundary (250X and 1000X); however, some slip within the monocarbide platelets was observed at 2000X, which indicated that this was not always true.

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Fig. 23. UC_{1.26} Heat-Treated First at 1600°C and Then at 2070°C (5.97% C; Specimen 20). The specimen appears to have been heated in the two-phase region (discussed in Fig. 17) since there are a few monocarbide platelets throughout the dicarbide-rich areas.

Fig. 24. UC_{1.30} Heat-Treated First at 1600°C and Then at 2000°C (6.13% C; Specimen 21), Showing Uranium Monocarbide and Dicarbide. The specimen appears to have been heated in a two-phase region. Left and center, bright field illumination; right, polarized light. Note that the microstructures of the monocarbide-sesquicarbide (Fig. 27) and monocarbide-dicarbide mixtures are very similar at 250X under bright field illumination, but at 1000X under polarized light they are markedly different. This microstructure is similar to the microstructures shown in Figs. 25 and 26.

Fig. 25. $UC_{1.29}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1900^{\circ}C$ (6.11% C; Specimen 22), Showing Uranium Monocarbide and Dicarbide. The specimen appears to have been heated in a two-phase region. This microstructure is similar to the microstructures shown in Figs. 24 and 26.

Fig. 26. $UC_{1.29}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1820^{\circ}C$ (6.09% C; Specimen 23), Showing Uranium Monocarbide and Dicarbide. The specimen appears to have been heated in a two-phase region. Left and center, bright field illumination; right, polarized light. This microstructure is similar to the microstructures shown in Figs. 24 and 25.

Fig. 27. $UC_{1.25}$ Hect-Treated at $1600^{\circ}C$ (5.93% C; Specimen 24), Showing Uranium Monocarbide (Dark) and Uranium Sesquicarbide (Light) Under Bright Field Illumination (Left and Center), and Under Polarized Light (Right) to Bring Out the Sesquicarbide Grain Structure. The needle-like precipitate is probably a trace of dicarbide which was not detected by X-ray diffraction. Note that the microstructures of the monocarbide-dicarbide (Figs. 24-26) and monocarbide-sesquicarbide mixtures are very much alike at 250X under bright field illumination, but at 1000X under polarized light they are markedly different. No grain structure was observed in the sesquicarbide phase in $UC_{1.10}$ (Fig. 14) or $UC_{1.20}$ (Fig. 20) specimens under polarized light.

Fig. 23. $UC_{1.41}$ Heat-Treated First at $1600^{\circ}C$ and Then at $2070^{\circ}C$ (6.66% C; Specimen 25). The specimen appears to have been heated in a region where the monocarbide and dicarbide form a solid solution.

Fig. 29. $UC_{1.41}$ Heat-Treated First at 1600°C and Then at 2000°C (6.63% C; Specimen 26), Showing Uranium Monocarbide and Dicarbide. The specimen appears to have been heated in a two-phase region. While the etchant did not develop any signs of dicarbide platelets within the monocarbide grains (the large dark grains), they are, in all probability, present. Note that the monocarbide platelets within the light dicarbide phase are much more apparent here than in Figs. 16-19 and 23-26, and that they appear to have a substructure similar to that of Fig. 22b. Left and center, bright field illumination; right, polarized light. This microstructure is similar to the microstructures shown in Figs. 30 and 31.

Fig. 30. $UC_{1.40}$ Heat-Treated First at 1600°C and Then at 1900°C (6.61% C; Specimen 27), Showing Uranium Monocarbide and Dicarbide. The specimen appears to have been heated in a two-phase region. Left and center, bright field illumination; right, polarized light. This microstructure is similar to the microstructures shown in Figs. 29 and 31.

Fig. 31. $UC_{1.41}$ Heat-Treated First at 1600°C and Then at 1820°C (6.62% C; Specimen 28), Showing Uranium Monocarbide and Dicarbide. The specimen appears to have been heated in a two-phase region. Left and center, bright field illumination; right, polarized light. This microstructure is similar to microstructures shown in Figs. 29 and 30.

Fig. 32. $UC_{1.39}$ Heat-Treated at $1600^{\circ}C$ (6.53% C; Specimen 29), Showing Uranium Sesquicarbide (Gray Matrix) and Uranium Monocarbide (Dark) Under Bright Field Illumination (Left and Center) and Under Polarized Light (Right) to Bring Out the Grain Structure of the Sesquicarbide.

Fig. 33. As-Cast $UC_{1.48}$ (6.95% C; Specimen 30), Showing Uranium Monocarbide (Dark) and Uranium Dicarbid (Light). The fine platelets within the grains indicate the presence of a high-temperature solid solution between monocarbide and dicarbide which precipitated upon cooling. Note the monocarbide-rich intergranular structure in contrast to the dicarbide-rich intergranular structure in as-cast $UC_{1.25}$ (Fig. 21).

Fig. 34. As-Cast $UC_{1.5}$ (7% C; Specimen 31), Showing Uranium Monocarbide (Dark) and Uranium Dicarbide (Light). This microstructure is similar to Fig. 33 and is presented only to show the appearance of specimens 32-38 and 41 (Figs. 35-41, 44) before heat-treatment.

Fig. 35. $UC_{1.55}$ Heat-Treated First at $1600^{\circ}C$ and Then at $2130^{\circ}C$ (7.25% C; Specimen 32). The specimen appears to have been heated in a region where the monocarbide and dicarbide form a solid solution. Note how the solid solution, upon cooling in the furnace, seems to have precipitated first into UC_{1+x} and UC_{2-y} phases, which, upon further cooling, separated into a monocarbide phase (dark) containing some dicarbide platelets and a dicarbide phase (light) containing monocarbide platelets. This microstructure is similar to the microstructures shown in Figs. 36 and 37.

Fig. 36. $UC_{1.5}$ Heat-Treated at $2000^{\circ}C$ (7% C; Specimen 33), Showing Uranium Monocarbide and Dicarbide. The specimen appears to have been heated in a single-phase region. This microstructure is similar to the microstructures shown in Figs. 35 and 37.

Fig. 37. UC-51 Heat-Treated First at 1600°C and Then at 2000°C (7.07% C; Specimen 34), Showing Uranium Monocarbide and D carbide. The difference between specimen 33 (Fig. 36) and specimen 34 is that specimen 34 received a prior heat-treatment at 1600°C to form the sesquicarbide (Fig. 44) and then was heated at 2000°C, while specimen 33 had no prior heat-treatment except the initial arc-melt.

Fig. 38. $UC_{1.49}$ Heat-Treated First at 1600°C and Then at 1900°C (6.98% C; Specimen 35), Showing Uranium Monocarbide and Dicarbide. The specimen appears to have been heated in a two-phase region. Note the substructure within the dark monocarbide platelets at 2000X. This microstructure is similar to that shown in Fig. 39.

Fig. 39. $UC_{1.48}$ Heat-Treated First at 1600°C and Then at 1820°C (6.93% C; Specimen 36), Showing Uranium Monocarbide and Dicarbide. The specimen appears to have been heated in a two-phase region. Note the substructure within the monocarbide platelets at 2000X. This microstructure is similar to that shown in Fig. 38.

Fig. 40. $UC_{1.48}$ Heat-Treated at $1600^{\circ}C$ to Form Sesquicarbide (Fig. 44), Then at $1900^{\circ}C$ to Decompose the Sesquicarbide (Fig. 38), and Finally at $1765^{\circ}C$ to Make Sesquicarbide Again (6.96% C; Specimen 37). This microstructure is similar to the microstructures shown in Figs. 41-44.

Fig. 41. $UC_{1.48}$ Heat-Treated at $1765^{\circ}C$ (6.94% C; Specimen 38), Showing Uranium Sesquicarbide with Traces of Monocarbide and Dicarbide. This microstructure is similar to Figs. 40 and 42-44.

Fig. 42. $UC_{1.51}$ Heat-Treated at $1720^{\circ}C$ (7.04% C; Specimen 39), Showing Uranium Sesquicarbide with Traces of Monocarbide and Dicarbide. This microstructure is similar to Figs. 40, 41, 43, and 44.

Fig. 43. $UC_{1.47}$ Heat-Treated at $1600^{\circ}C$ with One Brief Excursion to $1680^{\circ}C$ (6.89% C; Specimen 40), Showing Uranium Sesquicarbide with Traces of Monocarbide and Dicarbide. Note that the grain size is a little smaller than in Figs. 41 and 42, where a higher temperature was used. Heating this specimen for an additional 65 hr at $1600^{\circ}C$ had no effect on the amount of impurity in the sesquicarbide phase, although the grain size did increase slightly.

Fig. 44. $UC_{1.46}$ Heat-Treated at $1600^{\circ}C$ (6.87% C; Specimen 41), Showing Uranium Sesquicarbide with Traces of Monocarbide and Dicarbide. Note that the impurity is finer and the grains are more poorly defined than in specimen 40 (Fig. 43), which was very briefly heated to $1680^{\circ}C$ in addition to the major $1600^{\circ}C$ treatment.

Fig. 45. $UC_{1.49}$ Heat-Treated at $1275^{\circ}C$ (5.64% C; Specimen 42), Showing Uranium Sesquicarbide Under Bright Field Illumination (Left and Center), and Under Polarized Light (Right). The grains are quite small and tend to follow the platelet orientation of the original as-cast monocarbide-dicarbide mixture. The light precipitate (left) found along the grain boundary remaining from the original as-cast specimen is uranium dioxide, which was detected chemically and by x-ray diffraction analysis.

Fig. 46. $UC_{1.62}$ Heat-Treated First at 1600°C and Then at 2000°C (7.53% C; Specimen 43). The specimen appears to have been heated in a region where the monocarbide and dicarbide form a solid solution. This microstructure is similar to that in Fig. 47.

Fig. 47. $UC_{1.62}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1900^{\circ}C$ (7.55% C; Specimen 44), Showing Uranium Dicarbide and Monocarbide. The specimen appears to have been heated in a single-phase region. This microstructure is similar to that in Fig. 46.

Fig. 48. $UC_{1.62}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1820^{\circ}C$ (7.54% C; Specimen 45), Showing Uranium Dicarbide and Monocarbide. The specimen appears to have been heated in a two-phase region. Note that this microstructure is essentially identical to the one that is shown in Fig. 49, which contains a three-phase mixture of dicarbide, monocarbide, and sesquicarbide.

Fig. 49. $UC_{1.61}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1765^{\circ}C$ (7.50% C; Specimen 46), Showing Uranium Dicarbide Matrix (Light) with Sesquicarbide and Monocarbide. Note that this microstructure is essentially identical to that shown in Fig. 48, which contains only dicarbide and monocarbide.

Fig. 50. $UC_{1.59}$ Heat-Treated at $1600^{\circ}C$ (7.43% C; Specimen 47) Uranium sesquicarbide is the dark-gray phase under bright field illumination (left and center) whose grain structure is brought out by polarized light (right), and uranium dicarbide is the light phase. The trace of needle-like precipitate in the light dicarbide phase is probably monocarbide that was not detected in the x-ray diffraction analysis.

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Fig. 51. As-Cast $UC_{1.71}$ (7.95% C; Specimen 48), Showing Uranium Dicarbide with Fine Platelets of Uranium Monocarbide (Dark) Throughout the Grains. Note the blocky structure of the tetragonal dicarbide within the equiaxed grain structure of the high-temperature face-centered-cubic form.

Fig. 52. $UC_{1.78}$ Heat-Treated First at $1600^{\circ}C$ and Then at $2130^{\circ}C$ (8.2% C; Specimen 49), Showing Uranium Dicarbide (Light) and Monocarbide. The specimen appears to have been heated in a region where the monocarbide and dicarbide form a solid solution. The monocarbide platelets do not cross the twinning boundary, indicating that they precipitated after the dicarbide phase had transformed from the cubic to the tetragonal phase. Note also the substructures within both the monocarbide and dicarbide phases at 2000X, indicating that UC_{1+x} and UC_{2-y} phases precipitated first from the solid solution and that these, in turn, separated into the monocarbide and dicarbides. This microstructure is similar to the microstructure shown in Figs. 53-56, even though that in Fig. 56 contains sesquicarbide as well as the monocarbide and dicarbides.

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Fig. 53. $UC_{1.76}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1900^{\circ}C$ (8.15% C; Specimen 50), Showing Uranium Dicarbide and Monocarbide. This microstructure is similar to the microstructures shown in Figs. 52 and 54-56.

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Fig. 54. $UC_{1.73}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1820^{\circ}C$ (8.01% C; Specimen 51), Showing Uranium Dicarbide and Monocarbide. This microstructure is similar to the microstructures shown in Figs. 52-53 and 54-56.

Fig. 55. $UC_{1.72}$ Heat-Treated at $1765^{\circ}C$ (7.99% C; Specimen 52), Showing Uranium Dicarbide and Monocarbide. This microstructure is similar to the microstructures shown in Figs. 52-54 and 56.

Fig. 56. $UC_{1.74}$ Heat-Treated at $1700^{\circ}C$ (8.08% C; Specimen 53), Showing Uranium Dicarbide Matrix with Both Sesquicarbide and Monocarbide. It is impossible to differentiate the sesquicarbide from the monocarbide precipitate. Note that this microstructure is similar to Figs. 52-55, which did not contain any sesquicarbide.

Fig. 57. $UC_{1.70}$ Heat-Treated at $1600^{\circ}C$ (7.90% C; Specimen 54), Showing Uranium Dicarbide (Light) and Uranium Sesquicarbide (Large, Dark Areas That Were Purple Under the Microscope). The dark platelets throughout the dicarbide phase could be monocarbide, which was detected by x-ray diffraction analysis, and/or sesquicarbide. Polarized light did not develop any equiaxial grain structure within the sesquicarbide phase. Possibly these are single grain areas. This specimen cracked badly during heat-treatment.

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Fig. 58. As-Cast $UC_{1.78}$ ($8.24^{\circ}C$; Specimen 55), Showing Uranium Dicarbide with Fine Platelets of Monocarbide (Dark) Throughout the Grains. The monocarbide impurity is not readily apparent at 250X. This emphasizes the importance of examining microstructures at 1000X, as well as at the lower magnification.

Fig. 59. $UC_{1.79}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1900^{\circ}C$ (8.29% C; Specimen 56), Showing Uranium Dicarbide with Monocarbide Platelets. This microstructure is similar to the microstructures shown in Figs. 60-64 even though those in Figs. 63 and 64 contain sesquicarbide in addition to the dicarbide and monocarbide.

Fig. 60. $UC_{1.80}$ Heat-Treated First at $1600^{\circ}C$ and Then at $1820^{\circ}C$ (8.33% C; Specimen 57), Showing Uranium Dicarbide with Monocarbide Platelets. This microstructure is similar to the microstructures shown in Figs. 59, 61, and 62.

Fig. 61. $UC_{1.79}$ Heat-Treated at $1765^{\circ}C$ (8.27% C; Specimen 58), Showing Uranium Monocarbide Platelets (Dark) in Different Orientations Throughout the Dicarbide Matrix. All the platelets within a given dicarbide grain had the same orientation. The "striped" arrangement predominated, but significant amounts of other orientations were observed. Note that the platelets do not cross the dicarbide twinning boundary; this indicates that the monocarbide precipitated after the cubic-to-tetragonal transformation of the UC_{2-y} phase.

Fig. 62. $UC_{1.80}$ Heat-Treated at $1700^{\circ}C$ (8.34% C; Specimen 59), Showing Uranium Dicarbide with Monocarbide Platelets. This microstructure is similar to the microstructures shown in Figs. 59-61.

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Fig. 63a. $UC_{1.79}$ Heat-Treated at $1600^{\circ}C$ (8.26% C; Specimen 60). X-ray analysis indicated that the specimen is mostly uranium dicarbide with both monocarbide and sesquicarbide impurities. This microstructure is virtually identical to the microstructures in Figs. 59-62, which were dicarbide matrix with only monocarbide precipitate. It is impossible to differentiate the sesquicarbide from the monocarbide precipitate. About two-thirds of the specimen had this microstructure.

Fig. 63b. $UC_{1.79}$ Heat-Treated at $1600^{\circ}C$ (8.26% C; Specimen 60). About one-third of the specimen resembled the dark areas (actually dark reds and blues). No precipitate was observed within these areas under bright field illumination (left and center) or polarized light (right), although in all probability it was present and was not revealed by the etchant (see Fig. 64).

Fig. 64. $UC_{1.78}$ Heat-Treated at $1450^{\circ}C$ (8.25% C; Specimen 61), Showing Uranium Sesquicarbide and Monocarbide Platelets in a Dicarbide Matrix. This microstructure is similar to Fig. 63. The dark areas had the same "striped" structure as the light areas under the microscope, but, unfortunately, the dark red and blue colors photographed as a single phase.

Fig. 65. As-Cast $UC_{1.85}$ (8.54% C; Specimen 62), Showing Nearly Single-Phase Uranium Dicarbide.

Fig. 66. As-Cast $UC_{1.91}$ (8.80% C; Specimen 63; Combined-C/U Atom Ratio of 1.88), Showing Virtually Single-Phase Uranium Dicarbide. Note the blocky structure of the tetragonal dicarbide within the equiaxed grain structure of the high-temperature face-centered-cubic form. Spherical graphite particles have been detected in some specimens with this composition.

Fig. 67. As-Cast $UC_{1.92}$ (8.84% C; Specimen 64; Combined-C/U Atom Ratio of 1.90), Showing Uranium Dicarbide with a Trace of Spherical Graphite Particles. This microstructure is similar to Fig. 66 and is presented only to show the appearance of specimens 66 and 67 (Figs. 69 and 70) before heat-treatment.

Fig. 68. $UC_{1.91}$ Heat-Treated at $2130^{\circ}C$ (8.79% C; Specimen 65; Combined-C/U Atom Ratio of 1.87), Showing Uranium Dicarbide with Traces of Monocarbide (X-Ray Diffraction Analysis) and Graphite (Chemical Analysis). See the discussion of Fig. 69.

Fig. 69. $UC_{1.92}$ Heat-Treated at $2000^{\circ}C$ (8.81% C; Specimen 66; Combined-C/U Atom Ratio of 1.87). The larger platelets are probably graphite since X-ray fluorescence microprobe analysis showed a slight increase in the carbon concentration whenever the probe crossed a large platelet. The very fine platelets are presumed to be the trace of monocarbide detected in the X-ray diffraction analysis; however, this could not be confirmed with the microprobe since the platelets were smaller than the area covered by the microprobe. Note the contrast between this microstructure and that of the original as-cast button (Fig. 67).

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Fig. 70. $UC_{1.91}$ Heat-Treated at $1450^{\circ}C$ (8.80% C; Specimen 67; Combined-C/U Atom Ratio of 1.86), Showing Uranium Dicarbide with Traces of Monocarbide (X-Ray Diffraction Analysis) and Graphite (Chemical Analysis). This microstructure is similar to Fig. 69.

Fig. 71. As-Cast $UC_{1.93}$ (8.88% C; Specimen 68; Combined-C/U Atom Ratio of 1.86), Showing Uranium Dicarbide with Spherical- and Rod-Shaped Graphite. The graphite is more distinct under the microscope or in color photographs where the carbide is brightly colored and the graphite is black. The uranium monocarbide precipitate is apparently so fine that it is not visible here.

Fig. 72. As-Cast $UC_{1.97}$ (9.06% C; Specimen 69; Combined-C/U Atom Ratio of 1.84), Showing Uranium Dicarbide with Rod-Shaped Graphite and a Trace of a Very Fine Precipitate that is Probably the Uranium Monocarbide Detected by X-Ray Diffraction Analysis. Although this specimen has the stoichiometric composition for UC_2 , it contains large quantities of graphite and only a trace of monocarbide.

Fig. 73. $UC_{1.99}$ Heat-Treated at $2000^{\circ}C$ (9.10% C; Specimen 70; Combined-C/U Atom Ratio of 1.85), Showing Uranium Dicarbide, Rod-Shaped Graphite, and Small Platelets of Uranium Monocarbide and Probably Also of Graphite (see Fig. 69).

Fig. 74. $UC_{2.00}$ Heat-Treated at $1600^{\circ}C$ (9.14% C; Specimen 71; Combined-C/U Atom Ratio of 1.86), Showing Uranium Dicarbide, Rod-Shaped Graphite, and Small Platelets of Uranium Monocarbide and Probably Also of Graphite (see Fig. 69).

Fig. 75. $UC_{1.99}$ Heat-Treated at $1450^{\circ}C$ (9.12% C; Specimen 72; Combined-C/U Atom Ratio of 1.84), Showing Uranium Dicarbide, Rod-Shaped Graphite, and Small Platelets of Uranium Monocarbide and Probably Also of Graphite (see Fig. 69).

Fig. 76. $UC_{1.99}$ Heat-Treated at $1260^{\circ}C$ (9.14% C; Specimen 73; Combined-C/U Atom Ratio of 1.83), Showing Uranium Dicarbide, Rod-Shaped Graphite, and Small Platelets of Uranium Monocarbide and Probably Also of Graphite (see Fig. 69). The microstructures shown in Figs. 73-76 are virtually identical in spite of the range in heat-treatment temperatures (1260 to $2000^{\circ}C$).

Fig. 77. As-Cast $UC_{2.15}$ (9.78% C; Specimen 74; Combined-C/U Atom Ratio of 1.84), Showing Uranium Dicarbide, Graphite, and a Trace of a Fine Precipitate That is Probably the Uranium Monocarbide Detected by X-Ray Diffraction Analysis. Note how the amount of graphite increases with the increasing carbon content of the specimen beyond 8.8% ($UC_{1.91}$)(see Figs. 66, 67, 71, 72, and 78).

Fig. 78. As-Cast $UC_{2.4}$ (10.6% C; Specimen 75; Combined-C/U Atom Ratio of 1.86), Showing Uranium Dicarbide, Graphite, and a Fine Precipitate That is Probably the Trace of Uranium Monocarbide Detected by X-Ray Diffraction Analysis.

Fig. 79. $UC_{2.4}$ Heat-Treated 4 hr at $2000^{\circ}C$ (10.9% C; Specimen 76; Combined-C/U Atom Ratio of 1.87), Showing Uranium Dicarbide, Graphite, and Small Platelets of Uranium Monocarbide and Probably Also of Graphite (see Fig. 69).

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Fig. 80. $UC_{2.4}$ Heat-Treated at $1450^{\circ}C$ (10.8% C; Specimen 77; Combined-C/U Atom Ratio of 1.85), Showing Uranium Dicarbide, Graphite, and Small Platelets of Uranium Monocarbide and Probably Also of Graphite (see Fig. 69).

Fig. 81. As-Cast $U_{1.00}W_{0.10}C_{2.04}$ (84% U, 6% W, 8.6% C; Specimen 78), Showing Uranium Dicarbide, Graphite, and the Tungsten-Containing Phase (the Light Phase at the Grain Boundaries). Chemical analyses showed that at least 70% (and possibly all) of the tungsten was present as WUC_2 .

4. REFERENCES

1. D. K. Magnus, Trans. Am. Nucl. Soc. 7 (1), 110 (1964).
2. Heavy Water Organic Cooled Reactor, 1000 Mwe Nuclear Power Plant Preliminary Conceptual Design, AI-CE-Memo-6, Vols. 1 and 2 (1965).
3. R. D. MacDonald, W. G. Mathers, A. M. Tachis, and J. E. May, SAP-Clad Uranium Carbide Fuel Elements, AECL-2571 (1966).
4. P. R. Kasten et al., An Evaluation of Heavy-Water-Moderated Organic-Cooled Reactors, ORNL-3921 (1967); and Supplements A and B (to be published).
5. Euratom Scientific Activities ORGEL Program, Experimental Studies, EUR-1830.E, Part II (1964).
6. An Evaluation of Four Design Studies of a 1000 Mwe Ceramic Fueled Fast Breeder Reactor, COO-279 (1964).
7. W. V. Goeddel, The Development and Evaluation of Graphite-Matrix Fuel Compacts for the HTGR, GA-2289 (1961).
8. M. B. Sears and L. M. Ferris, Studies on the U-C Constitutional Diagram Between UC and UC₂ (in preparation).
9. M. W. Mallett, A. F. Gerds, and H. R. Nelson, J. Electrochem. Soc. 99, 197 (1952).
10. R. J. Gray, W. C. Thurber, and C. K. H. DuBose, Metal. Progr. 74, 65 (1958).
11. A. Accary, J. Nucl. Mater. 8, 281 (1963).
12. M. J. Bradley and L. M. Ferris, Inorg. Chem. 1, 683 (1962).
13. M. J. Bradley and L. M. Ferris, Inorg. Chem. 3, 189 (1964).
14. M. J. Bradley and L. M. Ferris, Inorg. Chem. 3, 730 (1964).
15. M. J. Bradley and L. M. Ferris, Inorg. Chem. 4, 597 (1965).
16. M. J. Bradley and L. M. Ferris, J. Inorg. Nucl. Chem. 27, 1557 (1965).
17. M. B. Sears, L. M. Ferris, and R. J. Gray, J. Electrochem. Soc. 113, 269 (1966).

18. M. J. Bradley, L. M. Ferris, T. Hikido, and J. W. Ullmann, The Effect of Irradiation on the Hydrolysis of Uranium Carbides. I. Preparation of Uranium Monocarbide Pellets for Irradiation, ORNL-3403 (1963).
19. L. M. Litz, A. B. Garrett, and F. C. Croxton, J. Am. Chem. Soc. 70, 1718 (1948).
20. M. W. Mallett, A. F. Gerds, and D. A. Vaughn, J. Electrochem. Soc. 98, 505 (1951).
21. A. E. Austin, Acta Cryst. 12, 159 (1959).
22. M. Atoji and R. C. Medrud, J. Chem. Phys. 31, 332 (1959).
23. B. D. Sharma, Acta Cryst. 16, 322 (1963).
24. A. L. Bowman, G. P. Arnold, W. G. Witteman, T. C. Wallace, and N. G. Nereson, Acta Cryst. 21, 670 (1966).
25. S. Takahashi, B. Ishii, K. Yamamoto, H. Uchikoshi, and Y. Akimoto, "Microstructures of U-C Alloys," in Compounds of Interest in Nuclear Reactor Technology, Vol. X of Nuclear Metallurgy, ed. by J. T. Waber, P. Chiotti, and W. N. Miner, IMD Special Report No. 13, The Metallurgical Society of the AIME, 1964, pp. 627-40.
26. W. B. Wilson, J. Am. Chem. Soc. 43, 77 (1960).
27. W. R. Laing, ORNL Analytical Chemistry Division, personal communication to M. B. Sears.
28. G. Goldberg, A. S. Meyer, Jr., and J. C. White, Anal. Chem. 32, 314 (1960).
29. A. B. Crowther and R. S. Large, Analyst 81, 64 (1956).
30. G. W. C. Milner, G. Jones, D. Crossley, and G. Phillips, The Determination of Nitrogen in Uranium Nitrides - Part II, AERE-R 4713 (1964).
31. P. E. Evans and T. J. Davies, J. Nucl. Mater. 10, 43 (1963).
32. R. R. Richard and E. I. Wyatt, ORNL, personal communication to M. B. Sears.
33. A. D. Horton and J. L. Botts, Nucl. Sci. Eng. 18, 97 (1964).
34. R. L. Martin, Anal. Chem. 34, 896 (1962).
35. E. L. Long, Jr., and R. J. Gray, Preparation of Metallographic Specimens Through Vibratory Polishing, ORNL-2494 (1958).

36. E. L. Long, Jr., and R. J. Gray, Metal Progr. 74, 145 (1958).
37. E. L. Long, Jr., J. T. Meador, and R. J. Gray, ASTM STP No. 285, American Society of Testing Materials, Philadelphia, Pa. (1960).
38. R. J. Gray and C. K. H. DuBose, A Micrographic Study of the Effect of Moisture in the Air on Arc-Cast Uranium Monocarbide and Uranium Dicarbide at Room Temperature over Extended Periods, ORNL-TM-56 (1961).
39. C. K. H. DuBose and R. J. Gray, Metallography of Pyrolytic Carbon Coated and Uncoated Uranium Carbide Spheres, ORNL-TM-91 (1962).
40. C. K. H. DuBose and R. J. Gray, Metallographic Examination of Pyrolytic-Carbon Coated and Uncoated Uranium Carbide Particles, ORNL-TM-521 (1963).
41. R. J. Gray and R. S. Crouse, Technical Papers of Nineteenth Metallography Group Meeting Held April 20-22, 1965, ORNL-TM-1161 (1966).

5. APPENDIX

5.1 Analytical Procedures

Uranium and Total Carbon. – Uranium and total carbon were determined by burning 0.7 g (UC_2) to 1 g (UC) of carbide, which had been crushed to $-10 +50$ mesh particles, in pure oxygen at $1000^\circ C$ for 2 hr.²⁷ The effluent gases were passed, first, through copper oxide ($650^\circ C$) to ensure complete combustion to CO_2 , then through an anhydrous trap to remove the water, and finally through an ascarite and anhydrous trap to sorb the CO_2 . The amount of total carbon was calculated from the weight of CO_2 sorbed in the ascarite trap, and the amount of uranium was calculated from the weight of U_3O_8 residue in the platinum combustion boat. To prevent premature ignition of the carbide, the combustion tube was cooled below $700^\circ C$ and filled with argon before the sample was introduced.

The analysis of specimen 78, which contained 6% tungsten, required a modification in the standard procedure. Since the combustion ash from the total carbon analysis consisted of a mixture of U_3O_8 and WO_3 , the uranium content could not be determined by weighing the ash. Therefore, it was necessary to leach the uranium from the ash with nitric acid and then to analyze the leachate for uranium.²⁷

Free Carbon. – A 0.5- to 1.0-g sample of carbide ($-10 +100$ mesh particles) was dissolved in refluxing acid and filtered through a Leco disposable filtering crucible (No. 528-30, Laboratory Equipment Corp., St. Joseph, Michigan).²⁷ The material held by the filter was washed with acetone and ether to dissolve any wax and was then dried at $100^\circ C$. The carbon in this material was determined as CO_2 in the Leco Low Carbon Analyzer. Initially, many of the samples were dissolved in 6 M HCl; later, however, 6 M HNO_3 , which gave faster dissolution and equally accurate results, was substituted for the HCl. A more-concentrated HNO_3 solution (10 M) was required for the dissolution of specimen 78, which contained 6% tungsten.

Oxygen. – Oxygen in the older specimens was determined by fluorination with $KBrF_4$.²⁸ More recently, oxygen has been determined by inert gas fusion, using a

Leco Oxygen Analyzer.²⁷ A 0.1- to 0.2-g sample was dropped into a bath of molten platinum metal contained in a graphite crucible. At 2200 to 2400°C, carbon that is dissolved in the platinum bath rapidly reduces oxides to CO, which is evolved and measured by a thermal conductivity cell. The fluorination and inert gas fusion procedures gave equally good results. For example, a uranium monocarbide specimen prepared at Atomics International analyzed 120, 250, and 140 ppm of oxygen (170 ppm, avg.) by inert gas fusion, and 138, 182, 248, 154, 178, 233, 123, 150, 111, and 193 ppm of oxygen (171 ppm, avg.) by fluorination.

Nitrogen. — In the analysis of uranium carbides for nitrogen, 0.25 to 0.5 g of crushed carbide was dissolved in 9 M H_3PO_4 -- 2.5 M H_2SO_4 .²⁷ The solution was then made basic, Devarda's alloy was added, and the ammonia that subsequently formed was steam-distilled into a receiver containing dilute sulfuric acid. Finally, the ammonia was determined spectrophotometrically, using sodium phenate as the indicator.²⁹ This Kjeldahl procedure is considerably faster than the Dumas method, and gives accurate results when the nitrogen is present in the specimen as uranium mononitride.³⁰ The Kjeldahl method does not yield quantitative nitrogen recovery from specimens containing the higher uranium nitrides;³⁰ however, the higher nitrides are readily decomposed to the mononitride by vacuum heat-treatment at 800 to 1150°C³¹ and probably would not be present in the carbide specimens used in this study since these specimens were either arc-cast or vacuum heat-treated at temperatures above 1250°C.

Tungsten. — Low concentrations (< 1%) of tungsten were determined by neutron activation analysis.³² The carbide was fused with KNO_3 - K_2CO_3 , and the resulting glass was dissolved in water. This water solution was irradiated for 5 min in a neutron flux of 6×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$, and then the activated tungsten was precipitated with a tungsten carrier as $\text{WO}_3 \cdot \text{H}_2\text{O}$. The precipitate was purified and ignited to WO_3 , and the gamma activity was subsequently determined by using a multichannel pulse-height analyzer. The specific activity was compared with reference tungsten standards that had been treated similarly.

The tungsten in specimen 78 was determined gravimetrically by leaching the carbide with 14 M HNO_3 , collecting the residue by filtration, burning the carbon (the free graphite in the original carbide) from this residue, and weighing the product (WO_3).²⁷

X-Ray Analyses. — X-ray powder patterns were determined with a Debye-Scherrer 114.59-mm-diam powder camera, using Cu K_α radiation. Microprobe analyses were conducted by using a Philips AMR/3 Electron Probe Microanalyzer.

5.2 Hydrolysis Procedure

The carbide specimen (3 to 4 g) was placed in the reaction vessel, 50 ml of water was placed in the funnel, and the apparatus was assembled as shown in Fig. 82. The reactants were preheated to the desired temperature in the constant-temperature bath (silicon oil or a water-glycerol mixture), which was controlled to $\pm 0.1^\circ\text{C}$, while the main reaction vessel and the water were flushed with helium to remove air from the system. The reaction was initiated by adding water to the carbide. Since the initial rate of hydrolysis was slow, the helium displaced by addition of water to the reaction vessel was vented through the pressure equalizer connected to the condenser. The pressure equalizer was then isolated from the rest of the system, which was maintained thereafter at atmospheric pressure by continual adjustment of the leveling bulb. The evolved gases were first collected in the gas buret, where the volume was measured, and then were transferred to an evacuated sample bulb. After gas evolution had ceased, the gas remaining in the reaction vessel was sampled by using the gas buret as a Toepler pump. The gelatinous residue was dissolved in 6 M HCl , the solution was filtered, and the filtrate was analyzed potentiometrically for uranium. The magnetic stirrer was used only during the residue dissolution step. Nonvolatile acid-insoluble waxes, found when the specimens contained uranium dicarbide or sesquicarbide, were recovered by washing the reaction vessel and filter first with acetone and then with ether and subsequently removing the solvents by evaporation. Any free carbon was collected on the filter.

Fig. 82. Apparatus for Measuring the Volume of Gas Evolved in the Reactions of Uranium Carbides with Aqueous Reagents.

Gas volumes were converted to standard conditions (0°C and 760 mm Hg pressure), assuming ideal gas behavior, and were corrected for the vapor pressure of water. Gas chromatography³³ gave an accurate and relatively complete analysis of the gaseous products; however, a complete carbon balance for the experiment could not be obtained when nonvolatile carbon-containing products were formed. The chromatographic peaks for all identified hydrocarbons were checked against known standards by using at least two different column packings. The hydrocarbons were also tested for unsaturation with a mercuric perchlorate column.³⁴ The amount of each unknown compound was estimated by using the calibration constant for the *n*-alkane that was eluted after the unknown. Since the samples contained helium from the initial atmosphere in the system, the compositions were normalized by dividing the amount (vol %) of each product in the gas sample by the sum of the products. In some cases, the amounts of helium (from the initial atmosphere in the system), hydrogen, and methane were also determined by mass spectroscopic analysis.^{13,14} The total carbon, as calculated from the chromatographic analyses, was corroborated by burning gas samples in oxygen over a hot platinum wire, using an Orsat apparatus.^{13,14}

5.3 Gaseous Products from the Hydrolysis of Uranium Carbides

The hydrolytic properties of many of these uranium carbide specimens have been discussed previously.¹²⁻¹⁶ The primary gaseous products obtained from the hydrolysis of specimens not included in refs. 12 to 16 are tabulated in Tables 4 to 6. Minor components such as the alkanes containing 5 to 8 carbon atoms have been grouped together. In all cases the ratios of the various C₂- to C₈-hydrocarbons were the same as those reported in ref. 14. Tables 4 and 6 are self-explanatory. In Table 5, the results for UC_{2.0} specimens show somewhat more than the ± 10% deviation expected, based on the precision of the gas chromatographic analyses. Specimens 69 through 73 were not taken from the same arc-cast button and contain varying amounts of tungsten (Table 3), which is known to have a catalytic effect on the hydrolysis reaction.¹⁵ Note also in Table 3 that these UC_{2.0} specimens contain considerably more tungsten than the other samples except for specimen 78, to which tungsten was added intentionally.

Table 4. Gaseous Products Obtained from the Hydrolysis
of Heat-Treated UC_{1.0} Specimens

Specimen No.	Heat- Treatment (°C)	Volume of Gas [ml (STP)/g carbide]	Composition of Gas (vol %)		
			Hydrogen	Methane	C ₂ - to C ₈ Hydrocarbons
avg. from ref. 13	as-cast	93	11	86	3
4	2000	91	10	85	5
5	1600	90	9	88	2
6	1275	88 ^a	13	83	4

^a1.9 wt % of original specimen was recovered as UO₂ after dissolution in 6 N HCl, of the hydrated uranium(IV) oxide that was formed by hydrolysis of the carbide.

Table 5. Gaseous Products Obtained from the Hydrolysis of Heat-Treated UC_{1.8}-UC_{2.3} Specimens

Total-C/U Atom Ratio	Specimen No.	Heat- Treatment (°C)	Volume of Gas [ml(STP) per g of carbide]	Composition of Gas (vol %)										Unidentified
				Hydrogen	Methane	Ethane	Propane	Butanes	C ₅ - to C ₈ -Alkanes	Ethene	Butenes	C ₅ - to C ₇ -Alkenes	Alkynes	
1.8	55	as-cast	43	29	28	29	0.8	3.8	1.0	1.4	3.4	2.0	0.9	1.3
	57	1820	43	30	28	27	0.9	3.7	1.2	1.3	3.3	2.1	1.1	1.3
	58	1765	46	33	27	26	0.8	3.3	1.1	1.3	3.6	2.2	1.2	1.4
	60	1600	42	31	26	28	0.9	3.7	1.3	1.4	3.6	2.1	1.2	1.4
	61	1450	44	43	15	26	0.8	3.5	1.5	1.4	3.8	2.5	1.2	1.3
1.9	64	as-cast	42	45	13	26	0.8	3.6	1.1	1.5	3.9	2.2	1.2	1.4
	66	2000	41	49	11	25	0.7	3.3	0.9	1.6	4.1	2.2	1.2	1.5
	67	1450	44	44	16	24	0.7	3.4	1.0	1.6	3.8	2.2	1.2	1.3
2.0	69	as-cast	43	40	15	28	1.0	4.4	1.2	1.4	5.0	2.2	0.4	1.1
	70	2000	39	33	17	33	1.0	5.2	1.1	1.6	5.1	1.8	0.7	1.2
	71	1600	41	34	16	34	1.0	4.7	0.9	1.7	4.8	1.3	1.3	0.8
	72	1450	44	47	18	22	0.6	2.9	0.6	1.8	3.3	1.1	1.1	1.0
	73	1260	48	55	12	22	0.6	2.7	0.6	1.2	3.3	1.5	0.4	0.9
2.3	75	as-cast	39	33	17	35	1.0	4.4	0.8	1.8	4.6	1.5	0.8	1.2
	76	2000	36	25	20	35	0.9	4.8	1.6	1.7	4.8	3.0	1.4	1.5
	77	1450	36	28	19	34	0.8	4.5	1.3	1.7	5.2	2.8	1.4	1.8

Table 6. Gaseous Products Obtained from the Hydrolysis of Heat-Treated $UC_{1.5}$ Specimens

Composition of Specimen	Specimen No.	Final Heat-Treatment (°C)	Volume of Gas [ml(STP) per g of carbide]	Composition of Gas (vol %)										
				Hydrogen	Methane	Ethane	Propane	Butanes	C ₅ - to C ₈ -Alkanes	Ethene	Butenes	C ₅ - to C ₇ -Alkenes	Alkynes	Unidentified
UC + UC ₂	30	as-cast	64	24	48	18	1.4	3.0	0.7	0.7	2.8	1.0	0.1	0.6
	31	as-cast	62	28	45	18	1.0	2.8	0.7	0.4	2.1	0.9	0.1	0.8
	33	2000	57	18	53	20	1.1	3.1	0.8	0.7	2.0	0.9	0.4	0.7
	34	2000	56	19	54	18	0.9	2.3	0.7	0.7	2.1	1.1	0.4	0.7
	35	1900	57	15	56	20	0.9	2.6	0.6	0.7	2.2	1.0	0.5	0.8
	36	1820	56	17	54	20	1.1	3.1	0.6	0.7	2.4	0.5	0.4	0.7
U ₂ C ₃	37	1765	62	64	5	20	0.6	2.8	0.8	1.1	3.0	1.1	0.4	0.7
	38	1765	63	57	5	25	0.8	3.4	0.9	1.4	3.5	1.3	0.6	1.2
	39	1720	60	56	2	27	1.1	3.7	0.9	1.6	4.3	1.3	0.7	1.1
	40	1600	61	58	2	26	0.7	4.0	0.9	1.2	4.2	1.1	0.4	0.9
	41	1600	63	57	5	25	0.8	4.0	0.9	1.4	3.7	1.0	0.5	0.8
	42	1275	62 ^a	65	5	20	0.7	2.8	0.4	1.4	3.7	0.5	0.4	0.5

^a3.3 wt % of original specimen was recovered as UO_2 after dissolution in 6 N HCl of the hydrated uranium(IV) oxide that was formed by hydrolysis of the carbide.

The values reported for the heat-treated specimens 70 through 73 in Table 5 fall within the range observed for similar arc-cast $UC_{2.0}$ specimens.¹³ Therefore, within the limits of experimental error, heat-treating the $UC_{2.0}$ specimens had no effect on their hydrolysis products.

5.4 Metallographic Procedure

Cutting. — Because the uranium carbides are brittle, specimens were prepared by breaking the sample buttons with a hammer. Attempts to cut the buttons with a conventional cut-off wheel resulted in fragmentation of the specimen.

Mounting. — The fragments were mounted in epoxy resin* in 1-1/4-in. mounts. The normal curing time was 6 to 8 hr at room temperature.

Grinding. — The mounted specimens were rough ground through 320-, 400-, and 600-grit silicon carbide papers, using a water-free silicone oil** as the vehicle.

Polishing. — Conventional metallographic polishing¹⁰ with motor-driven polishing wheels was used for some specimens; however, the semiautomatic vibratory polishing procedure³⁵⁻³⁷ gave better results and required a minimum of personal attention. Detailed preparation, examination, and photomicrography of uranium carbide fuels by vibratory polishing have been reported.³⁸⁻⁴⁰ For both conventional polishing and vibratory polishing, a slurry of silicone oil, Linde A alumina, and powdered graphite was added to a nylon cloth.

Etching. — The uranium carbides were etched with a solution of equal volumes of glacial acetic acid, 15.8 M (70%) nitric acid, and water. Uranium monocarbide, dicarbide, and sesquicarbide specimens were etched for 10-15, 15-30, and 10-30 sec, respectively. Etching times were influenced by the relative amounts of phase present

*Araldite No. 502 (10 parts by weight) and Hardener No. 951 (1 part by weight); products of Ciba Products, Fairlawn, New Jersey.

**Dow Corning 702 Fluid, Dow Corning Corp., Midland, Mich.

in the microstructure. The etching formed oxide interference films on the surface of the specimens; these films varied in color with the orientation and the chemical composition of the substrate.

Photomicrography. — The specimens were photographed on a Bausch and Lomb Research Metallograph with a carbon arc light source. Eastman Kodak Royal Pan film was used for the black-and-white photomicrographs shown in this report; it was processed in Eastman Kodak Polydol Developer. True-color reproductions of the microstructures have also been made,⁴¹ but are not included here.

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