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CONSTITUTION OF THE SYSTEMS OF
URANIUM AND CARBON WITH MOLYBDENUM,
NIOBIUM, RHENIUM, TUNGSTEN, AND YTTRIUM

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	1
URANIUM-CARBON-MOLYBDENUM SYSTEM	2
Background	2
Crystallography	2
Experimental Results	2
Ternary Sections	8
URANIUM-CARBON-NIOBIUM SYSTEM	15
Background	15
Crystallography	15
Experimental Results	15
Ternary Sections	17
URANIUM-CARBON-RHENIUM SYSTEM	17
Background	17
Crystallography	17
Experimental Results	17
Ternary Section	20
URANIUM-CARBON-TUNGSTEN SYSTEM	20
Background	20
Crystallography	23
Experimental Results	23
Ternary Section	25
YTTRIUM-CARBON SYSTEM	25
Background	25
Crystallography	28
Experimental Results	28
Binary Constitutional Diagram	29
URANIUM-CARBON-YTTRIUM SYSTEM	33
Experimental Results	33
Ternary Section	34
ACKNOWLEDGMENT	34
REFERENCES	38

CONSTITUTION OF THE SYSTEMS OF URANIUM AND CARBON WITH MOLYBDENUM, NIOBIUM, RHENIUM, TUNGSTEN, AND YTTRIUM

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The uranium-carbon-molybdenum system was found to contain only one ternary phase, $UMoC_2$, possessing a range of homogeneity from 46 to 50 a/o carbon. A pseudobinary tie line exists between UC and molybdenum below 1800 C. Between 1800 and 1900 C, UC and molybdenum react peritectically to form uranium liquid and $UMoC_2$. Pseudobinary systems also exist between $UMoC_2$ and UC, graphite, Mo_2C , and molybdenum. Nb_2C and NbC in intimate contact with liquid uranium at 1540 C contained less than 1 a/o uranium; the uranium contained no detectable niobium. The UC-NbC solid solution does not contain less than 49 a/o carbon at any composition containing more than 1 a/o uranium. The NbC corner of the NbC- Nb_2C -uranium region lies near 45 a/o carbon, 54 a/o niobium, and less than 1 a/o uranium. The uranium-carbon-rhenium system contains a ternary phase, $UReC_2$. Pseudobinary tie lines extend from UC to URe_2 , from UC to rhenium, and from $UReC_2$ to rhenium. Like in the uranium-carbon-molybdenum system, pseudobinary tie lines exist in the uranium-carbon-tungsten system at 1500 C between UC and tungsten and between UWC_2 and all the phases in the system except uranium. At 1500 C, the yttrium-carbon system contains two intermediate phases, a peritectically formed face-centered-cubic phase, YC, containing about 40 a/o carbon and an equiaxed and presumably cubic dicarbide, YC_2 , which transforms to a tetragonal structure below 1500 C. A complete series of solid solutions exists between UC and YC and, probably, between UC_2 and YC_2 . The UC-YC solid solution contains less than 50 a/o carbon at compositions containing as little as 8 a/o yttrium. Yttrium displaces uranium from the UC-YC solid solutions.

INTRODUCTION

As the development of a metal leads to the investigation of its binary phase relations with other elements, so the development of a compound such as uranium carbide leads to the development of its ternary phase relations with other elements. The constitution of the uranium-carbon systems with most of the more common metals of reactor construction were reviewed, on the basis of fragmentary information in the literature, in BMI-1441 (May 31, 1960).⁽¹⁾ The studies reported here represent an attempt to amplify, confirm, or amend the constitutional diagrams of some of the systems reported in BMI-1441.

(1) References at end.

URANIUM-CARBON-MOLYBDENUM SYSTEM

Background

The melting point of Mo_3C_2 (MoC) is about 2650 C. (2)

Mo_2C decomposes peritectically on heating at about 2400 C. (2)

UMoC_2 melts at about 2350 C. (3) A eutectic exists between UMoC_2 and carbon at 2200 C. A eutectic exists between UMoC_2 , UC_2 , and carbon at 2170 C.

An alloy of 43 a/o uranium, 43 a/o molybdenum, and 14 a/o carbon contained uranium monocarbide, molybdenum metal, and uranium metal. (4)

Alloys of uranium containing up to 44 a/o carbon and 6 a/o molybdenum or 38 a/o molybdenum and 5 a/o carbon contain uranium monocarbide in a matrix of molybdenum and uranium-molybdenum alloy. (5)

UMoC_2 forms on the high-carbon side of the UC -molybdenum tie line. (6)

A compound having the approximate composition $\text{U}_2\text{Mo}_5\text{C}_3$ has been reported. At 1500 C, pseudobinary tie lines extend between this phase and UC , UMoC_2 , Mo_2C , and molybdenum. (7)

The various carbides formed in this system do not dissolve in one another to any appreciable extent. (3, 4, 7, 8)

Crystallography

Mo_3C_2 (MoC) is face-centered cubic (NaCl type) above about 1800 C, with $a = 4.27\text{\AA}$. The compound is complex hexagonal below 1800 C, having four or more molecules per unit cell. Density is about 9 g per cm^3 . (9, 10)

Mo_2C is hexagonal close-packed (W_2C type), having one molecule per unit cell, with $a = 3.00$ and $c = 4.73\text{\AA}$. Density is 9.3 g per cm^3 .

UMoC_2 is orthorhombic (UCrC_2 type), having four molecules per unit cell, with $a = 5.61$, $b = 3.22$, and $c = 10.95\text{\AA}$. Density is 12.0 g per cm^3 . (11)

Experimental Results

The alloys shown in Table 1 were prepared by arc melting using the elemental materials. No weight losses were observed after each composition had been melted and turned over five times, so the final compositions were assumed to be the same as the nominal compositions. The cast alloys, weighing 50 g, were broken into several pieces, and the phases present were identified by metallographic methods, hardness

measurements, and X-ray diffraction techniques. Many of the alloys were annealed for various times at various temperatures and re-examined. The results of these examinations are summarized in Table 1.

TABLE 1. PHASES FOUND IN URANIUM-CARBON-MOLYBDENUM ALLOYS

Alloy	Nominal Composition			Phases Identified by Metallographic and X-Ray Methods(a)		
	a/o			As Cast	Annealed 3 Hr at 1500 C	Annealed 1/2 Hr at 1900 C
	U	C	Mo			
M-1	43	14	43	UC, Mo, (U, Mo) alloy	--	--
M-2	35	15	50	UC, Mo, (U, Mo) alloy, UMoC ₂	UC, Mo, (U, Mo) alloy	--
M-3	30	20	50	Mo, UC, UMoC ₂	UC, Mo, (U, Mo) alloy	--
M-4	25	25	50	UMoC ₂ , UC, Mo	UC, Mo, UMoC ₂	UMoC ₂ , Mo, UC ^(b)
M-5	20	30	50	UMoC ₂ , Mo, UC	UMoC ₂ , Mo, UC	UMoC ₂ , Mo, UC ^(b)
M-6	33	33	33 ^(c)	UMoC ₂ , UC, Mo	UC, Mo	UMoC ₂ , UC ^(b) , Mo
M-7	15	35	50	UMoC ₂ , Mo ₂ C, Mo	UMoC ₂ , Mo, Mo ₂ C	UMoC ₂ , Mo, Mo ₂ C
M-8	12	38	50	Mo ₂ C, UMoC ₂	--	--
M-9	20	40	40	UMoC ₂ , Mo	--	UMoC ₂ , Mo
M-10	29	42	29	UMoC ₂ , UC, Mo	UMoC ₂ , UC, Mo ^(d)	UMoC ₂ , UC, Mo
M-11	27	46 ^(c)	27	UMoC ₂ , UC, Mo	--	UMoC ₂
M-12	43	49	8	UC, UMoC ₂	--	--
M-13	25	50	25	UMoC ₂	UMoC ₂	--
M-14	21	57	22	UMoC ₂ , C	--	--
M-15	20	60	20	UMoC ₂ , C	--	--

(a) Phases are listed in order of decreasing volume.

(b) UC apparently was part of a liquid phase at 1900 C.

(c) Spot-check analyses showed nominal compositions to be correct within 1 a/o.

(d) Same result was achieved after 8 hr at 1500 C.

The cast structure of Alloy M-1 (43 a/o uranium-14 a/o carbon-43 a/o molybdenum) is shown in Figure 1. This structure shows molybdenum dendrites in a UC matrix with an intergranular residue of (U,Mo) alloy. It suggests the existence of a triangular, three-phase field having corners at UC, molybdenum, and (U,Mo) alloy. (4)

The annealed structures of Alloys M-2 and M-3 in Table 1 showed the same three phases as Alloy M-1, but the cast structures of these two alloys showed appreciable quantities of a phase which looked like UMoC₂ and which was apparently a carbon-deficient solid solution based on UMoC₂ containing as little as 46 a/o carbon. The X-ray patterns of UMoC₂ containing 46 a/o carbon and of UMoC₂ containing 50 a/o carbon are distinctly different, as shown in Figure 2. The X-ray pattern of the former was initially assumed to be associated with the phase U₂Mo₅C₃ reported previously(7), but it was not found at this composition, and it was subsequently obtained on the essentially single-phase alloy containing 27 a/o uranium, 46 a/o carbon, and 27 a/o molybdenum. Typical microstructures of UMoC₂ containing 46 and 50 a/o carbon are shown in Figure 3.

The as-cast structure of the Alloy M-3 in Table 1 is shown in Figure 4. The appearance of primary crystals of UMoC₂ in cast alloys of such low carbon contents

250X

RM15415

FIGURE 1. AS-CAST STRUCTURE OF 43 a/o URANIUM-14 a/o CARBON-43 a/o MOLYBDENUM ALLOY

Dark gray dendrites are molybdenum, light gray regions are UC, and intergranular phase is (U, Mo) alloy.

11021

FIGURE 2. X-RAY DIFFRACTION PATTERNS OF URANIUM-CARBON-MOLYBDENUM ALLOYS

- A: 27 a/o uranium-46 a/o carbon-27 a/o molybdenum alloy annealed 1/2 hr at 1900 C, showing unidentified structure plus a small amount of UC (Alloy M-11).
- B: 25 a/o uranium-50 a/o carbon-25 a/o molybdenum alloy annealed 3 hr at 1500 C, showing single-phase UMoC_2 .

250X

RM31193

a. 46 a/o Carbon, Annealed 1900 C

250X

RM31845

b. 50 a/o Carbon, As Cast

FIGURE 3. TYPICAL STRUCTURES OF UMoC_2 AT 46 a/o CARBON
AND 50 a/o CARBON

Striations are accentuated by Murikami's reagent.

is indicative of a high-melting phase which forms directly from a liquid of low carbon content at some high temperature. The disappearance of UMoC_2 on annealing at 1500 C is indicative of a peritectic reaction of the type: $\text{UMoC}_2 + \text{U (liquid)} = 2\text{UC} + \text{Mo}$, at some temperature above 1500 C.

250X

RM24314

FIGURE 4. AS-CAST STRUCTURE OF 30 a/o URANIUM-20 a/o CARBON-50 a/o MOLYBDENUM ALLOY

White needles are UMoC_2 , gray and black matrix contains UC and molybdenum.

Alloy M-4 (25 a/o uranium-25 a/o carbon-50 a/o molybdenum) and Alloy M-6 (33 a/o uranium-33 a/o carbon-33 a/o molybdenum) fall very nearly on a line from UC to molybdenum. The cast structures of these alloys were similar to that of alloy M-3 (shown in Figure 4) except that the amounts of primary UMoC_2 needles were much greater relative to the amounts of UC and molybdenum. When these two alloys were annealed at 1500 C, the resultant structures contained virtually no UMoC_2 . The structure of Alloy M-6 treated at 1500 C is shown in Figure 5. This structure shows the existence of a pseudobinary tie line from UC to molybdenum at 1500 C in agreement with the structure shown in Figure 1. However, when these same alloys were heated for 1/2 hr at 1900 C, the structure changed in a most drastic manner, as shown in Figure 6. Both samples showed signs of having been partly molten at 1900 C. With reference to Figure 6, the large, twinned crystals are UMoC_2 , which was present as a solid at 1900 C; the irregular, white globules around the edges of the UMoC_2 are molybdenum, at least part of which was present as a solid at 1900 C; the remaining gray and white matrix material is now a mixture of UC and molybdenum metal which was a uranium-base liquid at 1900 C. Figures 5 and 6 establish the existence of a peritectic reaction ($\text{UMoC}_2 + \text{liquid} = \text{UC} + \text{Mo}$) at a temperature between 1500 and 1900 C. A further heat treatment of the Alloy M-6 at 1800 C produced a UC-plus-molybdenum structure similar to that of Figure 5, so the peritectic temperature must be between 1800 and 1900 C.

250X

As Polished

RM27355

250X

Etched

RM27353

FIGURE 5. STRUCTURE OF 33 a/o URANIUM-33 a/o CARBON-33 a/o MOLYBDENUM ALLOY, ANNEALED 3 HR AT 1500 C

White phase is molybdenum. Matrix showing grain structure when etched is UC.

Alloy M-5 (20 a/o uranium-30 a/o carbon-50 a/o molybdenum) had a cast structure similar to that shown in Figure 4. This alloy, which is at the composition of the phase $U_2Mo_5C_3$ reported in the literature⁽⁷⁾, was found to contain three phases both as cast and as heat treated at 1500, 1800, and 1900 C. The only change which occurred during these heat treatments was that the phases tended to coarsen and spheroidize. The structure produced in this alloy at 1900 C is shown in Figure 7. This structure consists mainly of two phases: the gray phase showing longitudinal lines is identified as $UMoC_2$; the white phase is identified as molybdenum. The remainder represents liquid which decomposed into UC and molybdenum on cooling. The presence of such a small amount of liquid shows that this composition is near a pseudobinary tie line from $UMoC_2$ to molybdenum.

Alloys M-7, M-8, and M-9 (15 a/o uranium-35 a/o carbon-50 a/o molybdenum, 12 a/o uranium-38 a/o carbon-50 a/o molybdenum, and 20 a/o uranium-40 a/o carbon-40 a/o molybdenum) confirm the above tie and establish the existence of a three-phase field with corners at $UMoC_2$, Mo_2C , and molybdenum.

The structure of Alloy M-8 is shown in Figure 8. This structure shows only two phases, $UMoC_2$ and Mo_2C , and is apparently near a pseudobinary eutectic. Based on the amount of excess Mo_2C in this structure, the pseudobinary eutectic must be near 47 a/o molybdenum, 40 a/o carbon, and 13 a/o uranium.

Alloys M-10, M-11, and M-12 (29 a/o uranium-42 a/o carbon-29 a/o molybdenum, 27 a/o uranium-46 a/o carbon-27 a/o molybdenum, and 43 a/o uranium-49 a/o carbon-8 a/o molybdenum) establish the existence of a three-phase field with corners at $UMoC_2$, molybdenum, and UC at temperatures up to the peritectic temperature, where the UC-molybdenum tie line disappears. The structures of Alloys M-11 and M-13 are shown in Figure 3. Changes in the relative amounts of UC and molybdenum in the structures of Alloys M-10 and M-11 as a function of temperature of heat treatment show that the homogeneity range of $UMoC_2$ increases slightly with increasing temperature.

Alloy M-12 in Table 1 (43 a/o uranium-49 a/o carbon-8 a/o molybdenum) had the as-cast structure shown in Figure 9. This structure shows primary dendritic crystals of UC in a eutectic matrix which consists primarily of UC and $UMoC_2$. The eutectic composition appears to be near 13 a/o molybdenum.

Alloy M-14 (21 a/o uranium-57 a/o carbon-22 a/o molybdenum) had the as-cast structure shown in Figure 10. This is apparently the eutectic composition on a pseudobinary tie line from graphite to $UMoC_2$.

Ternary Sections

The ternary phase relationships derived from data in the literature and from the above studies may be summarized in terms of ternary isothermal sections, as shown in Figures 11, 12, and 13. The number 3 is used on these sections to designate a three-phase field, the components of which may be found at the corners of each such field. Vertical sections from UC to molybdenum and from graphite to uranium-50 a/o molybdenum alloy are shown as Figures 14 and 15.

750X

RM27756

FIGURE 6. STRUCTURE OF 33 a/o URANIUM-33 a/o CARBON-33 a/o MOLYBDENUM ALLOY ANNEALED 1/2 HR AT 1900 C

Striated phase is UMoC_2 . Black-outlined, white globules are molybdenum. Gray and white matrix is a mixture of UC and molybdenum which was liquid at 1900 C.

750X

RM27761

FIGURE 7. STRUCTURE OF 20 a/o URANIUM-30 a/o CARBON-50 a/o MOLYBDENUM ALLOY ANNEALED 1/2 HR AT 1900 C

Long gray phase is UMoC_2 . White areas are molybdenum. Minor, dark gray phase is UC, which was part of an intergranular liquid at 1900 C.

750X

RM26060

FIGURE 8. AS-CAST STRUCTURE OF 12 a/o URANIUM-38 a/o CARBON-50 a/o MOLYBDENUM ALLOY

A few primary white needles of Mo_2C are visible in a matrix of a eutectic containing UMoC_2 and Mo_2C .

250X

RM14596

FIGURE 9. AS-CAST STRUCTURE OF 43 a/o URANIUM-49 a/o CARBON-8 a/o MOLYBDENUM ALLOY

Black phase is UC; white phase is UMoC_2 .

500X

RM27195

FIGURE 10. AS-CAST STRUCTURE OF 21 a/o URANIUM-57 a/o CARBON-22 a/o MOLYBDENUM ALLOY

White phase is UMoC_2 ; black phase is graphite.

FIGURE 11. URANIUM-CARBON-MOLYBDENUM SYSTEM AT 1500 C

FIGURE 12. URANIUM-CARBON-MOLYBDENUM SYSTEM AT 1800 C

FIGURE 13. URANIUM-CARBON-MOLYBDENUM SYSTEM AT 2000 C

FIGURE 14. SECTION FROM URANIUM MONOCARBIDE TO MOLYBDENUM

FIGURE 15. SECTION FROM CARBON TO URANIUM - 50 a/o MOLYBDENUM ALLOY

URANIUM-CARBON-NIOBIUM SYSTEM

Background

The melting point of NbC varies over its range of homogeneity and reaches a maximum of about 3500 C at a composition near 47 a/o carbon. Nb₂C decomposes peritectically on heating to about 3100 C. (12)

The existence of complete solubility between NbC and UC has been established. (9, 13, 14) The liquidus line for the pseudobinary system UC-NbC is a smooth curve between the terminal compositions. (13)

The (U, Nb)C solid solution exists in equilibrium with carbon at compositions which increase in NbC content with increasing temperature. The tendency for carbon to react with (U, Nb)C to form UC₂ and a (U, Nb)C solution richer in NbC increases with increasing temperature. UC₂ dissolves a negligible amount of niobium. (15)

The (U, Nb)C solid solution exists in equilibrium with carbon above 54 mole per cent NbC at 1600 C, above 55 mole per cent NbC at 1800 C, and above 63 mole per cent at 2000 C. (16)

Niobium displaces uranium from UC. (17) The uranium contains essentially no niobium. (18)

Crystallography

NbC is face-centered cubic (NaCl type), having four molecules per unit cell, with $a = 4.47\text{\AA}$ in equilibrium with graphite. Density is 7.8 g per cm³.

Nb₂C is hexagonal close-packed (L'3 type), having one molecule per unit cell, with $a = 3.12$ and $c = 4.97\text{\AA}$ in equilibrium with NbC. Density is 7.9 g per cm³.

Experimental Results

An alloy was prepared by arc melting to consist of UC₂ plus approximately 10 a/o niobium. The structure of the cast alloy is shown in Figure 16. This structure consists of primary dendrites plus a eutectic. The primary dendrites have the etching characteristics of the NbC-rich (Nb, U)C solid solution. The relative amounts of the primary dendrites and eutectic show that the eutectic composition contains much less than 10 a/o niobium and probably less than 5 a/o niobium. It may be inferred that the eutectic temperature is similar to the minimum between pure UC and UC₂, since the constituents of the eutectic are apparently nearly pure UC₂ and a (U, Nb)C solid solution containing an appreciable amount of NbC, roughly all the niobium in the eutectic. This is in agreement with the above-mentioned finding that UC₂ dissolves a negligible amount of niobium.

A uranium-carbon alloy containing 49.7 a/o carbon was heated in contact with niobium at 1540 C. When sectioned, several thick two-phase zones were observed at the contact interface. From the niobium side these zones were identified as niobium-uranium solid solution plus Nb_2C , Nb_2C plus uranium metal, and $(\text{Nb}, \text{U})\text{C}$ solid solution plus uranium metal. Electron-probe microanalyses were obtained of the various phases at several points in these zones. At a point near the interface between the Nb_2C and the $(\text{Nb}, \text{U})\text{C}$ zones, the Nb_2C particles were found to contain between 0.3 and 0.7 a/o uranium. At this point, the $(\text{Nb}, \text{U})\text{C}$ contained only 0.6 a/o uranium and the metallic uranium obtained no niobium. It is considered likely that the metallic uranium contained traces of niobium and carbon in liquid solution at 1540 C, but that this was divorced from the liquid on cooling. No information was obtained from the electron-probe microanalyzer with regard to the carbon contents of any of the phases so that the following additional studies were undertaken.

The seven NbC-rich alloys shown in Table 2 were prepared by arc melting. The cast alloys were sectioned and analyzed for carbon and uranium. The phases present were identified by metallographic observation and by hardness measurements. The minor phases present were identified as uranium metal and Nb_2C , and the combined volume of these was determined by point counting. Using these data (also shown in Table 2) and the lever law, several compositions corresponding to the solubility limit for uranium in $(\text{Nb}, \text{U})\text{C}$ and in Nb_2C were calculated. Alloys N-1 and N-2 indicate that a composition of 14 a/o uranium-48 to 49 a/o carbon-balance niobium lies on the solubility-limit line for uranium in $(\text{Nb}, \text{U})\text{C}$. Alloy N-3 indicates that a composition of 2 a/o uranium-49 a/o carbon-balance niobium lies on the solubility-limit line for uranium in NbC. Alloy N-4 indicates that at 46 a/o carbon and 53 a/o niobium, NbC will contain less than 1 a/o uranium in solution. The appearance of Nb_2C in Alloy N-5 shows that the NbC corner of the ternary region, NbC plus Nb_2C plus uranium metal, lies very near 45 a/o carbon, 54 a/o niobium, and less than 1 a/o uranium. The presence of NbC in Alloy N-7 suggests that the ternary region, NbC plus Nb_2C plus uranium metal, is very extensive and that the Nb_2C corner of this region extends at least to the lower limit of the existence range of Nb_2C at temperatures near the solidus. Since Nb_2C forms by peritectic reaction, this point may shift to higher carbon contents at lower temperatures.

TABLE 2. VOLUME OF MINOR PHASES FOUND IN AS-CAST NIOBIUM-URANIUM-CARBON ALLOYS

Alloy	Analyzed Composition, a/o			Minor Phases Present	
	U	C	Nb ^(a)	Identity	Amount Present, volume per cent
N-1	20.2	44.5	35	Uranium metal	5
N-2	14.2	47.8	38	Not identified ^(b)	1.4
N-3	10.1	44.9	45	Uranium metal	8
N-4	5.2	44.1	50	Uranium metal	4.4
N-5	5.2	39.7	55	Nb_2C , uranium metal ^(b)	15
N-6	5.3	34.2	60	Nb_2C , uranium metal	12
N-7	5.2	27.8	67	Nb_2C , uranium metal ^(c)	29

(a) By difference.

(b) Major phase, $(\text{Nb}, \text{U})\text{C}$, had a hardness of 3200 KHN.

(c) Minor phase, Nb_2C , had a hardness of 1780 KHN.

Ternary Sections

The ternary phase relationships derived from data from the literature and from the above studies may be summarized in terms of ternary isothermal sections. Figure 17 shows a section at 1300 C. At this temperature UC_2 is unstable and U_2C_3 dominates the high-carbon, high-uranium portion of the diagram. Since NbC and Nb_2C are much more stable than UC, liquid uranium metal dominates the low-carbon, high-uranium portion of the diagram. Figure 18 shows a section at 1700 C. Figure 19 shows a section at 2200 C which illustrates the growing stability and range of homogeneity of UC_2 with increasing temperature.

URANIUM-CARBON-RHENIUM SYSTEM

Background

Eutectic melting is observed between UC and rhenium metal at about 1900 C. (19)

Crystallography

$UReC_2$ is orthorhombic ($UCrC_2$ type), having four molecules per unit cell, with $a = 5.52$, $b = 3.20$, and $c = 10.88$ Å. Density is 15.5 g per cm^3 .

Experimental Results

The four alloys shown in Table 3 were prepared by arc melting to determine the presence or absence of possible pseudobinary tie lines in the uranium-carbon-rhenium system at and below 50 a/o carbon. The alloys were prepared from spectrographic graphite, biscuit uranium, and commercial rhenium bar stock. A spectrographic analysis of the rhenium bar indicated no tungsten in this material. The arc-melted buttons were broken into several pieces and examined by X-ray diffraction and metallographic methods. A piece of each alloy was wrapped in tantalum foil and heat treated for 3 hr at 1500 C. The heat-treated pieces were further examined by metallographic methods, and Alloy R-4, which appeared to be radically changed by the heat treatment, was further examined by X-ray diffraction.

The phases found by metallographic and X-ray examination both before and after heat treatment at 1500 C were the same, and it must be concluded that there are no major changes in the uranium-carbon-rhenium system between 1500 C and the solidus temperature in the region of compositions examined. The phases identified are shown in Table 3. The as-cast structure of the $UReC_2$ phase (Alloy R-1) is shown in Fig-20. A small amount of excess rhenium is apparently present in the microstructure, but this was not detected by X-ray. The $UReC_2$ phase is isostructural with $UCrC_2$. Alloy R-1 had a hardness of 1390 kg per mm^2 . The as-cast structure of Alloy R-2 is shown in Figure 21. This structure consists of a few primary dendrites of rhenium

250X

RM16622

FIGURE 16. AS-CAST STRUCTURE OF AN ALLOY OF UC_2 PLUS 10 at% NIOBIUM

Structure shows primary NbC-rich dendrites plus a (U, Nb)C- UC_2 eutectic.

FIGURE 17. URANIUM-CARBON-NIOBIUM SYSTEM AT 1300 C

FIGURE 19. URANIUM-CARBON-NIOBIUM SYSTEM AT 2200 C

metal in a background composed of the UC-rhenium eutectic. The UC-rhenium eutectic is evidently near 35 a/o uranium, 35 a/o carbon, and 30 a/o rhenium. The as-cast structure of Alloy R-4 in Table 3 is shown in Figure 22. This structure consists of a primary dendrite of URe_2 in a background composed of the UC- URe_2 eutectic. The UC- URe_2 eutectic is evidently near 41 a/o uranium, 29 a/o carbon, and 35 a/o rhenium.

TABLE 3. PHASES FOUND IN URANIUM-CARBON-RHENIUM ALLOYS

Alloy	Nominal Composition, a/o			Phases Identified by Metallographic and X-Ray Methods
	U	C	Re	
R-1	25	50	25	$\text{UReC}_2^{(a)}$
R-2	30	30	40	Rhenium, UC
R-3	35	25	40	UC, URe_2 , rhenium
R-4	40	20	40	UC, URe_2

(a) Alloy hardness was 1390 kg per mm^2 .

Ternary Section

The ternary phase relationships derived from the above data are shown in Figure 23.

URANIUM-CARBON-TUNGSTEN SYSTEM

Background

WC decomposes on heating at about 2750 C. W_3C_2 exists as a stable phase only in the temperature range from 2525 to 2780 C. W_2C melts congruently at 2800 C and exists over a composition range from approximately 28 a/o to 33 a/o carbon. ⁽²⁰⁾

A ternary compound UWC_2 exists between UC and WC. ⁽¹¹⁾ UWC_2 melts at 2575 C and has a hardness of 1900 kg per mm^2 . A eutectic exists between UWC_2 and graphite at 2360 C. A ternary eutectic exists between UWC_2 , UC_2 , and graphite at 2275 C. ⁽³⁾

Melting has been observed between UC and tungsten at 2280 C. ⁽²¹⁾ Melting has been observed between UC and W_2C at 2480 C, and between UC and WC at 2430 C. ⁽²²⁾

WC dissolves no UC ⁽⁸⁾, but UC dissolves a small amount of WC. The solubility of tungsten in UC has been reported as 5 a/o ⁽⁸⁾, 2 to 4 a/o ⁽²³⁾, and 1 a/o tungsten. ⁽²⁴⁾

250X

RM22072A

FIGURE 20. AS-CAST STRUCTURE OF 25 a/o URANIUM-50 a/o CARBON-25 a/o RHENIUM ALLOY

Orthorhombic crystals of UReC_2 , microcracks, and trace quantities of rhenium are visible.

500X

RM22073A

FIGURE 21. AS-CAST STRUCTURE OF 30 a/o URANIUM-30 a/o CARBON-40 a/o RHENIUM ALLOY

White, primary dendrites of rhenium metal in a eutectic background mixture of UC and rhenium are shown.

750X

RM22075A

FIGURE 22. AS-CAST STRUCTURE OF 40 a/o URANIUM-20 a/o CARBON-40 a/o RHENIUM ALLOY

White, primary dendrite of URe_2 is visible in a eutectic background mixture of UC and URe_2 .

FIGURE 23. URANIUM-CARBON-RHENIUM SYSTEM AT 1500 C

A ternary section of the uranium-tungsten-carbon system at 1500 C shows pseudobinary tie lines between UC and tungsten and between UWC_2 and UC, tungsten, W_2C , WC, carbon, UC_2 , and U_2C_3 . (25)

Crystallography

WC is hexagonal, having one molecule per unit cell, with $a = 2.90$ and $c = 2.93\text{\AA}$. Density is 15.5 g per cm^3 .

W_3C_2 is face-centered cubic, with $a = 4.13\text{\AA}$. (20)

W_2C is hexagonal close packed, having one molecule per unit cell, with $a = 2.99$ and $c = 4.72\text{\AA}$. Density is 17.2 g per cm^3 .

UWC_2 is orthorhombic (UCrC_2 type), having four molecules per unit cell, with $a = 5.62$, $b = 3.24$, and $c = 10.96\text{\AA}$. Density is 14.8 g per cm^3 . (11)

Experimental Results

A number of alloys containing more than 50 a/o carbon, more than 30 a/o uranium, plus small amounts of tungsten, were prepared by arc melting. The structure of one such as-cast alloy is shown in Figure 24. The structure of this alloy, having a nominal composition of 65 a/o carbon, 32 a/o uranium, and 3 a/o tungsten, shows primary, rounded dendrites of UC_2 plus an interdendritic eutectic presumed to consist of UWC_2 and UC_2 . The lack of a secondary precipitate in the UC_2 dendrites plus the relatively large amount of UWC_2 in the eutectic in this structure indicates that there is no solubility of tungsten in UC_2 . Examination of this alloy and other alloys containing more tungsten suggests that the UC_2 - UWC_2 eutectic is near 15 a/o tungsten, and that a UC- UWC_2 eutectic exists near 10 a/o tungsten. The solubility of tungsten in UC is less than 2 a/o (4 mole per cent WC) at low temperatures. The solubility increases with temperature and may exceed 5 mole per cent WC at the eutectic temperature.

The three tungsten-rich alloys shown in Table 4 were prepared by arc melting to determine the pseudobinary tie lines at compositions below 50 a/o carbon. The alloys were prepared from spectrographic graphite, biscuit uranium, and commercial tungsten bar stock. The arc-melted buttons were broken into several pieces and examined by X-ray diffraction and metallographic methods. A piece of each alloy was wrapped in tantalum foil and heat treated for 3 hr at 1500 C. Metallographic examination of the heat-treated alloys disclosed changes in the distribution of the phases present, but no gross changes in the amounts of the phases. The phases identified are shown in Table 4.

The heat-treated structure of Alloy W-1 is shown in Figure 25. This structure shows large primary particles of UWC_2 and a slightly coarsened eutectic of W_2C and UWC_2 . The W_2C - UWC_2 eutectic is evidently near 50 a/o tungsten, 40 a/o carbon, and 10 a/o uranium.

500X

RM16612

FIGURE 24. AS-CAST STRUCTURE OF AN ALLOY OF 65 a/o CARBON, 32 a/o URANIUM, AND 3 a/o TUNGSTEN (UC_2 PLUS 3 a/o TUNGSTEN)

Primary, rounded dendrites of UC_2 plus an interdendritic eutectic are shown.

750X

RM22078A

FIGURE 25. STRUCTURE OF 15 a/o URANIUM-45 a/o CARBON-40 a/o TUNGSTEN ALLOY AS HEAT-TREATED 3 HR AT 1500 C

Gray phase is UWC_2 ; white phase is W_2C .

TABLE 4. PHASES FOUND IN URANIUM-CARBON-TUNGSTEN ALLOYS

Alloy	Nominal Composition, a/o			Phases Identified by Metallographic and X-Ray Methods
	U	C	W	
W-1	15	45	40	UWC_2 , W_2C
W-2	20	40	40	UWC_2 , W, UC
W-3	25	25	50	W, UC

The heat-treated structure of Alloy W-2 is shown in Figure 26. This structure shows needlelike crystals of UWC_2 in a eutectic matrix of UWC_2 , tungsten, and UC. The eutectic composition evidently contains much more tungsten than the composition of this alloy. The heat treatment has caused a precipitate to form in the UWC_2 phase, suggesting that UWC_2 has a higher solubility for uranium and tungsten near the solidus temperature than at 1500 C. This observation is in agreement with the finding of an X-ray pattern in Alloys W-2 and W-3 corresponding to the low-carbon pattern of UMoC_2 (Figure 2).

The heat-treated structure of Alloy W-3 is shown in Figure 27. This structure shows coarse tungsten metal particles in a eutecticlike matrix consisting of fine particles of tungsten in a UC field. The cast structure of this alloy contained an acicular phase which was probably UWC_2 . It seems likely that the eutecticlike structure is the product of the peritectic reaction, $\text{UWC}_2 + \text{U (liquid)} = 2\text{UC} + \text{W}$; a reaction directly comparable to that found in the uranium-molybdenum-carbon system. On the basis of the amount of coarse tungsten present in the structure shown in Figure 27, the UC-W peritectic or eutectic reaction evidently occurs near 40 a/o carbon, 38 a/o uranium, and 22 a/o tungsten.

Ternary Section

The data obtained above are in agreement in all important particulars with the ternary section reported by Rudy, et al. (25) A ternary section at 1500 C is shown as Figure 28.

YTTRIUM-CARBON SYSTEM

Background

At least two, and probably three, carbides exist in the binary yttrium-carbon system. The lowest carbon phase has a wide range of existence from $\text{YC}_{0.25}$ to

750X

RM22077A

FIGURE 26. STRUCTURE OF 20 a/o URANIUM-40 a/o CARBON-40 a/o TUNGSTEN ALLOY AS HEAT TREATED 3 HR AT 1500 C

Major white phase is UWC_2 . Globular white phase is tungsten metal. Dark gray phase is UC.

750X

RM22076A

FIGURE 27. STRUCTURE OF 25 a/o URANIUM-25 a/o CARBON-50 a/o TUNGSTEN ALLOY AS HEAT TREATED 3 HR AT 1500 C

White phase is tungsten metal. Dark gray phase is UC.

FIGURE 28. URANIUM-CARBON-TUNGSTEN SYSTEM AT 1500 C

$YC_{0.40}$ (20 to 29 a/o carbon). (26) An alloy containing 12 w/o (50 a/o) carbon had a melting point of 1950 C and a hardness of 120 kg per mm². (27) Above 1900 C, YC melted and decomposed, forming volatile yttrium and a liquid rich in carbon. (27)

Yttrium dicarbide has a melting point over 2300 C. (28)

Crystallography

YC is face-centered cubic (carbon-deficient NaCl structure), having four yttrium atoms per unit cell, with $a = 5.10\text{\AA}$ in equilibrium with yttrium and $a = 5.12\text{\AA}$ in equilibrium with YC_2 . Density is 5.5 g per cm³.

Y_2C_3 exhibits low symmetry, and is not isostructural with Pu_2C_3 . (26)

YC_2 is tetragonal (CaC_2 type), having two molecules per unit cell, with $a = 3.66$ and $c = 6.17\text{\AA}$. Density is 4.53 g per cm³. At temperatures of 1500 C and above, YC_2 has an allotropic modification which is probably isostructural with UC_2 ; i. e. face-centered cubic.

Experimental Results

The five yttrium-carbon alloys listed in Table 5 were prepared by arc melting. Analyses obtained on three of the alloys produced results checking the nominal compositions within 2 a/o. The structure of Alloy BY-1 is shown in Figure 29. This photomicrograph shows a single phase identified by X-ray examination as tetragonal YC_2 . The needles are indicative of a solid-state martensitlike phase transformation, presumably from a congruently melting, high-temperature, cubic allotrope represented by the equiaxed structure, to the tetragonal structure present at room temperature. This alloy had a hardness of 410 kg per mm². This structure was not materially altered by a heat treatment of 3 hr at 1500 C, showing that the allotropic transformation temperature is below 1500 C.

TABLE 5. PHASES FOUND IN YTTRIUM-CARBON ALLOYS

Alloy	Nominal Carbon Content, a/o	Phases Identified by Metallographic and X-ray Methods	Lattice Parameter of YC Phase, A
BY-1	66	YC_2 (tetragonal)	--
BY-2	60	YC_2 , YC	--
BY-3	50(a)	YC, YC_2	5.12
BY-4	35(b)	YC, yttrium	5.10
BY-5	20(c)	YC, yttrium	5.10

(a) Chemical analysis showed 50 a/o carbon.

(b) Chemical analysis showed 37 a/o carbon.

(c) Chemical analysis showed 21 a/o carbon.

After annealing for 3 hr at 1500 C, Alloy BY-2 in Table 5 was identified as largely YC_2 plus some YC. This result shows that, if Y_2C_3 exists, it probably forms by peritectoid reaction at a lower temperature.

Alloy BY-3 had a hardness of 580 kg per mm^2 , exhibited a submetallic luster similar to that of mill scale (Fe_3O_4), and reacted readily with water to form acetylene and probably other gases. The microstructure of the alloy after annealing for 3 hr at 1500 C is shown in Figure 30. This photomicrograph shows a white phase identified as tetragonal YC_2 . A needlelike substructure within these particles (not developed in this photomicrograph) confirmed that the YC_2 was above its allotropic transformation temperature at 1500 C. The gray, major phase present is YC having a lattice parameter of 5.12A. Clearly YC does not exist at its stoichiometric composition, and this photomicrograph showing about 25 volume per cent YC_2 in an alloy at 50 a/o carbon suggests that the upper limit of the range of existence of YC is about 40 a/o carbon.

Alloy BY-4 in Table 5 is shown in Figure 31 after annealing for 3 hr at 1500 C. This microstructure shows spheroidized islands of YC in a eutectic matrix. This microstructure confirms that the melting point of YC is above 1500 C and that a eutectic, melting below 1500 C, exists between YC and yttrium metal. This alloy, containing about 35 a/o carbon and showing a structure containing about 15 volume per cent yttrium metal, suggests that the lower limit of the range of existence of YC is also about 40 a/o carbon. A lattice parameter of 5.10A was obtained for the YC in this alloy, so YC must have a slight range of homogeneity.

The cast structure of the above alloy showed dendrites of YC plus other phases which could not be positively identified. The presence of YC_2 was suggested by some of the X-ray lines; and the microstructure showed signs of reactions between the phases during cooling, indicating that YC forms by peritectic reaction and that the critical composition is near but below 35 a/o carbon.

The cast structure of Alloy BY-5 in Table 5 also showed about 30 volume per cent primary dendrites of YC in a eutectic matrix. This structure, shown in Figure 32, locates the eutectic composition near 15 a/o carbon. When this alloy was annealed at 1500 C, a structure indicating incipient or partial melting resulted, showing that the eutectic temperature is very near 1500 C. The yttrium metal in the alloy agglomerated into a massive, irregular network. A small amount of an oriented (Widmanstätten) precipitate formed in the yttrium, showing that yttrium dissolves some carbon, perhaps up to 2 a/o, at 1500 C.

Binary Constitutional Diagram

A binary constitutional diagram for the yttrium-carbon system which is consistent with the available data is shown as Figure 33. YC_2 is presumed to have a congruent melting point and, therefore, a eutectic must exist between it and graphite. The black triangle on the YC_2 composition at about 1300 C indicates an allotropic transformation at an unknown temperature below 1500 C. The data on Y_2C_3 are not clear, and it is indicated as forming by a peritectoid reaction below 1500 C.

100X

RM22836

FIGURE 29. AS-CAST STRUCTURE OF 33 a/o YTTRIUM-66 a/o CARBON ALLOY

Martensitlike needles of tetragonal YC_2 formed within the equiaxed grain structure of a presumed high-temperature, cubic allotrope of YC_2 .

500X

RM23349

FIGURE 30. STRUCTURE OF A 50 a/o YTTRIUM-50 a/o CARBON ALLOY, AS ANNEALED 3 HR AT 1500 C

About 25 volume per cent of tetragonal YC_2 appears in a gray-mottled matrix of YC .

500X

RM24472

FIGURE 31. STRUCTURE OF 65 a/o YTTRIUM-35 a/o CARBON ALLOY,
AS ANNEALED 3 HR AT 1500 C

Black spheroids of YC are present in a eutectic matrix
consisting of YC and yttrium metal.

500X

RM23443

FIGURE 32. AS-CAST STRUCTURE OF 80 a/o YTTRIUM-20 a/o
CARBON ALLOY

Primary dendrites of YC are visible in a yttrium-YC
eutectic matrix.

FIGURE 33. YTTRIUM-CARBON CONSTITUTIONAL DIAGRAM

URANIUM-CARBON-YTTRIUM SYSTEM*

Experimental Results

The alloys listed in Table 6 were prepared in the form of 50-g buttons by arc melting the elemental materials. The cast structure of Alloy Y-1 is shown in Figure 34. This structure shows primary, gray dendrites of YC, brilliant white spheroids of uranium metal, and a eutectic containing primarily yttrium metal and YC. The structure of the same alloy after annealing for 3 hr at 1500 C is shown in Figure 35. The spheroids of uranium show a cored appearance which suggests that liquid uranium dissolves appreciable yttrium at 1500 C. The yttrium has formed an intergranular network. A trace of a Widmanstätten precipitate may be seen in the yttrium, confirming the finding that appreciable carbon is soluble in yttrium at 1500 C. The markings on the YC are the result of oxidation during specimen preparation; this stage of oxidation represents an intermediate condition between that shown in Figure 30, where only very faint marks are visible on the YC, to that shown in Figure 31, where the oxidation products have formed a continuous layer of loose powder on the surface of the YC particles.

TABLE 6. PHASES FOUND IN URANIUM-CARBON-YTTRIUM ALLOYS

Alloy	Nominal Composition, a/o			Phases Identified by Metallographic and X-ray Methods	Lattice Parameter of FCC (U, Y)C Phase, Å
	U	C	Y		
Y-1	10	20	70	YC, yttrium, uranium	5.10
Y-2	25	25	50(a)	YC, uranium, yttrium	5.04, 5.11
Y-3	40	25	35	(Y,U)C, uranium	5.04
Y-4	25	35	40	(Y,U)C, uranium	5.02, 5.04
Y-5	20	40	40	(Y,U)C, uranium	5.01, 5.02
Y-6	33	33	33	(Y,U)C, uranium	5.00
Y-7	45	35	20	(U,Y)C, uranium	5.00
Y-8	25	50	25	(U,Y)C, YC ₂	4.99
Y-9	42	50	8	(U,Y)C, YC ₂	--
Y-10	30	60	10	(U,Y)C ₂ , UC	4.96, 4.96

(a) Chemical analysis showed 27 a/o carbon, 25 a/o uranium.

The appearance of large amounts of uncombined uranium metal in this alloy containing only 10 a/o uranium shows that yttrium displaces uranium from uranium carbide and that the carbide-rich corner of the three-phase field, monocarbide-uranium-yttrium, occurs at a composition where YC contains little, if any, uranium in solution.

Alloy Y-2 in Table 6 showed structures which were qualitatively identical, but quantitatively different from the first alloy. Much more metallic uranium and much less metallic yttrium were observed.

*See the preceding section on the yttrium-carbon system for available background and crystallography data.

Alloys Y-3 through Y-7 all contained a face-centered-cubic carbide and uranium metal, both as cast and after annealing at 1500 C. The face-centered-cubic carbide showed lattice parameters varying continuously, as noted in Table 6, and this was identified as a continuous solid solution between UC and YC; i. e. (U,Y)C. The structures were dendritic as cast, but became equiaxed when annealed at 1500 C. A drastic coarsening which occurred during annealing was attributed to the presence of liquid uranium.

Alloys Y-8 through Y-10 in Table 6, containing 50 and 60 a/o carbon, were dendritic as cast, and did not become equiaxed when annealed for 3 hr at 1500 C. The structure of Alloy Y-8, 25 a/o uranium-50 a/o carbon-25 a/o yttrium after annealing at 1500 C is shown in Figure 36. This structure consists of dendritic (U,Y)C plus an interdendritic material identified as containing YC₂. This structure shows that at this composition, (U,Y)C contains less than 50 a/o carbon. Alloy Y-9, 42 a/o uranium-50 a/o carbon-8 a/o yttrium, also contained a small amount of YC₂, suggesting that the (U,Y)C solid solution may contain less than 50 a/o carbon even at this low yttrium content.

Alloy Y-10 contained a tetragonal phase having lattice parameters of $a = 3.54$ and $c = 6.12 \text{ \AA}$. Since these are intermediate to those of UC₂ ($a = 3.51$, $c = 5.98 \text{ \AA}$) and those of YC₂ ($a = 3.66$, $c = 6.17 \text{ \AA}$), it seems likely that a complete series of solid solutions exists between UC₂ and YC₂. The cast and annealed structures of this alloy are shown in Figure 37. The cast structure is believed to show mainly the (U,Y)C₂ phase, which is severely cored with respect to metal atoms and appreciably sub-stoichiometric. The entire structure has apparently undergone the martensitlike transformation to the tetragonal allotrope. An appreciable amount of essentially pure UC is present in the alloy, suggesting that pure YC₂ has virtually no solubility for (U,Y)C. The annealed structure is believed to show the high-yttrium cores of the (U,Y)C₂ phase essentially unchanged by the heat treatment. The lower carbon, higher uranium portions of the (U,Y)C₂ phase have decomposed into a eutectoid structure, presumably by precipitating additional UC. The lattice parameters for the (Y,U)C₂ solid solution given above were obtained on the annealed alloy, so it seems likely that the high-yttrium dendrite cores contain at least 15 a/o yttrium. Thus, the range of homogeneity with respect to carbon content of (U,Y)C₂ containing 15 a/o yttrium or more is quite small at temperatures above 1500 C. Below 10 a/o yttrium the range of homogeneity of (U,Y)C₂ must approach that of UC₂.

Ternary Section

The ternary phase relationships derived from the above data are shown as a ternary isothermal section at 1500 C in Figure 38.

ACKNOWLEDGMENT

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500X

RM23445

FIGURE 34. AS-CAST STRUCTURE OF A 10 a/o URANIUM-20 a/o CARBON-70 a/o YTTRIUM ALLOY

Gray dendrites of YC, bright white spheroids of uranium, and a eutectic of yttrium and YC are shown.

500X

RM24473

FIGURE 35. STRUCTURE OF A 10 a/o URANIUM-20 a/o CARBON-70 a/o YTTRIUM ALLOY ANNEALED 3 HR AT 1500 C

Irregular crosspatched particles of YC, bright white spheroids of uranium, and matte gray intergranular network of yttrium containing a trace amount of a Widmanstätten precipitate are visible.

500X

RM23352

FIGURE 36. STRUCTURE OF A 25 a/o URANIUM-50 a/o CARBON-25 a/o YTTRIUM ALLOY ANNEALED 3 HR AT 1500 C

Dendrites of (U, Y)C plus an interdendritic material containing YC_2 are evident.

500X

As Cast

RM22852

750X

Annealed 3 Hr at 1500 C

RM23353

FIGURE 37. STRUCTURES OF 30 a/o URANIUM-60 a/o CARBON-10 a/o YTTRIUM ALLOY

Cast structure shows cored $(U, Y)C_2$ plus some UC. Annealed structure shows residual, high-yttrium cores of the $(U, Y)C_2$ plus eutectoidlike decomposition product of the low-yttrium portions of the $(U, Y)C_2$.

FIGURE 38. URANIUM-CARBON-YTTRIUM SYSTEM AT 1500 C

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WC:DLK/dnm