

An X-Ray Study of the System Uranium Monocarbide-Uranium Dicarbide-Beryllium Carbide

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Mixed carbide preparations within the system uranium monocarbide-uranium dicarbide-beryllium carbide were investigated after heating and quenching. X-ray diffraction methods were used to identify the phases found and to determine the degree of interaction. Carbide alloys were studied after treatments at 1,700° and 1,900° C, and a constitutional diagram for the 1,700° C level is presented. No ternary compounds were identified within the system. The limit of solubility of beryllium carbide in uranium monocarbide at 1,700° and 1,900° C was found to be 20 mole percent and 40 mole percent, respectively. Lattice parameters based on X-ray patterns in the back-reflection region failed to indicate any other interactions, but evidence is presented to indicate some solid solution among the uranium carbides without lattice parameter change. The room-temperature stability of uranium sesquicarbide (U_2C_3), which has been reported by other investigators, was verified. X-ray diffraction data were obtained for this cubic compound, using CuK_α radiation.

1. Introduction

Uranium, as a metal and in the form of various compounds, is the usual source of energy in nuclear reactors. As a moderator and structural material for piles operating at temperatures above the useful range for metals, some form of beryllium is among the foremost of the ceramic materials considered because of favorable cross-sectional properties and high thermal conductivity. For applications other than reactors, the carbides of these elements have been investigated and have been found to be suitable for special high-temperature applications, for example, crucibles.

An uranium carbide, later shown to have been UC_2 , was prepared by Moissan [1]¹ in 1896. Other workers [2, 3, 4, 5, 6, 7, 8, 9, 10, 11] established the structure and determined some of the properties of the three uranium carbides, UC, U_2C_3 , and UC_2 . Beryllium carbide, discovered in 1895 by Lebeau [12], remained almost a laboratory oddity until recently. Stackelberg and Quatrum [13] in 1934 published the crystallographic structure of Be_2C , and Kielland and Tronstad [14] found it served a useful purpose as an intermediate product in the production of beryllium chloride. Beryllium carbide was little used as a refractory because other materials were available, which were more stable with respect to air and moisture and were less toxic.

In nuclear reactors, temperatures must be maintained at the highest possible levels for good efficiency. The materials used in the construction of reactors must, therefore, be stable at the temperatures involved, and, in addition, must be compatible with each other. The favorable nuclear properties of the uranium carbides and beryllium carbide made desirable an investigation of combinations of these materials. The present study was undertaken to determine the constitution of alloys resulting from solid-state reaction within the system UC- UC_2 - Be_2C .

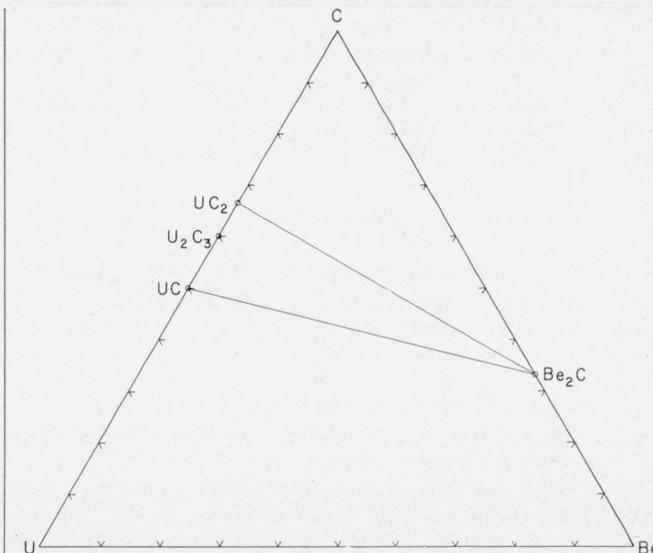


FIGURE 1. Relation of the end members of the system UC- UC_2 - Be_2C to that of the constituent elements, in mole percent.

Figure 1 shows the relation of the end members of this system to that of the constituent elements (U, Be, and C).

2. Materials

The uranium-carbon alloys used in this study were supplied by Battelle Memorial Institute. They were prepared by melting the materials in an induction furnace and remelting in argon in an arc furnace. The uncombined carbon of the arc-melted alloys was usually not over 0.03 percent by weight. The chemical compositions of the starting materials are given in table 1. The uranium-carbon alloys, designated by A following the alloy number in table 1, were made available for this study by M. W. Mallett et al. [9,11] after the completion of work

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. Chemical composition of materials

Material	Chemical composition (percentage by weight) ^a						
	U ^b	C	Free C	BeO	N ₂	H ₂ O	Be
Alloy 361	95.28	4.72	---	---	---	---	---
Alloy 369	88.3	11.7	---	---	---	---	---
Alloy 137A	95.6	4.4	---	---	---	---	---
Alloy 112A	93.68	6.32	---	---	---	---	---
Alloy 66A	93.07	6.93	---	---	---	---	---
Alloy 81A	92.5	7.5	---	---	---	---	---
Alloy 100A	91.0	9.0	---	---	---	---	---
Be ₂ C	---	39.35	0.67	0.61	0.01	0.14	59.22

^a The uranium-carbon alloys were supplied and analyzed by Batelle Memorial Institute. The beryllium carbide was supplied and analyzed by Brush Beryllium Co.

^b Uranium by difference.

^c Carbon by difference.

on the uranium-carbon system. Alloys 361 and 369 were freshly prepared for this study, after it was found that the older alloys had "aged" and no longer gave reproducible results. The data in this report were obtained on mixtures of alloys 361, 369, and beryllium carbide.

The beryllium carbide was of 98.3-percent purity, which was the highest quality available at the time of its purchase. The impurities were beryllia (BeO), carbon, beryllium nitride (Be₃N₂), and moisture.

3. Equipment

Figure 2 shows the inductively heated quenching furnace used for all heat treatments in this study. The base of the furnace consists of a 12-in. cube made of ¼-in. steel plate with all-welded construction. A fused-silica tube, with a 5-in. inside diameter, is set in a groove in the top of the base, and a vacuum-tight seal is obtained by means of a neoprene "O" gasket and a clamping ring. The furnace head is attached to the top of the silica tube by means of a similar arrangement and is water-cooled. An induction coil, consisting of eight turns, is placed concentric with and midway along the silica tube.

The prism and window on the furnace head provide a means for temperature measurement and observation of specimens with an optical pyrometer mounted in a horizontal position. A neoprene "O" gasket forms a vacuum-tight seal between the tempered glass window and the furnace head. The optical pyrometer was calibrated with the window and prism in the line of sight by the Temperature Measurement Section of the National Bureau of Standards. A Kovar insulated terminal is soldered in place through the head to act as a fuse-wire support and electrode for the quenching current. The head itself serves as the other electrode.

The susceptor and other structural parts of the furnace were machined from suitable carbon shapes. The susceptor assembly is mounted concentric with the silica tube at its midpoint, and the assembly is supported by a carbon pipe 1½-in. outside diameter by 1-in. inside diameter, which extends to a hole in the top of the furnace base. The pipe also

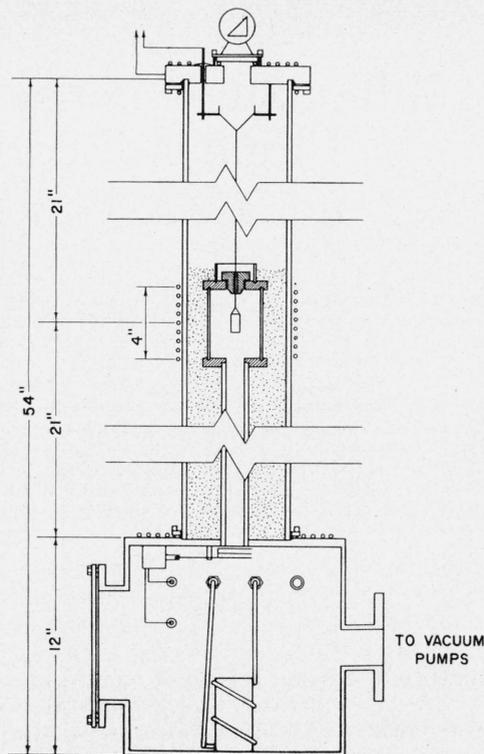


FIGURE 2. Schematic drawing of an inductively heated furnace used for heating and quenching carbide alloys in controlled atmospheres.

serves as a guide to direct the specimen to the quench cup and to retain the thermal insulation. The entire space above the furnace base around the pipe and susceptor assembly is solidly packed with carbon-black insulation to approximately ¼ in. below the upper rim of the stack on top of the susceptor assembly. Twelve to 14 deep holes, formed in the escape of adsorbed gases during evacuation and heating.

Within the furnace base, a solenoid-operated shutter assembly serves as a radiation shield under the lower end of the carbon pipe. Electricity is brought into the base by means of two Kovar insulated terminals soldered through the side wall. The cup, containing about 750 ml of a quenching oil, is a thin-walled brass tube closed at the lower end. Because of the small heat capacity of the cup and the necessity for as rapid cooling as possible, a water-cooling jacket of ¼-in. copper tubing was placed around the cup. The water inlet and outlet, as well as the atmosphere inlet, consists of ¼-in. pipe nipples welded through the sidewall of the furnace base. Access to the interior of the furnace base is obtained by a 6-in. pipe flange welded to one side of the base. The flange is provided with a cover plate and rubber gasket. A standard 2-in. pipe flange welded to the opposite side of the furnace base permits connection to the vacuum system.

Specimen holders used with the furnace consist of two general types: (1) refractory metal holders sus-

pended from the furnace head, when specimens are to be quenched, and (2) carbon or graphite crucibles, when specimens are to be cooled in the furnace. When specimens are to be quenched, the sample cup consists of a hollow cylinder, $\frac{5}{8}$ -in. in diameter and 1 in. tall, with a removable bottom. The entire assembly is shaped from 0.010-in. molybdenum. A bail of 0.025-in. molybdenum wire is provided. The cylinder containing the specimen is suspended from a 0.010-in. molybdenum wire attached to a platinum fuse wire strung between two supports on the furnace head. The molybdenum support wire extends through the $\frac{3}{16}$ -in. sight hole in the susceptor cover plug. In cases where it is not necessary to quench the specimen, and a refractory metal holder is desired, the platinum fuse wire and the 0.010-in. molybdenum support wire are replaced with a 0.040-in. molybdenum wire. The second type of specimen holder used in the furnace is fabricated from graphite or carbon rods. This holder is a hollow cylindrical crucible with an external flange to support it from the susceptor cover to allow the main body of the crucible to extend well into the hot zone of the furnace.

Before heating any specimens in the furnace, the parts were outgassed by heating the furnace to 2,000° to 2,100° C in vacuum. When not in use, the furnace was continuously pumped by a small auxiliary mechanical pump to maintain a pressure of approximately 50μ of mercury in the chamber at all times. If, however, the furnace was not to be used for an extended period, it was evacuated and filled with helium or argon. If the furnace had been maintained under reduced pressure, either during a heating period or during an idle period, it was always filled with helium or argon before exposing the interior to the air. This procedure minimized the adsorption of air on the carbon susceptor and on the carbon-black insulation. A motor-generator, rated at 75 kw at 9,600 cps, supplied power to the furnace. About 10 to 12 min. were required to reach a temperature of 1,900° C, and about 3 kw were required to maintain the temperature at that level. The specimen temperature was easily controlled to within ± 5 deg C by making small manual adjustments of the field excitation of the generator.

X-ray diffraction patterns were obtained with a high-angle goniometer spectrometer, using Cu K_{α} radiation. The diffracted X-ray intensities were recorded on a strip chart on which 1 in. was equivalent to 1 deg 2θ .

4. Methods

4.1. Preparation and Treatment of Alloys

The starting materials from which the preparations were compounded (see table 1) were obtained in two conditions. The uranium-carbon alloys were received in ingot form. The ingots were coarsely crushed in a "diamond" mortar, and were further reduced in a boron carbide mortar to pass a No. 325 U. S. Standard Sieve. These operations were per-

formed in a dry box in an atmosphere of carbon dioxide. The beryllium carbide was obtained in powdered form that passed a No. 325 U. S. Standard Sieve.

Five-gram batches of the appropriate amounts of the various starting materials were weighed on an analytical balance. The powdered materials were blended by grinding together in a boron carbide mortar, within a dry box, prior to pressing. Specimens for solid-state reaction were pressed in hardened steel molds into pellet form, usually $\frac{3}{8}$ -in. diameter and approximately $\frac{3}{8}$ to $\frac{1}{2}$ in. high. The specimens were placed in graphite cups within the molybdenum cup, so that contamination due to heating in contact with molybdenum was avoided. After the furnace was assembled, with specimens in place, the chamber was "pumped down" to a pressure of 1μ of mercury and then filled with argon. The pumping and refilling with argon was repeated once before heating was started. After a 2-hr heat treatment at the elevated temperature (either 1,700° or 1,900° C), the specimen assembly was cooled rapidly by dropping it into the cold oil. The quenching oil was removed from the specimens by soaking them overnight in carbon tetrachloride. The cleaned, dry pellets were crushed and ground in a boron carbide mortar within the dry box, to pass a No. 200 U. S. Standard Sieve. The fine powders were stored in a desiccator, usually not longer than 3 days, before they were subjected to X-ray analysis.

The results obtained for the constitution of mixed carbides within the system UC-UC₂-Be₂C, after the treatment described above, are based on room-temperature X-ray analyses of the quenched crystalline phases and on the lattice parameters.

A uniform period of 2 hr at the elevated temperature was selected, based on a series of experiments on alloy preparations involving solid-state reactions between mixtures of UC and Be₂C. The degree of reaction, as indicated by the unit-cell size of the resulting solid solutions, was evaluated after total reaction times of 2, 4, and 6 hr, with grinding and repressing between heat treatments. It is reasonable to assume that a 6-hr total reaction time with intermediate grinding and repressing at 2-hr intervals is more conducive to the attainment of equilibrium than is a single 6-hr treatment. No significant differences in lattice parameters of the UC solid solutions were observed between the alloys heated for 2, 4, or 6 hr. The shortest of these reaction periods was selected for convenience and to minimize compositional changes, such as carbon "pickup" and beryllium loss due to dissociation of the beryllium carbide.

4.2. X-Ray Methods

The lattice parameters for cubic compounds and solid solutions were evaluated by taking the average of the values obtained from the last five diffraction peaks in the back-reflection region of the X-ray pattern. The parameters of the tetragonal UC₂ compound and solid solutions were evaluated by taking the average of the values obtained from those

reflections that had the greatest contribution to the desired parameter. The "a" parameter was found by taking the average of the values obtained from the (*hk*0) reflections (200), (220), (310), (400), and (330), and the "c" parameter was found by appropriate calculations, using the formula

$$\frac{l^2}{c^2} = \frac{1}{d^2} - \frac{h^2 + k^2}{a^2}$$

for the diffraction reflections (103), (004), (114), (204), (105), (215), (116), (206), (305), and (107).

4.3. Chemical Methods and Precision

Early in the investigation, it was believed that chemical analysis of the alloys after heat treatment would prove of value in interpreting the results of the X-ray analyses and in more accurately locating the phase boundaries that exist in the system UC-UC₂-Be₂C. The varying degrees of instability of the uranium-carbon alloys and of beryllium carbide, with respect to air and moisture, made it desirable to analyze preparations as soon as possible after heat treatment. Unfortunately, analytical procedures for the separation and analysis of uranium, beryllium, and carbon, in the form of mixed carbides, were not available. It was necessary to develop new techniques and adapt other techniques for use in this study.

The methods that are described for the separation and analysis of uranium, beryllium, and carbon are not intended to represent a completely developed, standard method of analysis, but are presented as a guide to other workers.

Some of the powdered, quenched preparations that were analyzed by X-ray methods were analyzed chemically for uranium, beryllium, iron, and carbon as follows:

a. Uranium

Duplicate samples of approximately 0.50 g were weighed into 125-ml Erlenmeyer flasks. Nitric and perchloric acids were added, and the sample was digested for 2 hr on a hot plate. When solution of the sample was complete, a second portion of nitric acid was added.

The solution was then transferred to a special continuous extractor, similar in design to the one described by Rodden and Warf [15], except that a Friedrichs condenser was used without an extension tube. The solution was extracted for 1½ hr with diethyl ether, at the end of which time the uranium had been quantitatively transferred to the boiler flask. The aqueous layer remaining in the extractor tube contained ammonium nitrate, beryllium, and any iron that might have been present as an impurity.

After evaporation of the ether, the uranium extract was fumed with sulfuric acid to remove any organic matter. The solution was then diluted, and the uranium was precipitated as ammonium diuranate with carbonate-free ammonium hydroxide solution. The precipitate was filtered on Whatman No. 42 filter paper, drained, and ignited in a platinum

crucible at 1,000° C for 1 hr. The ignited precipitate was cooled and weighed as U₃O₈.

b. Beryllium

The aqueous layer remaining after the extraction was transferred to a beaker, evaporated to dryness, and the ammonium nitrate volatilized by the method of J. Lawrence Smith [16]. Beryllium was determined by one of two methods. If more than 2 percent by weight was indicated by the nominal composition of the sample, a gravimetric method was used, but if less was indicated, a fluorimetric method was used.

For the gravimetric determination of beryllium, the solution remaining after the ammonium nitrate volatilization was diluted, and the beryllium was precipitated with ammonium hydroxide as the hydrous oxide. The precipitate was filtered on a Whatman No. 41H filter paper, drained, and ignited in a platinum crucible at 1,000° C for 1 hr. The ignited precipitate was cooled and weighed as BeO.

For the fluorimetric determination of beryllium, the solution from the ammonium nitrate volatilization was diluted in a volumetric flask, and suitable aliquots were transferred to 50-ml volumetric flasks. These aliquots were treated according to the method of Fletcher, White, and Sheftel [17], and the fluorescence of the resulting solutions was compared with that of fluorescent uranium glass standards in a photoelectric fluorimeter designed and built at the Bureau by E. L. McGandy.

c. Iron

Iron was present in small quantities in all the alloys tested. No sample was found that contained more than 0.35 nor less than 0.10 percent of iron. Approximately, one in every three samples was tested for iron. For this determination, an aliquot was removed from the solution after ammonium nitrate volatilization and transferred to a 25-ml volumetric flask. This was treated according to a standard method described by Sandell [18], using orthophenanthroline as a colorimetric reagent. The optical density of the resulting solution was compared with that of standard solutions in a Beckman model B spectrophotometer.

d. Carbon

The carbon content of samples containing no beryllium was determined by ignition in porcelain boats in an oxygen train at 1,000° C. It was found, however, that this temperature was too low to completely decompose the samples containing beryllium carbide. Samples containing beryllium carbide were decomposed at higher temperatures, obtained in a modified inductively-heated combustion furnace, with the aid of a special flux containing copper as a combustion catalyst. In the determination of small amounts of carbon in beryllium metal, J. J. Tregoning [19] described the use of copper as a combustion catalyst.

A special flux, consisting of 0.80 g of open-hearth iron (NBS Standard Sample 55) and 0.90 g of powdered copper, was added to a combustion crucible. About 0.20 g of the carbide was then accurately weighed in the crucible, and the mixture was blended, placed in the inductively heated combustion furnace, and burned in a stream of purified oxygen. The carbon dioxide formed was absorbed in ascarite contained in a Nesbitt bulb.

Because the samples could not be dried at 110° C without some oxidation taking place, several of them were checked for moisture content by a special procedure. For this purpose, a crucible, 15 mm in diameter, 15 mm high, and having a 2-mm wall thickness, was machined from graphite. About 0.20 g of sample was weighed accurately into the crucible, and placed in the inductively heated combustion furnace. The sample was heated at approximately 1,200° C in a stream of dried helium, and the evolved moisture was absorbed in magnesium perchlorate contained in a Nesbitt bulb.

The standard deviation of an individual analysis, as well as the estimated precision that might be obtained when 2 or 3 determinations are made, is given in table 2. These data were derived from the uranium, beryllium, and carbon analyses made of the mixed carbide alloys. The lack of standard samples of these mixed carbides and the time limitation imposed by the expiration of the investigation prevented the accumulation of sufficient data to justify any definite statements concerning the accuracy of the analytical methods.

The results of analyses of various preparations in the system UC-UC₂-Be₂C are given in table 3. The data were selected as being typical of the results obtained, as well as indicating the compositional

range over which the various elements occurred in the alloys. The nominal composition was included in the table to show that the analyzed compositions were in reasonably good agreement with the intended compositions. The uranium and beryllium percentages are the average of duplicate determinations, and the carbon values represent the average of three determinations. The sum of the percentages of the constituent elements found is less than 100 percent in every case. The departure from 100 percent is found, in general, to increase with increasing amounts of beryllium carbide in the alloy. In most instances smaller departures from 100 percent were found for the alloys heat-treated at 1,900° C than for the alloys heat-treated at 1,700° C. The results have been corrected for the small amount (less than 2% by weight) of moisture found and are expressed on the basis of the dry material. The

TABLE 2. Estimated standard deviation and precision of analytical methods

Element	Compositional range (% by weight)	Method of analysis	Degrees of freedom on which standard deviation is based ^a	Estimated standard deviation of an individual analysis ^b	Estimated standard deviation of average ^c for—	
					n=2	n=3
U.....	55 to 95	Gravimetric...	53	0.34	0.24	0.20
Be.....	0 to 2	Fluorimetric...	22	.036	.025	.021
Be.....	2 to 12	Gravimetric...	34	.21	.15	.12
C.....	4 to 12	Combustion..	146	.088	.062	.051

^a See [21] for definition of statistical terms and description of methods.

^b Standard deviation of an individual analysis = $\sqrt{(\text{sum of squares})/(\text{degrees of freedom})}$.

^c Standard deviation of average = $(\text{standard deviation of individual analysis})/\sqrt{(\text{number of determinations})}$.

TABLE 3. Typical analyses of alloys within the system UC-UC₂-Be₂C

Alloy	Temperature of heat treatment	Nominal composition						Analyzed composition ^a (percentage by weight)			
		Mole percent			Percentage by weight			U	Be ^b	C	Total
		UC	UC ₂	Be ₂ C	U	Be	C				
	°C										
85.....	1,700	92	8	-----	94.83	-----	5.17	93.4	-----	4.85	98.2
85.....	1,900	92	8	-----	94.83	-----	5.17	93.9	-----	5.18	99.1
187.....	1,700	80	20	-----	94.29	-----	5.71	93.8	-----	5.64	99.4
187.....	1,900	80	20	-----	94.29	-----	5.71	93.8	-----	5.52	99.3
150.....	1,700	21.7	78.3	-----	91.17	-----	8.83	91.7	-----	7.90	99.6
150.....	1,900	21.7	78.3	-----	91.17	-----	8.83	91.2	-----	7.99	99.2
101.....	1,700	10	90	-----	91.25	-----	8.75	89.6	-----	8.37	98.0
101.....	1,900	10	90	-----	91.25	-----	8.75	91.0	-----	8.50	99.5
118.....	1,700	65	25	10	92.72	0.78	5.97	92.2	0.84	6.37	99.4
118.....	1,900	65	25	10	92.72	.78	5.97	91.4	.64	6.33	98.4
181.....	1,700	35	55	10	91.30	.77	7.93	90.1	.59	8.00	98.7
181.....	1,900	35	55	10	91.30	.77	7.93	90.6	.64	8.10	99.3
91.....	1,700	50	10	40	87.49	4.42	8.09	83.6	4.44	7.61	95.6
91.....	1,900	50	10	40	87.49	4.42	8.09	85.6	4.41	8.09	98.1
92.....	1,700	45	15	40	87.17	4.40	8.43	83.6	3.97	7.11	94.7
92.....	1,900	45	15	40	87.17	4.40	8.43	85.9	3.99	8.61	98.5
93.....	1,700	40	20	40	86.85	4.39	8.76	81.8	4.14	7.52	93.5
93.....	1,900	40	20	40	86.85	4.39	8.76	84.5	4.46	8.72	97.8
98.....	1,700	15	45	40	85.29	4.31	10.40	81.0	3.87	9.69	94.6
98.....	1,900	15	45	40	85.29	4.31	10.40	83.6	3.98	10.1	97.8
108.....	1,700	25	5	70	73.89	13.06	13.05	71.0	10.6	11.1	92.7
109.....	1,700	20	10	70	73.43	12.98	13.58	69.6	10.7	11.5	91.8
111.....	1,700	10	20	70	72.54	12.82	14.64	67.4	11.9	13.7	93.0

^a The uranium and beryllium values are the average of two determinations; the carbon values are the average of three determinations.

^b Beryllium was determined by a fluorimetric method for amounts less than 2 percent by weight, and by a gravimetric method for amounts greater than 2 percent by weight.

percentage of iron, in those specimens which were analyzed for iron content, was found to be too low (less than 0.35% by weight) to account for the departure from 100 percent.

Both the uranium carbides [1] and beryllium carbide are known to be unstable in the presence of air and moisture. The alloys heat-treated at 1,700° C were stored in desiccators for several months longer than those heat-treated at 1,900° C. In view of the instability of these carbides with respect to air, it is reasonable to assume that the departure of these analyses from 100 percent may be attributed, in part, to oxidation of the specimens that occurred during storage periods of as long as 18 months. In all cases, the specimens were ground to pass a No. 200 U. S. Standard Sieve for X-ray analysis shortly after heat treatment and were stored in this condition. The expiration of the investigation prevented the determination of oxygen content.

The results of the chemical analyses of the alloys were not substituted for the nominal compositions for several reasons:

First, due to oxidation or hydration, the chemical composition of the samples is believed to have changed during the interval between X-ray and chemical analyses.

Second, some doubt exists concerning the cause of the failure of the analysis to total 100 percent. Even if the cause is definitely attributed to oxygen, there are no valid assumptions that can be made to permit the calculation of the composition that existed at the time of heat treatment.

Third, all of the heated alloys were not analyzed, and confusion would result from the attempt to correlate data in which part of the alloys were considered on the basis of nominal composition, and part on the basis of analyzed composition.

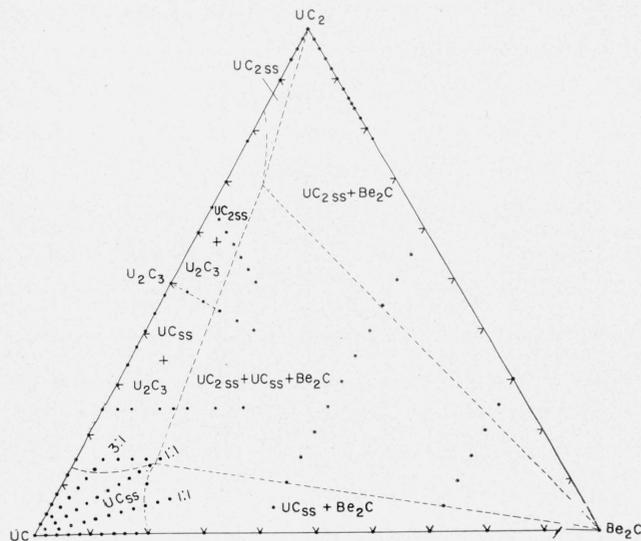


FIGURE 3. Phases identified in the system UC-UC₂-Be₂C, in mole percent.

The alloys were heated for 2 hours at 1,700° C, in argon and then oil-quenched. Dots refer to preparations studied.

5. Results and Discussion

5.1. Isothermal Section at 1,700° C

An isothermal section at 1,700° C was made of interactions within the system UC-UC₂-Be₂C and in the binary boundary systems that are included. A constitutional diagram, prepared from the data, is shown in figure 3. This figure represents the constitution of alloys after a 2-hr heat treatment at 1,700° C and is not intended to represent an equilibrium phase diagram.

a. The Binary System UC-Be₂C

Data are presented in table 4 and figure 4 showing the relation between lattice parameters and composition in the system UC-Be₂C after quenching in oil from 1,700° C. It can be seen that small additions of Be₂C increase the unit-cell size of the UC phase. At the limit of solubility, 20 mole percent (or 2.9 wt percent) of Be₂C, the volume of the UC unit-cell was increased by 1.6 percent. The broken line in figure 4 represents the type of results obtained early in the

TABLE 4. Composition and UC lattice parameters in the system UC-Be₂C

Preparations were heated 2 hr at 1,700° C in argon and then oil-quenched.

Alloy	Nominal composition		UC _{ss} parameters	
	Be ₂ C	UC	Oil-quenched (rapid cooling)	Quenched in less rapid cooling media ^a
	Mole %	Mole %	A	A
44	0	100	4.962	4.963
55	2	98	4.964	4.965
56	4	96	^b 4.967	4.968
57	6	94	^b 4.970	4.972
59	8	92	4.972	-----
43	10	90	4.974	4.973
173	12	88	4.979	-----
174	14	86	4.981	-----
42	20	80	4.988	4.972
41	30	70	4.985	4.972
40	40	60	4.989	4.972
39	50	50	4.988	4.973
37	70	30	4.992	4.974

^a These data obtained on specimens that were cooled either in molten tin (mp 232° C) or on tantalum wool.

^b Pellets missed oil quench-cup. They were cooled less rapidly than those which were oil-quenched.

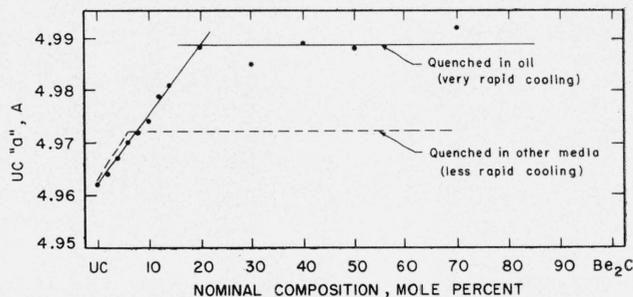


FIGURE 4. Lattice parameters of uranium carbide solid solutions in mixtures of UC and Be₂C.

The preparations were heated for 2 hours at 1,700° C in an argon atmosphere and then quenched in oil.

investigation, when the specimens were dropped onto tantalum wool or into molten tin in a cooler part of the furnace rather than into quenching oil. The furnace quench, which resulted in a less rapid cooling, indicated a much lower solubility limit for Be_2C in UC (6 mole percent) than was obtained with the oil quench (20 mole percent). Because precipitation or ex-solution occurs readily in these alloys, it seems likely that X-ray examination with high-temperature equipment might show a still higher solubility for the same temperature.

b. The Binary System UC-UC₂

The uranium-carbon system has been studied in other laboratories [10, 11]. The conflicting nature of the proposed diagrams, the need for determining lattice parameter values, and the degree of interaction between phases made desirable a reinvestigation of that portion of the system between UC and UC₂.

Uranium sesquicarbide, U₂C₃, was observed in the present investigation consistent with the conditions of stress and temperature described by Mallett, Gerds, and Vaughan [9]. The X-ray diffraction pattern described by Mallett was obtained with Fe K radiation and contained 23 lines with $a=8.088 \pm 0.001$ Å. The pattern, obtained with Cu K α radiation, in this study, contained 14 additional high-angle reflections with $a=8.089 \pm 0.001$ Å, based on the high-angle reflections. Because the pattern, obtained with Cu K α radiation, has not been published, it is given in table 5. The pattern was obtained from a sample consisting of 50 mole percent of UC₂ and 50 mole percent of UC heated at 1,600° C in argon and cooled to room temperature in the furnace.

The results obtained in the present study are given in table 6. The data indicate that UC enters into a solid-state reaction with as much as 27 mole percent of U₂C₃ (13.5 mole percent of UC₂), to yield a single-phase region of UC solid solutions. These solid solutions show no significant lattice parameter change over this range of composition. It was found that alloy mixtures, such as 194 (table 6) with a carbon content sufficient to correspond to 24 mole percent of U₂C₃, showed only the pattern of UC solid solution after heat treatment. Experiments performed, using the X-ray methods previously described, showed that 5 mole percent of U₂C₃ could easily be detected in the presence of 95 percent of UC. For this reason, the first six alloys of table 6 were considered to be one-phase solid solutions, regardless of the fact that no parameter change was observed.

An independent estimate of the limit of solid solution was obtained from a comparison of the relative intensities of U₂C₃ and UC_{ss} reflections of the X-ray patterns of two-phase alloys between 24 and 95.2 mole percent U₂C₃ (12 and 47.6 mole percent of UC₂), with the relative intensities of known, unheated mixtures of UC and U₂C₃. The (220) reflection of UC at 2θ equals 52.1° and the (510/439)

TABLE 5. X-ray diffraction data for the cubic compound U₂C₃ obtained with copper K α_1 radiation

hkl	Cu K α_1	d	a
	2 θ	Å	Å
211	27.00	3.300	-----
220	31.26	2.859	-----
310	35.07	2.556	-----
321	41.76	2.161	-----
400	44.80	2.021	-----
332	53.07	1.724	-----
422	55.61	1.651	-----
510/431	58.10	1.586	-----
521	62.88	1.477	-----
440	64.98	1.434	-----
530	67.46	1.387	-----
611/532	71.89	1.312	-----
620	74.06	1.279	-----
541	76.21	1.248	-----
631	80.46	1.193	-----
444	82.55	1.1676	-----
710/543	84.63	1.1442	-----
721/633/552	88.81	1.1008	-----
642	90.89	1.0809	-----
730	92.97	1.0621	-----
732/651	97.13	1.0274	-----
800	99.25	1.0111	-----
741	101.36	0.9956	-----
653	105.63	.9668	-----
660/822	107.79	.9534	-----
750/831/743	109.98	.9404	-----
752	114.48	.9159	-----
840	116.76	.9045	8.0904
833/910	119.14	.8933	8.0892
761/921/655	124.03	.8722	8.0888
664	126.56	.8623	8.0893
754/930/851	129.20	.8527	8.0891
932/763	134.79	.8343	8.0893
844	137.82	.8256	8.0887
853/941	141.01	.8171	8.0888
772/10,1,1	148.21	.8009	8.0884
862/10,2,0	152.40	.7931	8.0884
Average.....			8.0890

TABLE 6. Composition and lattice parameters in the system UC-UC₂

Preparations were heated 2 hr at 1,700° C in argon and then oil-quenched.

Alloy	Nominal composition		Lattice parameters of stable phases		
	UC ₂	UC	UC _{ss}	U ₂ C ₃	UC _{2ss} (a*) ^a
	Mole %	Mole %	Å	Å	Å
44-----	0	100	4.962	-----	-----
88-----	2	98	4.961	-----	-----
87-----	4	96	4.964	-----	-----
86-----	6	94	4.964	-----	-----
85-----	8	92	4.964	-----	-----
194-----	12	88	4.966	-----	-----
186-----	15	85	4.964	8.09	-----
187-----	20	80	4.965	8.090	-----
188-----	25	75	4.964	8.090	-----
84-----	30	70	4.965	8.089	-----
149-----	33.7	66.3	4.968	8.089	-----
192-----	40.5	59.5	4.967	8.090	-----
89-----	50	50	4.968	8.089	-----
146-----	60	40	-----	8.089	(b)
83-----	70	30	-----	8.090	4.196
150-----	78.3	21.7	-----	8.090	4.195
101-----	90	10	-----	-----	4.194
81-----	94	6	-----	-----	4.193
80-----	96	4	-----	-----	4.194
79-----	98	2	-----	-----	4.194
67-----	100	-----	-----	-----	4.195

^a $a^* = \sqrt[3]{a^2c}$.

^b Phase identified, but in an amount too small to permit a determination of the lattice parameter.

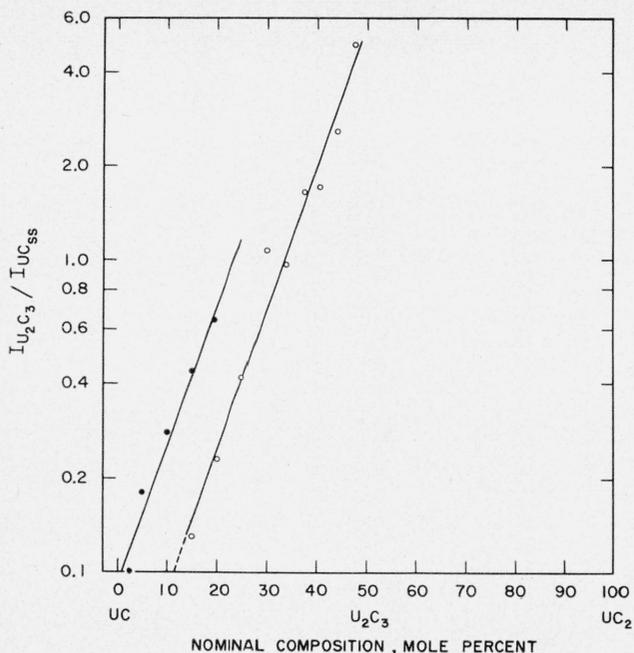


FIGURE 5. X-ray intensity ratio as a function of composition, for alloys between UC and UC_2 .

Solid circles represent data obtained from unheated mixtures. Open circles represent data obtained from alloys heated for 2 hr at $1,700^\circ\text{C}$ in argon.

reflection of U_2C_3 at 2θ equals 58.1° were selected for the intensity comparison of the heated and the unheated mixtures.

The ratios of $I_{U_2C_3}/I_{UC}$, when plotted against composition on rectangular coordinate paper, appeared to follow a curved line. When the same data were plotted on semilogarithmic paper, a more nearly linear relationship was obtained. For this reason, the data were fitted by curves of the form $y=ab^x$, using the method of least squares. These are the straight lines through the data points in figure 5.

From the curves, the intensity ratios associated with a given U_2C_3 content may be found for both the heated alloys and the known mixtures. The much smaller intensity ratio of a heated alloy, as compared with that of a known mixture of the same composition, indicate that the amount of "free" U_2C_3 has decreased as a result of the heat treatment. The distance between the curves, measured parallel to the x -axis, represents the amount of decrease in "free" U_2C_3 . The value obtained from the curves in this way, about 20 mole percent of U_2C_3 (10 mole percent of UC_2), may be used as an estimate of the solubility limit of U_2C_3 in UC, and confirms the presence of solid solubility without parameter change.

The single-phase region of UC_2 solid solutions extends to about 32 mole percent of U_2C_3 (16 mole percent of UC), without appreciable parameter change. An insufficient number of alloys was examined in the field $UC_{2ss}+U_2C_3$ to allow an estimate of the solubility limit based on intensity measurements. No evidence has been found for a single-phase field for U_2C_3 at $1,700^\circ\text{C}$.

TABLE 7. Composition and lattice parameters in the system UC_2 - Be_2C

Preparations were heated 2 hr at $1,700^\circ\text{C}$ in argon and then oil-quenched.

Alloy	Nominal composition		Lattice parameters $UC_2(a^*)^a$
	UC_2	Be_2C	
	Mole %	Mole %	\AA
67	100	—	4.195
74	98	2	4.196
75	96	4	4.196
76	94	6	4.193
77	92	8	4.194
66	90	10	4.195
195	88	12	4.194
196	86	14	4.195
78	85	15	4.194
197	84	16	4.194
198	82	18	4.196
199	78	22	4.195
62	30	70	4.195

$$^a a^* = \sqrt[3]{a^2c}$$

c. The Binary System UC_2 - Be_2C

Data are presented in table 7 for alloy preparations in the UC_2 -rich end of the system. It can be seen that Be_2C has no effect on the UC_2 unit-cell size in the quenched alloys obtained after heating 2 hr at $1,700^\circ\text{C}$ in argon. In this particular binary system, involving the carbides of a very heavy metal and a very light metal, the X-ray method for the identification of phases is especially inadequate because of the wide difference in X-ray absorption characteristics. On the basis of X-ray evidence alone, there is no indication of solubility of Be_2C in UC_2 .

d. Ternary Alloys Within the System UC- UC_2 - Be_2C

The data obtained on ternary alloys along several sections within the system UC- UC_2 - Be_2C are given in tables 8 and 9. Although the alloys are not identified by number in figure 3, the compositions given in the tables should identify the individual alloys along the respective section lines.

The alloys described in table 9 are, with few exceptions, within the UC single-phase field. The data give a satisfactory representation of the parametric surface within this region. It can be seen that the parameter increase along the sections, in the direction away from UC, is greatest along the 1:1 section. Vertical sections through the parametric surface, perpendicular to the 1:1 section, would show parameter maxima near the 1:1 section.

Five sections were studied (table 8), which extend into or cross the three-phase field in figure 3. For alloys along the sections, the UC_{ss} parameters increased to a value of $a=5.002 \pm 0.005 \text{ \AA}$ and then remained essentially constant. Those alloys that had UC_{ss} parameters within these limits were considered to be within the three-phase area and were used in locating the three-phase boundary. Along those sec-

TABLE 8. Composition and lattice parameters along several sections within the system UC-UC₂-Be₂C

Preparations were heated for 2 hr at 1,700° C in argon and then oil-quenched.

Alloy	Nominal composition			Lattice parameters			
	UC	UC ₂	Be ₂ C	UC _{ss}	UC _{2ss} (a*) ^a	U ₂ C ₃	Be ₂ C
	Mole %	Mole %	Mole %	A	A	A	A
40.....	60	---	40	4.989	(b)	---	---
90.....	55	5	40	4.987	(b)	---	---
91.....	50	10	40	4.998	(b)	---	---
92.....	45	15	40	5.000	(b)	---	---
93.....	40	20	40	5.002	4.198	---	(b)
94.....	35	25	40	5.005	4.197	---	(b)
95.....	30	30	40	5.007	4.196	---	(b)
96.....	25	35	40	5.005	4.194	---	(b)
97.....	20	40	40	5.001	4.195	---	(b)
98.....	15	45	40	---	4.191	---	(b)
99.....	10	50	40	---	4.192	---	(b)
100.....	5	55	40	---	4.192	---	(b)
37.....	30	---	70	4.992	(b)	---	4.342
108.....	25	5	70	5.000	(b)	---	4.342
109.....	20	10	70	5.000	(b)	---	4.342
110.....	15	15	70	5.001	4.198	---	4.342
111.....	10	20	70	---	4.195	---	4.342
112.....	5	25	70	---	4.197	---	4.341
62.....	---	30	70	---	4.195	---	4.342
177.....	35	65	---	(b)	4.196	8.090	---
178.....	35	62.5	2.5	---	4.196	8.089	---
179.....	35	60	5	---	4.198	8.090	---
180.....	35	57.5	7.5	(b)	4.197	8.089	---
181.....	35	55	10	5.004	4.196	---	---
182.....	35	52.5	12.5	5.002	4.198	8.091	---
183.....	35	50	15	5.003	4.197	---	---
188.....	75	25	---	---	4.964	(b)	8.090
189.....	72.5	25	2.5	4.970	(b)	8.089	---
117.....	70	25	5	4.976	(b)	8.088	---
118.....	65	25	10	4.991	(b)	8.089	---
190.....	62.5	25	12.5	5.002	(b)	8.090	---
119.....	60	25	15	5.003	(b)	---	---
120.....	55	25	20	5.004	(b)	---	---
121.....	50	25	25	5.002	(b)	---	---
68.....	48.1	48.1	3.8	4.976	4.197	8.090	---
69.....	46.2	46.2	7.6	4.995	4.200	---	---
70.....	44.9	43.6	11.5	5.007	4.195	---	---
71.....	42.9	41.6	15.4	5.005	4.201	---	---
72.....	40.2	40.3	19.5	5.005	4.198	---	---

^a $a^* = \sqrt[3]{a^2c}$.

^b Phase identified but in an amount too small to permit a determination of the lattice parameter.

tions where U₂C₃ and UC_{ss} were identified, the disappearance of U₂C₃ indicated that the boundary of the three-phase area had been crossed and was used in locating the boundary.

The stability relations of uranium sesquicarbide are not clearly understood. The conditions of stress and temperature necessary to form or stabilize U₂C₃, as described by Mallett et al. [9], were verified in the present work with the same alloys. As these alloys "aged," the sesquicarbide failed to appear, either in binary or ternary mixtures. Mixtures made from the freshly prepared alloys, 361 and 369, however, gave results compatible with those reported by Mallett.

U₂C₃ was found in the present experiments as a constituent phase in only a limited portion of the ternary diagram. It was not found in any preparation that contained more than 12.5 mole percent of Be₂C.

Three possible forms of an equilibrium phase diagram might be postulated. In the first such form, figure 6, a join would connect U₂C₃ and Be₂C. In this form of diagram the absence of U₂C₃ within the central portion of the system, under the conditions

TABLE 9. Composition and lattice parameters of UC solid-solution alloys within the system UC-UC₂-Be₂C

Preparations were heated 2 hr at 1,700° C in argon and then oil-quenched.

Alloy	Nominal composition		Lattice parameters	
	UC	UC ₂ :Be ₂ C	UC	U ₂ C ₃
	Mole %	Mole %	A	A
151.....	95	3:1	4.966	---
152.....	92.5	3:1	4.968	---
153.....	90	3:1	4.967	---
154.....	87.5	3:1	4.969	---
155.....	85	3:1	4.971	(a)
156.....	82.5	3:1	4.974	---
157.....	80	3:1	4.972	8.090
158.....	97.5	1:1	4.963	---
159.....	95	1:1	4.966	---
160.....	92.5	1:1	4.969	---
161.....	90	1:1	4.969	(a)
162.....	87.5	1:1	4.976	---
163.....	85	1:1	4.977	(a)
164.....	82.5	1:1	4.984	---
165.....	80	1:1	4.989	---
204.....	77.5	1:1	4.992	---
205.....	75	1:1	4.993	---
206.....	72.5	1:1	4.997	---
203.....	70	1:1	4.998	---
166.....	95	1:3	4.969	---
167.....	92.5	1:3	4.972	---
168.....	90	1:3	4.976	---
169.....	87.5	1:3	4.981	---
170.....	85	1:3	4.981	---
171.....	82.5	1:3	4.987	---
172.....	80	1:3	4.982	---
208.....	77.5	1:3	4.986	---
209.....	75	1:3	4.988	---
210.....	72.5	1:3	4.989	---
200.....	77.5	2:1	4.980	8.090
201.....	75	1.5:1	4.992	---
202.....	72.5	1.2:1	4.997	---
207.....	75	1:1.5	4.992	---

^a Phase identified, but in an amount too small to permit a determination of the lattice parameter.

of the present experiments, would result from the nonattainment of equilibrium, and U₂C₃ would increase at the expense of UC₂ or UC as equilibrium was approached. In the second form of an equilibrium diagram, U₂C₃ would not appear. The presence of the U₂C₃ phase in the alloys would be a non-equilibrium condition, and the amount of U₂C₃ would decrease as equilibrium was approached. Another possible explanation of the occurrence of U₂C₃, within the ternary system, is one requiring the postulation of a compound in the UC-Be₂C system at about 25 to 35 percent of Be₂C. X-ray patterns within this region indicate a cubic, single-phase material with parameters slightly larger than UC, and have been interpreted merely as a solid solution of Be₂C in UC, with beryllium substituting for carbon in the interstitial uranium-carbon compound. It is possible, however, that a compound 3UC·Be₂C or 2UC·Be₂C may exist and form a complete series of solid solutions with pure UC. Binary joins would exist between both U₂C₃ and UC₂ and the postulated compound. This explanation would satisfactorily explain the observed occurrence of U₂C₃, without postulating varying amounts of stress on a material that does not seem to have a varying composition. The possible occurrence of a hypothetical compound is suggested as a convenient method for making the results compatible with the phase rule, but no defi-

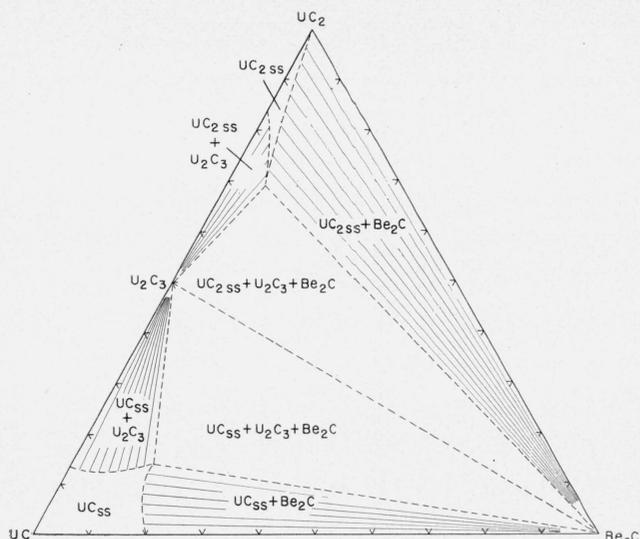


FIGURE 6. Most probable equilibrium diagram for the system UC-UC₂-Be₂C at 1,700° C, in mole percent.

nite evidence of its occurrence was found. Of these three possible forms of an equilibrium diagram for the system, it is believed that the first, figure 6, is the most probable.

The boundary between the fields of UC_{ss} and UC_{ss}+U₂C₃ is clearly established because 1- and 2-phase alloys in these regions can be readily differentiated by X-ray methods. The boundary between the fields of UC_{ss} and UC_{ss}+Be₂C, on the other hand, can only be approximated, because the X-ray method fails to distinguish between 1- and 2-phase ternary alloys involving UC_{ss} and Be₂C.

The data and discussion of alloys in table 6 indicate the extent of the UC₂ single-phase alloys in the binary system UC-UC₂. Evidence has not been obtained to prove or to disprove the existence of single-phase UC₂ alloys in the binary system UC₂-Be₂C. The assignment of a field to single-phase UC₂ alloys is in recognition of its existence rather than an approximation of the extent of the field.

5.2. Isothermal Study at 1,900° C

a. The Binary System UC-UC₂

The composition and lattice parameters of constituent phases of the alloys heated at 1,900° C are given in table 10. All preparations intermediate between the carbide end members are shown to consist of the two phases UC and UC₂. There is no apparent relation between composition and unit-cell size.

b. The Binary System UC-Be₂C

The composition and X-ray data for alloys between UC and Be₂C are given in table 11. Alloys 35, 36, and 37 are not on the join between UC and Be₂C because of an excess of carbon. With the starting materials then available, additions of either beryllium

TABLE 10. Composition and lattice parameters in the system UC-UC₂

Preparations were heated 2 hr at 1,900° C in argon and then oil-quenched.

Alloy	Nominal composition		Lattice parameters	
	UC	UC ₂	UC	UC ₂ (a*) ^a
	Mole %	Mole %	A	A
44	100	0	4.963	---
85	92	8	4.965	(b)
187	80	20	4.967	(b)
84	70	30	4.968	4.207
192	59.5	40.5	4.963	4.199
89	50	50	4.966	4.201
146	40	60	4.964	4.200
83	30	70	4.963	4.197
150	21.7	78.3	4.965	4.199
101	10	90	(b)	4.197
67	---	100	(b)	4.202

^a a* = $\sqrt[3]{a^2c}$.

^b Phase identified but in an amount too small to permit a determination of the lattice parameter.

TABLE 11. Composition and lattice parameters in the system UC-Be₂C

Preparations were heated for 2 hr at 1,900° C in argon and then oil-quenched.

Alloy	Nominal composition			Lattice parameters		
	UC	UC ₂	Be ₂ C	UC _{ss}	UC ₂	Be ₂ C
	Mole %	Mole %	Mole %	A	A	A
44	100	0	0	4.963	---	---
43	90	0	10	4.970	---	---
42	80	0	20	4.978	---	---
41	70	0	30	4.982	---	---
40	60	0	40	4.990	---	---
39	50	0	50	4.987	(a)	---
38	40	0	60	4.993	(a)	---
37	29.6	0.4	70	4.995	(a)	(a)
36	19.3	.7	80	4.996	(a)	(a)
35	9.1	.9	90	5.002	(a)	4.342
26	---	---	100	(a)	(a)	4.343

^a Phase identified, but in an amount too small to permit a determination of the lattice parameter.

or uranium metal would have been required to yield compositions on the join. Both the volatilization of beryllium and the gain in carbon from the specimen holder, during heating, could have resulted in further departures from the binary join. The occurrence of UC₂ in the alloys at the Be₂C end of the system may have resulted from these types of compositional changes. The tabulated data show UC solid solutions with increasing lattice parameters between 0 and 40 mole percent (7.4 wt percent) Be₂C. The marked change in slope of the parameter-composition curve at 40 mole percent of Be₂C indicates the limit of solubility of Be₂C in UC. Thus, it can be seen that the solubility of Be₂C in UC is twice as large at 1,900° C as it was found to be at 1,700° C. An explanation for the smaller slope within the two-phase region is given in section 5.3.

c. The Binary System UC₂-Be₂C

The data obtained for the alloys within this system, reacted at 1,900° C, are given in table 12. The lattice parameters of the UC₂ phase showed no systematic variation with composition. Be₂C could be positively identified only in those mixtures made up to contain 40-mole percent (7 wt percent) or more

TABLE 12. Composition and lattice parameters in the system UC₂-Be₂C

Preparations were heated for 2 hr at 1,900° C in argon and then oil-quenched.

Alloy	Nominal composition		Lattice parameters		
	UC ₂	Be ₂ C	UC ₂ (a*) ^a	UC	Be ₂ C
	Mole %	Mole %	A	A	A
67	100	---	4.202	(b)	---
66	90	10	4.196	(b)	(b)
65	80	20	4.200	(b)	(c)
73	70	30	4.197	(b)	(c)
64	60	40	4.198	(b)	(b)
63	50	50	4.196	(b)	(b)
47	40	60	4.200	(b)	(b)
62	30	70	4.199	(b)	(b)
61	20	80	4.199	(b)	4.343
60	10	90	4.202	(b)	4.343
26	---	100	(b)	(b)	4.343

^a a* = √(a²c).

^b Phase identified, but in an amount too small to permit a determination of the lattice parameter.

^c Identification of the phase questionable.

TABLE 13. Composition and lattice parameters along several sections within the system UC-UC₂-Be₂C

Preparations were heated for 2 hr at 1,900° C in argon and then oil-quenched.

Alloy	Nominal composition			Lattice parameters		
	UC	UC ₂	Be ₂ C	UC	UC ₂ (a*) ^a	Be ₂ C
	Mole %	Mole %	Mole %	A	A	A
40	60	---	40	4.990	---	(b)
90	55	5	40	4.995	(b)	---
91	50	10	40	4.989	(b)	---
92	45	15	40	4.998	(b)	---
93	40	20	40	4.999	(b)	(b)
94	35	25	40	5.002	(b)	---
95	30	30	40	5.004	(b)	---
96	25	35	40	4.998	4.203	---
97	20	40	40	5.005	(b)	---
98	15	45	40	(b)	4.198	---
99	10	50	40	(b)	4.200	---
100	5	55	40	(b)	4.195	---
64	---	60	40	---	4.198	(b)
179	35	60	5	4.982	4.204	---
181	35	55	10	4.992	4.204	---
183	35	50	15	4.992	4.204	---
117	70	25	5	4.986	(b)	---
118	65	25	10	4.993	(b)	---
119	60	25	15	5.005	(b)	---
120	55	25	20	4.998	(b)	---
121	50	25	25	5.005	(b)	---

^a a* = √(a²c).

^bPhase identified, but in an amount too small to permit a determination of the lattice parameter.

of Be₂C. UC reflections could be identified in the X-ray patterns of all mixtures. The persistent occurrence of UC, in these alloys, may reflect the need for still more rapid cooling to prevent the dissociation of UC₂. The data indicate no solubility in the system UC₂-Be₂C.

d. Ternary Alloys in the System UC-UC₂-Be₂C

A limited number of ternary alloy preparations on three sections were reacted at 1,900° C, and the data obtained are given in table 13. There appears

to be little change in the parameters of either UC or UC₂ in the alloys heated at 1,900° C. All of the ternary alloys, however, do have somewhat larger UC_{ss} parameter values than do those alloys consisting only of UC and UC₂ (table 10).

The dissociation temperature of uranium sesquicarbide [9] is 1,800° C, and therefore this phase does not appear in alloys reacted at 1,900° C. Thus, the disappearing phase technique cannot be employed in the location of a three-phase region.

5.3. Discussion of X-Ray Results

The diffraction intensities, obtained by the X-ray Geiger counter method, for the carbides of uranium are, in general, rather weak. Although the X-ray patterns for cubic UC and U₂C₃ are sharp, the pattern for tetragonal UC₂ is diffuse, making accurate parameter determinations difficult. All of the solid solutions formed in this system give comparatively weak intensities, the preparations increasingly distant from the pure compounds having increasingly poor patterns. These weak intensities are due, primarily, to the greater degree of disorder that is generally found in solid solutions.

Another difficulty encountered in the interpretation of the X-ray patterns is the inability to identify small amounts of Be₂C in the presence of large amounts of any of the uranium carbides. This is due to the fact that beryllium is a much lighter element than uranium and has much less diffracting power. Free beryllium carbide cannot be recognized in the diffraction pattern in amounts less than about 25 to 35 mole percent. Therefore, the limits of solid solution must be found by changes in the slope of the parameters of the uranium-carbide component plotted against composition, as in figure 4. The disappearing phase method is of no value in locating the boundary between single-phase and two-phase areas where one of the phases is beryllium carbide.

Very heavy and very light atoms differ greatly in abilities to reflect and transmit X-rays. Because the uranium carbides are practically opaque to X-rays, the X-ray beam is diffracted from the extreme surface of the X-ray spectrometer sample. In beryllium carbide, on the other hand, the X-ray beam may penetrate readily, and diffraction occurs throughout the whole thickness of the sample. This results in broadened peaks, the centers of which are slightly in error. When an X-ray sample is composed of a small amount of a heavy material, such as uranium monocarbide, and a large amount of a light material, such as beryllium carbide, the position of the UC diffraction peaks will be effectively displaced toward lower 2θ angles or larger d values. The end result is to cause an error in the parameter measurement of the UC, which is a function of the amount of dilution with Be₂C. The slope of the UC_{ss} parameter curve within the two-phase region (alloys 35 to 39, table 11) can be partly attributed to this error of "dilution."

X-ray results indicate that Be_2C enters into solid solution in UC to a considerable extent, resulting in an increase of the lattice parameter of the UC. As the beryllium atom has a much smaller radius than that of the uranium atom, this increase in parameter cannot be due to a substitution of Be for U. The beryllium atom, however, is slightly larger than the carbon atom and could partially replace carbon in the interstitial sites between the uranium atoms in six-fold coordination. The only other available positions for the beryllium atoms in the UC structure are those of the empty sites comparable to those occupied by fluorine in the fluorite-type structure. The beryllium atoms occupy these latter positions in Be_2C , which has the antiferite-type structure. It seems highly unlikely that the beryllium atom could occupy the same position in the UC solid solution that has the NaCl-type structure, where both the corners and the faces of the unit-cell are occupied by uranium atoms, with carbon atoms filling the interstices.

Equilibrium conditions seem to be very difficult to obtain in this system. Small amounts of UC_2 were almost always indicated in the X-ray patterns for samples that might be expected to consist of a single UC phase. The reason for this occurrence is not clear, but probably represents an unmixing reaction during quenching.

Uranium dicarbide has the same crystallographic structure as CaC_2 and other alkaline-earth dicarbides, which all undergo a phase transformation to a cubic form at elevated temperatures [20]. These cubic forms are stable only at elevated temperatures. It is possible that UC_2 also has a cubic form at some elevated temperature. The possibility of such a phase transformation might well be tested with high-temperature X-ray equipment.

5.4. General Observation

Suitable compacts were obtained by pressing fine-powder mixtures at a pressure of 60,000 psi in hardened steel molds without binders. The specimens, so formed, were free from cracks and strong enough to permit handling. After the heat treatment at either 1,700° or 1,900° C, the pellets were hard and sound, even after the rather extreme thermal shock as a result of oil-quenching.

It was found that soaking in carbon tetrachloride was required to remove completely the quenching oil. This suggested the presence of some open pores in the heated specimens.

During the heating period the carbides were extremely sensitive to small amounts of oxygen in the furnace atmosphere. Crumbling of the pellet surface was an indication of oxygen contamination. Any oxygen contamination in the specimen was also shown by the presence of uranium-dioxide reflections in the X-ray pattern.

A comparison of the lattice parameters of the UC solid solutions in preparations heated in contact

with graphite, molybdenum, or tantalum was made. The smaller parameters, which resulted from heating in contact with molybdenum or tantalum, indicated that reactions occurred for these combinations. For this reason, graphite cups were used to avoid reactions with the refractory metals.

6. Summary

Alloys within the system UC- UC_2 - Be_2C were prepared, heat-treated in the solid state in argon at 1,700° and 1,900° C, and analyzed by X-ray methods to determine the crystalline phases present. The findings may be summarized as follows:

1. Uranium monocarbide forms single-phase alloys with as much as 20 mole percent of beryllium carbide at 1,700° C, and approximately 40 mole percent at 1,900° C.

2. Solid solutions of Be_2C in UC have larger lattice parameters than either of the end members. It is believed that beryllium atoms partially replace the smaller carbon atoms of the UC structure.

3. Uranium monocarbide interacts with as much as 27 mole percent of uranium sesquicarbide (13.5 mole percent of uranium dicarbide) during the treatment at 1,700° C to form single-phase alloys.

4. Uranium dicarbide interacts with as much as 32 mole percent of uranium sesquicarbide (16 mole percent of uranium monocarbide) during the treatment at 1,700° C to form single-phase alloys.

5. No solubility of either the monocarbide or the dicarbide of uranium in uranium sesquicarbide is indicated.

6. The limitations of the X-ray methods prevent any definite statement about the interaction of Be_2C and UC_2 .

7. Several possible explanations are offered with regard to the occurrence of U_2C_3 within a very restricted portion of the system.

8. The various interactions outlined above have shown no deleterious effects on the physical structure of the mixed carbide alloys. The preparations were hard and sound, even after the rather extreme thermal shock due to oil-quenching. In a like manner, the solid-solution alloys showed no improvement, insofar as was incidentally observed, in their stability to air and moisture over the individual pure carbides.

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