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Limited Solid Solutions of Uranium and Thorium Dicarbides

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The quasi-binary system ThC_2–UC_2 has been studied across the entire composition range by thermal analysis, isothermal annealing experiments from 1600 to 2100°, and room-temperature and high-temperature X-ray diffraction. The system exhibits complete miscibility at elevated temperatures with alloys having cubic symmetry. At lower temperatures, a miscibility gap about 7 mole % wide exists in the range of 60 to 67 mole % UC_2. In this region two nonisomorphic tetragonal phases coexist. One of these phases is a UC_2-type tetragonal phase with $c/a = 1.653$. The other phase is a ThC_2-type tetragonal phase with $c/a = 1.275$. The transitions from cubic to tetragonal are diffusionless and unquenchable. A tentative phase diagram is proposed, and the coexisting phases are discussed in terms of the high-temperature structures of the pure materials.

Introduction

The use of the actinide carbides as highly refractory fuels and fertile materials for high-temperature nuclear reactors[1] has prompted the study of the phase equilibria of these systems.

Uranium dicarbide is known to have a body-centered tetragonal structure, while thorium dicarbide has a monoclinic structure.[5] Thus, without more detailed considerations, a miscibility gap in the binary system might be predicted. However, the system was studied by Brett, Law, and Livey[6] in 1958, and they reported complete miscibility, although the crystallinity of samples in the middle ranges of composition was poor. Conversely, in 1961, Benesovsky and Rudy[7] reported a miscibility gap about 30 mole % wide at 1700° which persisted to 1900°. Benesovsky and Rudy annealed samples prepared from the individual carbides for 16 hr,[7] while Brett, Law, and Livey prepared their samples by arc melting.[6] Neither author presented lattice parameters obtained from the X-ray measurements, nor was it certain in either case that equilibrium had been attained. In view of the conflicting data and the importance of the results to future carbide-fueled reactors, a resolution of the problem was indicated and this research was undertaken.

Apparatus and Procedures

Annealing experiments were carried out in a tantalum tube furnace under high vacuum ($<10^{-4}$ torr). Samples were prepared from ThO_2, UO_2, and graphite. They were converted to the dicarbides in graphite crucibles in a vacuum induction furnace and then melted briefly to ensure homogeneity. After cooling, the samples were transferred to the tantalum tube furnace for annealing. The heating element was a tantalum tube 6 in. long, 1.25–1.75 in. in diameter, with a 0.010-in. wall shielded by seven turns of tantalum foil. This arrangement provided a constant temperature zone about 1 in. long. The furnace was capable of sustained operation at 2300°. The vacuum dome was a double-walled aluminum pressure vessel which was cooled by water flowing between the walls. The sample loading port was equipped with a 4-in. gate valve which permitted the sequential attachment of a quartz window and a "Pyrovane" temperature controller, or a "quenching mechanism," without contamination of the furnace atmosphere. The quenching mechanism consisted of a brass plate through which a 0.25-in. diameter steel tube could be lowered into the vacuum chamber and inside the tantalum heater tube to within 0.5 in. of the sample. The sample was quenched by subjecting it to a high-pressure stream of helium while a mechanical vacuum pump simultaneously evacuated the helium from the vessel. Using this technique, samples could be cooled from 2100 to 1600° in 15 sec and to 600° in an additional 17 sec. While faster cooling rates could certainly be attained by immersion of the sample in a liquid (oil or liquid metal), this procedure eliminated the problem of sample contamination and was more readily adaptable to our furnace design.

Thermal analysis experiments were carried out in a high-frequency induction furnace. A schematic diagram of the furnace assembly and the associated infrared thermal analysis unit is shown in Figure 1. The induction heating unit was a 10-kc, 30-kw motor generator set. The radiation emitted from the sample passed through either a Pyrex or quartz window and was focused on the plane of a Kodak infrared detector (Ektron detector). The infrared detector was connected as one leg of a simple Wheatstone bridge circuit. The output of the bridge circuit was fed to the *y* axis of a recorder, where the heating and cooling curves were plotted as a function of time. A heating and cooling curve for a carbide sample from room temperature to 2500° and back could be completed in about 6 min. Details of the furnace design, construction, and operation will be given in a forthcoming publication.[8]

Heating and cooling curves were obtained from the output of the detector. Absolute temperatures were obtained with a standard microoptical pyrometer which was periodically calibrated against a tungsten-ribbon lamp certified by the Bureau of Standards. Temperature interval marks were recorded on the chart paper by a remote marker mechanism as the sample was either heated or cooled. In the absence of reliable emittance values for the carbide, and in view of the fact that the samples approached (but were not truly) black bodies and had varying surface conditions, the data are reported assuming an emissivity of unity. The total error due to both operator error and non-black body conditions is estimated to be ±20 and ±50° at 1400 and 2500°, respectively.

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(1) The Ultra High Temperature Reactor Experiment (UHTREX) reactor[2] at the Los Alamos Scientific Laboratory uses only a uranium dicarbide fuel, while the Dragon reactor[3] of the Organization for European Economic Cooperation and the Peach Bottom Atomic Power Station[4] utilize mixed carbide fuels.

(2) "Status Report on Ultra High Temperature Reactor Experiment (UHTREX) for Four-Month Period Ending September 20, 1962," Los Alamos Scientific Laboratory Report LAMS-2782, Oct 1962.

(3) C. A. Rennie, *et al.*, *Nucl. Eng.*, **5**, No. 50, 1 (1960).

(4) P. Fortescue, *et al.*, *Nucleonics*, **18**, 86 (1960).

(5) P. K. Gantzel and N. L. Baldwin, *Acta Cryst.*, **17**, 772 (1964).

(6) N. Brett, D. T. Law, and D. Livey, *J. Inorg. Nucl. Chem.*, **12**, 44 (1960); also United Kingdom Atomic Energy Authority Report AERE-M/R-2574, 1958.

(7) F. Benesovsky and E. Rudy, *Monatsh. Chem.*, **92**, 1186 (1961).

(8) S. Langer, N. L. Baldwin, and F. Kester, to be published.

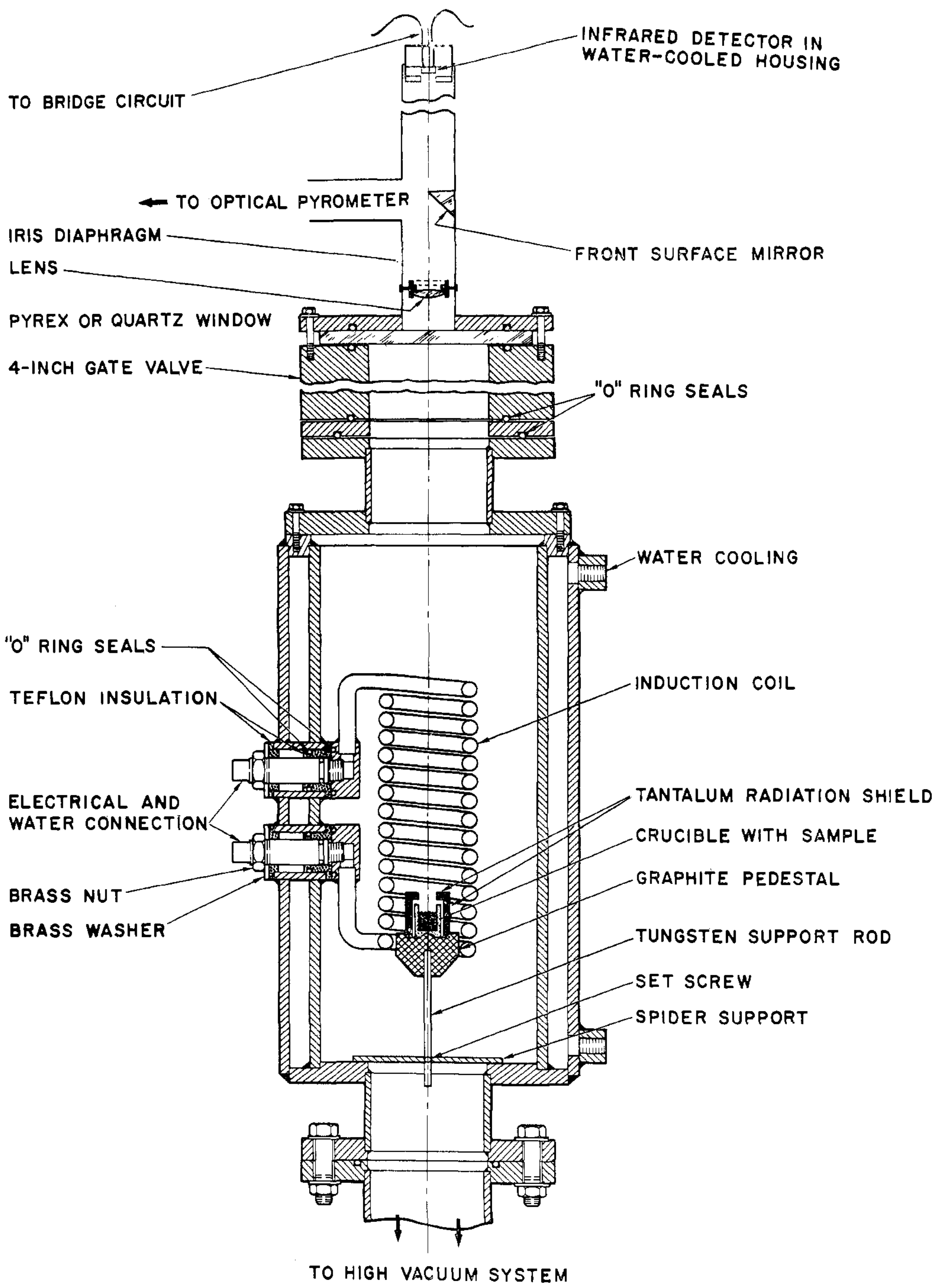

Figure 1.—Thermal analysis apparatus.

Thermal analysis samples were prepared from appropriate mixtures of the corresponding dioxides and graphite powder. These mixtures were heated in the induction furnace at gradually increasing temperatures while maintaining the pressure at about 10^{-3} torr. Complete outgassing and carburization were assured by annealing the sample at 2200° for 2 hr, during which time the pressure dropped to $<10^{-5}$ torr.

Heating and cooling curves were run on the sintered samples. These curves were repeated after the sample had been melted and consolidated in order to determine whether any change had taken place during melting. In general, the thermal arrests observed on the sintered samples were of insufficient intensity to permit precise evaluation of the temperature of the thermal effects. It was clear, however, even in the sintered samples, that the thermal effects corresponding to those observed on the melted material had been detected. Other than the increased sharpness of the thermal breaks, no significant differences between the sintered and fused material were noted.

After the thermal analyses were completed, the samples were rapidly transferred to an argon atmosphere glove box where they were sectioned for X-ray, metallographic, and chemical analysis.

Room-temperature X-ray studies were carried out using a 114.6-mm Debye–Scherrer camera filled with hydrogen. Lindemann glass capillaries were loaded and sealed with Apiezon Q in the inert atmosphere drybox and, finally, fusion sealed on removal from the drybox. Both Cu Kα and Cr Kα radiations were used in the X-ray studies. The Cr Kα radiation was particularly useful since the longer wavelength increased the diffracting angles, thus lowering the relative angular errors. The increased dispersion facilitated indexing of lines at higher θ values. Details of the procedure and an analysis of the room-temperature pattern of ThC_2 are presented in ref 5.

X-Ray studies of the thermal expansion and crystallographic transitions of thorium–uranium dicarbides were carried out in a high-temperature high-vacuum Norelco diffractometer attachment (Model 86N). The carbide samples were ground in an inert atmosphere drybox, immersed in mineral oil with benzene to thin the carbide–mineral oil mixture, then transferred onto a tantalum carbide[9] or rhenium high-temperature stage in open air. Slight warming under vacuum removed the mineral oil.

Measurement of the sample temperatures in the high-temperature X-ray camera posed an especially difficult problem. The combination of a heated reflective stage with a dispersed sample, clearly at a temperature lower than that of the stage, both with unknown and probably changing emissivities, made it obvious that the true sample temperature could not be determined with any degree of confidence. Our efforts were directed toward monitoring the relative temperature of the stage to ensure that it was in the proper temperature range for the pattern being observed. Therefore, the transition temperatures reported herein were determined by the thermal analysis experiments.

The metallographic examination was carried out using standard techniques, but minimizing exposure of the sample to the atmosphere. Air etching was sufficient to bring out the grain structure of the samples which were normally kept under oil. The characteristic, banded, martensitic structure of the ThC_2 phase was clearly visible under polarized light after etching.

Chemical analyses consisted of X-ray spectrographic analysis for uranium and thorium (accurate to ±1%) and combustion analysis for total carbon. Dissolution of the carbide and weighing of the carbon residue (or burning of the residue to CO_2) provided an analysis for free carbon. Oxygen, nitrogen, and hydrogen were determined by standard vacuum fusion techniques.

Results

The data obtained in the annealing experiments are given in Table I. The compositions of the samples were obtained by chemical analysis of the specimens after annealing. In all cases, the analyzed metal compositions agreed (within the analytical errors) with the prepared compositions. All samples were analyzed for both total and free carbon. Unfortunately, however, analysis of some of the samples was delayed for as long as 2 months after submission, and the carbon results were clearly unreliable. A typical analysis, based on the metallographic appearance of the samples, past experience with these carbides, and the reliable analyses on a few specimens run during the later stages of this work, would be: combined carbon, 8.8 to 9.3 wt %; free carbon, 0.1 to ~6 wt %; total carbon, ~9.0 to ~14 wt %; oxygen, 100 to 500 ppm; nitrogen, 1 to 25 ppm; hydrogen, 6 to 35 ppm.

Room-temperature X-ray diffraction patterns for all compositions were indexed, and lattice constants were derived which described the positions of all observed lines to within the accuracy of their measurement (usually about 0.1° θ for film measurements).

TABLE I

LATTICE CONSTANTS OF ANNEALED AND THERMAL ANALYSIS SAMPLES[a]

Mol-% UC_2[b]	Annealing Temp (°C)	Phases Present According to X-ray Data			Mol-% UC_2[b]	Annealing Temp (°C)	Phases Present According to X-ray Data		
		ThC_2 (Mono)	ThC_2 (Tetr)	UC_2 (Tetr)			ThC_2 (Mono)	ThC_2 (Tetr)	UC_2 (Tetr)
9.1	1610	x			32.5	1960	x		
9.1	1820	x			32.5	2180	x		
9.1	2120	x			33.1	1660[c]	x		
11.1	1590	x			33.5	1620	x		
11.1	2100	x			39.8	[c,d]		x	
11.2	[c,d]	x			48.6	1950		x	
14.3	1630[c]	x			48.8	2260		x	
14.3	1800[c]	x			49.1	1660[c]		x	
14.4	1580	x			50.1	1630		x	
14.4	1770	x			56.3	1750		x	
14.4	2110[c]	x			56.7	1590		x	
14.4	2120	x			59.9	2110		x	
14.4	[c,d]	x			60.2	1390		x	x
16.5	2110	x			60.2	1520		x	x
16.7	1590	x			60.2	1810		x	
16.7	1790	x			62.0	1660		x	x
16.8	1660[c]	x			62.0	1810		x	x
16.8	1810[c]	x			62.0	2160		x	x
16.9	2120[c]	x			62.4	1710		x	x
17.0	[c,d]	x			62.7	2040		x	x
19.3	1890	x			62.9	1830			x
19.3	2130	x			63.0	2050			x
19.4	[c,d]	x			63.1	1690			x
19.7	1660[c]	x			65.6	1840			x
19.9	1580	x			65.6	2070			x
25.0	1620	x			66.1	1660[c]			x
25.0	2060[c]	x			66.9	1630		x	x
25.1	1630[c]	x			79.2	1790			x
25.2	1800[c]	x			79.2	1790			x
25.2	2170	x			79.5	2120			x
25.2	[c,d]	x			79.9	1610[c]			x
25.3	1810	x							

[a] An extended form of this table giving compositions, annealing temperatures, X-ray lattice parameters, and unit cell volumes has been deposited as Document No. 9068 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. [b] Compositions are based on chemical analysis. [c] Indicates that sample was furnace-cooled from the annealing temperatures. All other annealed samples were quenched. [d] Thermal analysis sample.

The room-temperature X-ray diffraction studies showed that a single carbide phase was present in the range 0 to 60 mole % UC_2. This phase was of the thorium dicarbide type, and in the range 0 to 48 mole % UC_2 monoclinic lattice parameters were necessary to account for the observed X-ray patterns. From 48 to 60 mole % UC_2, tetragonal lattice parameters adequately represented the observed pattern. Indeed, this tetragonal structure was similar to one of the high-temperature structures of pure ThC_2.[10] In the range 67 to 100 mole % UC_2, a UC_2-type tetragonal phase was present. Both the ThC_2- and the UC_2-type tetragonal phases were observed in the X-ray diffraction photographs in the range 60 to 67 mole % UC_2.

The X-ray diffraction data from the annealed samples are given in Table I. The lattice parameters for each sample were obtained by a least-squares extrapolation FORTRAN program on an IBM-7090 computer.[5]

The lattice parameters for the ThC_2-type phase in Table I are plotted *vs.* the mole fraction (x) of UC_2 in Figure 2. The parameters[11] can be readily described in the monoclinic phase region by the equations[12]

$$\left.\begin{aligned} A_0 &= 8.287 - 0.534x + 0.201x^2 \\ b_0 &= 4.230 - 0.162x - 0.481x^2 \end{aligned}\right\} \quad 0 \leq x < 0.48$$

$$C_0 = 10.569 - 0.381x - 0.303x^2 \quad 0 \leq x < 0.60$$

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(9) Prepared by carburizing the metal prior to the experiment.

(10) P. K. Gantzel, *et al.*, *Advan. X-ray Anal.*, **8**, 78 (1965).

(11) A_0 and C_0 are used to denote the choice of unconventional monoclinic axes for ThC_2. The choice of these axes has been discussed by Gantzel and Baldwin.[5]

(12) No functional relationship is apparent for the monoclinic β angle.

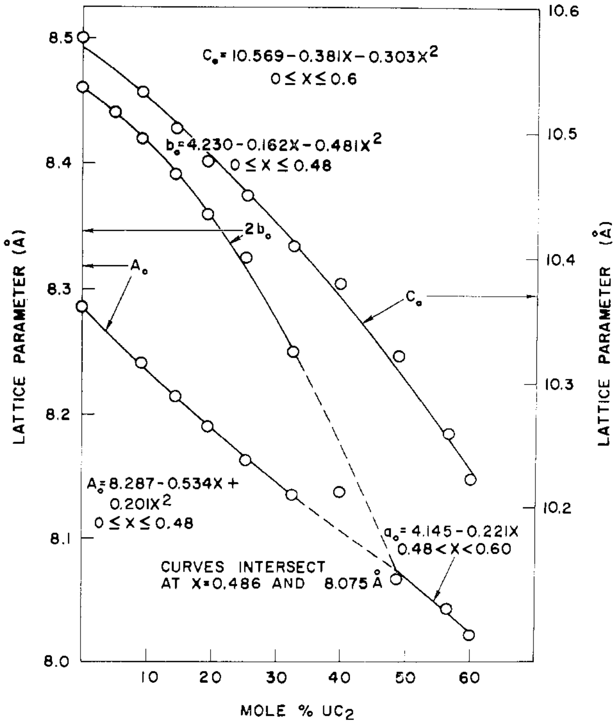

Figure 2.—Lattice parameters of ThC_2 phases.

and in the tetragonal phase region by the equation

$$a_0 = 4.145 - 0.221x \quad 0.48 < x < 0.60$$

For the tetragonal phase, the lattice constant c_0 is given by $C_0/2$ from above.

The lattice parameters of the UC_2-type tetragonal phase in Table I are plotted *vs.* composition in Figure 3. The parameters of this phase are given by the equations

$$\left.\begin{aligned} a_0 &= 4.225 - 1.214x + 0.516x^2 \\ c_0 &= 5.908 + 0.504x - 0.410x^2 \end{aligned}\right\} 0.67 \leq x \leq 1.00$$

In the composition range from 60 to 67 mole % UC_2, the lattice parameters of the coexisting phases are given by the values at the respective boundaries of this region.

Photomicrographs showing the microstructure of four typical compositions are shown in Figures 4–7. The twinned-herringbone structures in Figures 4 and 5 are typical of thorium dicarbide, which appears to undergo at least one and perhaps two martensitic transformations.[13] Stringers of primary phase graphite are evident. The area surrounding these primary phase graphite stringers is typically devoid of excess graphite and is, perhaps, a measure of the distance which the graphite can diffuse from the time the eutectic temperature is passed to some temperature at which diffusion has essentially ceased. Metallographically, it is clear that, other than graphite, only a single-carbide phase is present in these samples. This is also true of the high-UC_2 samples shown in Figures 6 and 7.

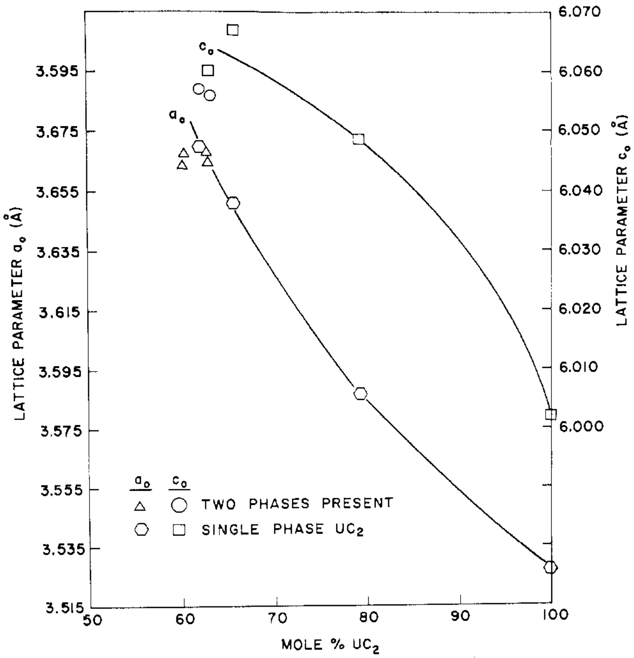

Figure 3.—Lattice parameters of UC_2 phase.

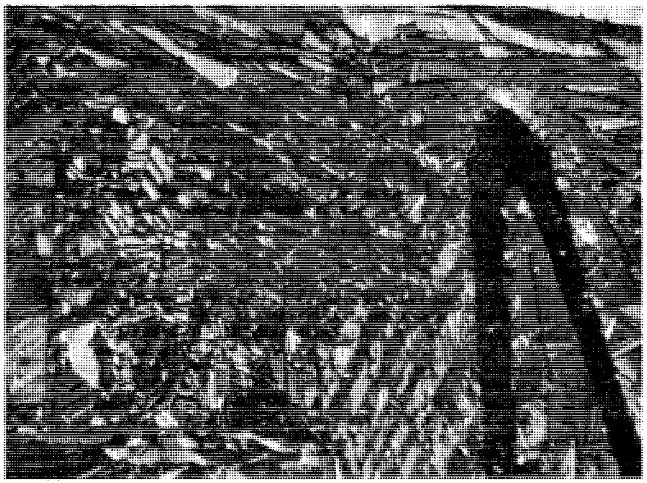

Figure 4.—Photomicrograph of ThC_2; 640× (polarized).

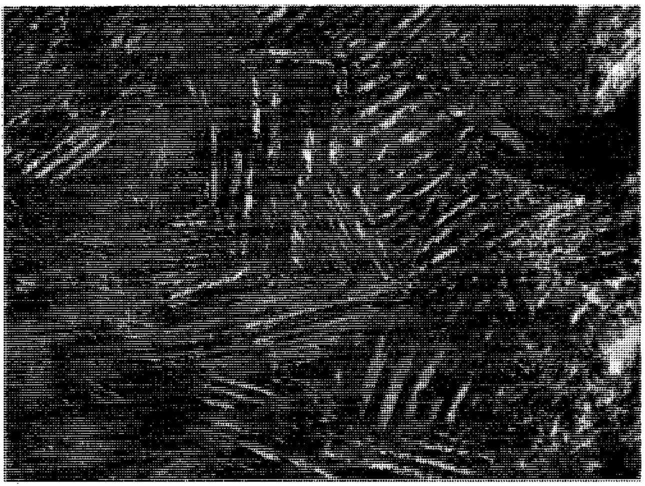

Figure 5.—Photomicrograph of 20 mole % UC_2; 250× (polarized).

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[13] S. Langer, *et al.*, "Studies in the Thorium-Carbon Binary System," in "Proceedings of the International Conference on Compounds of Potential Interest in Nuclear Reactor Technology," J. T. Waber, P. Chiotti, and W. N. Miner, Ed., The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, 1964, pp 359–386.

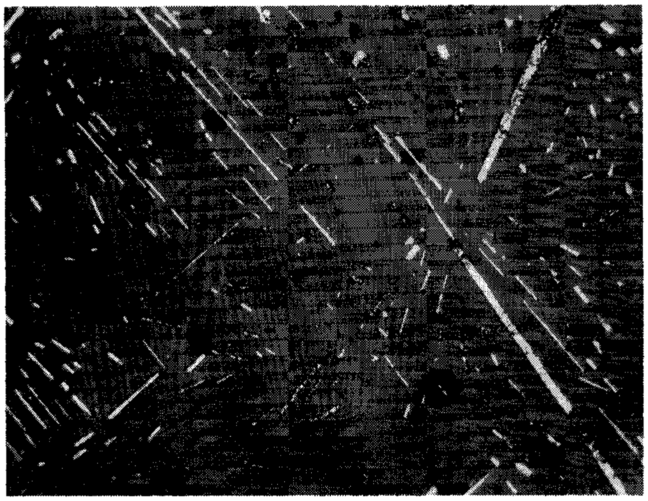

Figure 6.—Photomicrograph of 80 mole % UC_2; 250× (polarized).

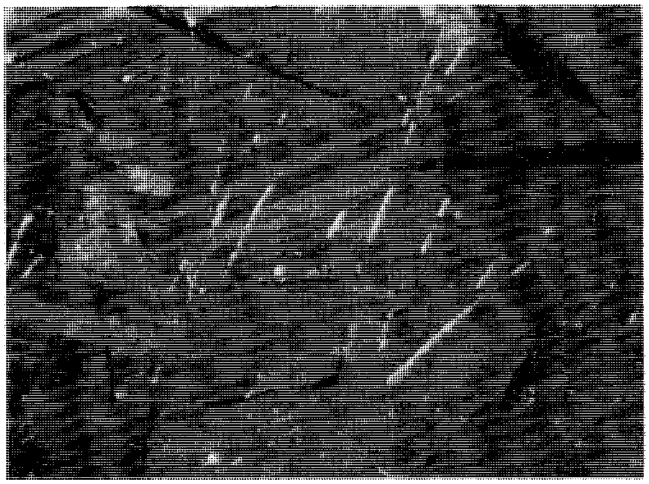

Figure 7.—Photomicrograph of UC_2; 250× (polarized).

The photomicrographs of Figures 4 and 5 show the fine subbands running almost perpendicular to the longer main bands. This structure is typical of ThC_2, and its similarity to structures in other alloys exhibiting diffusionless transformations has been pointed out.[10,13] These fine subbands are normally absent in high-UC_2 photomicrographs. It is not clear, however, whether these subbands disappear at ThC_2 contents below 80 mole %; if so, they might be attributed to the lower temperature transition (monoclinic to tetragonal) of thorium carbide, which is not detected in samples with lower thorium content.

Some of the results of thermal analysis experiments are given in Table II. Measurements were made of the transition temperatures and melting points of the ternary alloys. The melting point data are subject to much larger errors and the results are best described as falling in a band centered at about 2470 ± 70°, as shown in Figure 8.[14] The data actually represent the eutectic temperatures between the cubic solid solution carbide phases and graphite. The variations are random, and no melting point minimum was observed in the quasi-binary system.

The data on the transition temperatures show considerable hysteresis with the temperature determined on heating being, in some cases, almost 100° higher than the points determined from cooling curves. Such behavior is common in substances which undergo martensitic transformations, and the phase transitions in both UC_2[16] and ThC_2[13] have been reported to be of this type. The UC_2 transition from a low-temperature, body-centered tetragonal structure to a cubic structure occurs at 1820 ± 20°.[17] Thorium dicarbide has been shown by thermal analysis and high-temperature X-ray diffraction to undergo two polymorphic transitions at average temperatures of 1422 ± 28° and 1480 ± 21°.[18] The room-temperature structure is monoclinic,[5] while the high-temperature form has been identified as cubic.[13] The intermediate-temperature phase is tetragonal.[13] It has not been possible to quench-in the high-temperature forms of either UC_2 or ThC_2, nor any of the intermediate compositions of the UC_2–ThC_2 system.

The thermal analysis data for the transitions are plotted in Figure 9. It should be noted that the low-temperature transition of the ThC_2-type phase is observed only in samples containing less than 20 mole % uranium. This is in agreement with a gradual degeneration of the ThC_2 monoclinic structure into a ThC_2-type tetragonal structure (see Discussion). The minimum temperature of the high-temperature transition appears to be about 1100° on cooling at about 50 mole % UC_2. For a given Th/U ratio, the transition temperatures are less precisely known than for the pure carbides.

During the final stages of this work, Hill and Cavin[19] reported that UC_2 and ThC_2 formed a complete series of solid solutions with a face-centered cubic structure at 1500°. Unfortunately, their experimental points did not include compositions within the region of immiscibility proposed in this work. However, their report prompted study in the high-temperature X-ray camera of quenched compositions in which two carbide phases were detected. A sample of two-phase material (62 mole % UC_2) quenched from 1655° was examined as a function of temperature and showed the presence of two tetragonal phases (UC_2-type and ThC_2-type) up to the transition temperature (~1150°). Above this temperature, only a single-phase cubic structure was detected, while the two-phase tetragonal material returned on cooling. In contrast, material outside the region of the miscibility gap showed a single-phase tetragonal (or monoclinic) structure below and a single-phase cubic structure above the transition temperature.

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[14] The data for pure ThC_2 and UC_2 are taken from ref 13 and 15, respectively.

[15] M. G. Bowman and W. G. Witteman, "Studies Within the System UC–UC_2. Phase I Studies," USAEC Report TID-7676, 1961, p 121.

[16] R. Chang, *Acta Cryst.*, **14**, 1097 (1961).

[17] W. B. Wilson, *J. Am. Ceram. Soc.*, **43**, 77 (1960).

[18] These numbers are a revised average of the data presented in ref 12. The maximum temperature change has been 5° (see Table III).

[19] N. A. Hill and O. B. Cavin; see abstract of paper, *Bull. Am. Ceram. Soc.*, **43**, No. 4, 325 (1964).

Table II

Transition Temperatures of ThC_2–UC_2 Alloys

UC_2, mole %	Monoclinic-to-tetragonal transition temp, °C[a]			Tetragonal-to-cubic transition temp, °C[a]			Solidus temp,[b] °C
	Heating	Cooling	Hysteresis	Heating	Cooling	Hysteresis	
9.1	1286	1271	15	1390	1341	49	. . .
9.1	1354	1298	56	1462	1391	71	2499
11.1	1374	1335	39	1506	1478	28	2469
14.4	1225	1201	24	1341	1327	14	2361
14.4	1246	1230	16	1369	1335	34	. . .
16.9	1271	1245	26	1435	1394	41	2549
17.0	1229	1191	38	1371	1314	57	2401
19.4	1219	1165	54	1387	1309	78	3432
24.7	1232	1193	39	1389	1362	27	2511
25.0	. . .	. . .	. . .	1325	1290	35	2432
25.2	. . .	. . .	. . .	1346	1282	64	. . .
32.9	. . .	. . .	. . .	1287	1230	57	2479
50.2	. . .	. . .	. . .	1206	1059	147	2397
60.2	. . .	. . .	. . .	1218	1100	118	. . .
66.9	. . .	. . .	. . .	1265	1181	84	2510
77.5	. . .	. . .	. . .	1431	1377	54	2436

[a] The transition temperatures recorded are the average values for several measurements in each experiment. [b] The solidus temperature is the average of the temperatures observed on melting and freezing.

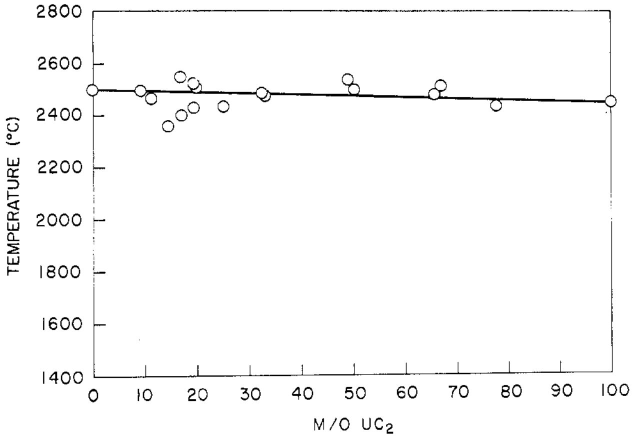

Figure 8.—Quasi-binary eutectic temperatures; $(Th,U)C_2$–C system.

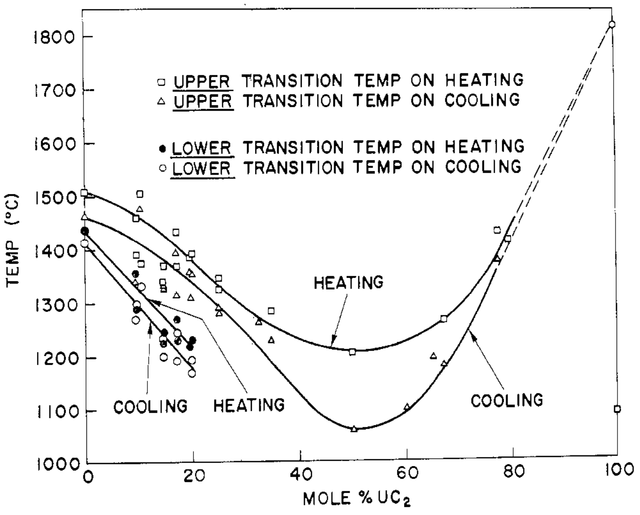

Figure 9.—Solid-state transition temperatures in the ThC_2–UC_2 system.

Discussion

The results of metallographic and X-ray diffraction studies of the alloy samples show the absence of the wide miscibility gap reported by Benesovsky and Rudy[7] and also differ from the earlier results of Brett, Law, and Livey,[6] which showed complete miscibility.

The X-ray diffraction studies of Hill and Cavin,[19] and the high-temperature X-ray studies of samples with UC_2 contents of 62 mole % reported here, show quite clearly that the pseudo-binary system exhibits a complete series of solid solutions with cubic symmetry at 1500° and quite probably at all temperatures above those of the phase transitions in the individual alloys.

The annealing studies reported in this paper show that UC_2–ThC_2 samples annealed at 1600° and above are quenched to a single-phase tetragonal (or monoclinic) structure for all compositions except those in the range from 60 to 67 mole % UC_2, where two distinct tetragonal phases are produced. Also, it is clear from the high-temperature X-ray data that the tetragonal phase(s) are produced during the quenching process and that only a single cubic phase is present at the annealing temperature.

There are, however, some anomalous data which suggest that the quenched system does, in some cases, retain a part of the equilibria present at high temperatures. Samples at the extremities of the immiscibility region can, at times, be quenched to a single tetragonal phase. At other times, two phases are produced. Samples with compositions in the center of this region (62 to 63 mole % UC_2) are always quenched to two-phase material. In these samples, the driving force for the precipitation of the second phase thus appears to always be sufficient to cause nucleation and growth during the quench. For compositions close to the two-phase boundary, however, the driving force appears to be insufficient to ensure the precipitation of the second phase in all cases. A small degree of supersaturation of the coexisting phases is therefore possible, and this results in some uncertainty in the precise composition limits of the miscibility gap.

It is appropriate, at this point, to raise the question of the attainment of equilibrium in the three annealing studies now published on the UC_2–ThC_2 system.

The study by Brett, Law, and Livey[6] utilized arc-melted samples, but no details on the heat treatment of the arc-melted material are given. Photomicrographs of samples annealed at 1900° (for an unspecified time) are shown; however, the reported poor crystallinity in the central portion of the diagram may be considered an indication of a tendency toward immiscibility.

One of their samples[6] had a composition of 59.4 mole % UC_2, which is just at the high-thorium boundary of the proposed miscibility gap. The metallographic observation of the sample states: "Mainly a single phase with some banded grains. Small amounts of a second phase which rapidly air etches." This is the only indication in their paper of the possible presence of a region of immiscibility. However, these authors had no X-ray indication of the presence of a second phase. Conversely, in the present work two phases are clearly evident on X-ray examination, but a second carbide phase could not be detected with the optical microscope, with the electron microscope, or with statistically valid precision in the electron microprobe analyzer (see below).

Benesovsky and Rudy[7] annealed samples prepared from the individual dicarbides by cold pressing and sintering. The alloys were then annealed for 16 hr at 1700°. It is doubtful that diffusion in carbides is sufficiently rapid at that temperature to permit complete solution of a mixture of two phases in the indicated annealing time. Some alloys were also annealed at 1900°, and immiscibility was also observed in these samples. At the annealing temperatures in the studies of Benesovsky and Rudy,[7] single-phase cubic solid solutions are the equilibrium phases. The presence of two-phase material over a wide composition range (30 mole %) implies that equilibrium (*i.e.*, single-phase cubic solid solution) was not attained at the annealing temperature.

At the start of the anneals in this study, the materials present were single-phase solid solutions of UC_2 and ThC_2 prepared by melting in a graphite crucible. Thus, the equilibrium phases at the annealing temperatures were present. Except in the region from 60 to 67 mole % UC_2, a single-tetragonal (or monoclinic) carbide phase was obtained in quenching. In the miscibility gap region, however, the decomposition[20]

$$(U,Th)C_2(\text{cubic}) = (U,Th)C_2(\text{tetragonal}) + (Th,U)C_2(\text{tetragonal})$$

occurs. Since precipitation of the two phases occurs in a composition region where the transition temperatures are of the order of 1200°, it is likely that the two phases, if present, would be precipitated during a similar transition at higher temperatures. Thus, a wider miscibility gap than that observed is not likely. The boundaries of the proposed two-phase region may, therefore, be estimated from the over-all composition of alloys exhibiting immiscibility. The analytical data indicate a two-phase region about 7 mole % wide.

An additional comment regarding the possible effects of varying carbon content of the samples should be made. All the data reported herein have been obtained in a region of the ternary system where an excess of free carbon was present and are, therefore, isoactivity data. However, the variation of the carbon content of the carbide phase with Th/U ratio is unknown. Uranium dicarbide has been reported by Bowman and Witteman[15] to exhibit carbon contents from $UC_{1.89}$ to $UC_{1.94}$, while ThC_2 exists over the range $ThC_{1.68}$ to $ThC_{2.04}$, as shown by Langer, *et al.*[13] The carbon content of the carbide phase is thus not constant in solutions of UC_2 and ThC_2.

Room-temperature lattice parameters for samples annealed at various temperatures are given in the extended version of Table I and are shown in Figures 1 and 2. A gradual metamorphosis from the monoclinic ThC_2 structure to a tetragonal structure with increasing UC_2 content is apparent from the convergence of the A_0 and $2b_0$ axis curves depicted in Figure 2. The accelerated approach of these two curves, shortly before their intersection, appears to indicate that in the region 45 to 60 mole % UC_2 the structure of the single-phase solid solution is truly tetragonal, rather than asymptotically approaching this condition. The close correspondence between the tetragonal solid solution (at room temperature) and the high-temperature form of ThC_2[10] is indicated by the similar c/a ratios (1.277 ± 0.001 for ThC_2 at 1460° and 1.275 ± 0.0005 for $(Th_{0.4}U_{0.6})C_2$) at room temperature. However, the $(Th,U)C_2$ tetragonal form is not identical with the tetragonal species produced by the addition of ThC_2 to UC_2, as shown by the c/a ratios of the two species. The c/a ratio of ThC_2 remains constant with increasing UC_2 content throughout the monoclinic and tetragonal $(Th,U)C_2$ regions, but the ratio is then punctuated by a sudden change to 1.653 for $Th_{0.37}U_{0.63}C_2$ as the UC_2-type tetragonal phase appears. With further decrease in ThC_2 content, the c/a ratio gradually climbs to 1.702 for pure UC_2. The c/a ratios are shown in Figure 10.

The unit cell volumes[21] of the annealed samples are given in the extended form of Table I with the monoclinic cell volumes reduced to conform to the size of the unit cells of the tetragonal phases. A smooth continuous curve for all compositions can be drawn from ThC_2 to UC_2 (Figure 11). The unit cell volumes (in A^3) for all three structures are given by the equation[21]

$$V = 92.63 - 12.68x - 13.26x^2 + 7.86x^3 \qquad 0 \leqq x \leqq 1.00$$

where x is the mole fraction of UC_2.

From room temperature up to its transition to cubic, a sample of $(Th_{0.4}U_{0.6})C_2$ exhibited a volume expansion

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[20] The notation $(U,Th)C_2$ (tetragonal) is used to designate a tetragonal solid-solution phase high in uranium, while the notation $(Th,U)C_2$ (tetragonal) is used for the analogous tetragonal phase high in thorium.

[21] For the actual monoclinic volume in the region $0 \leqq x \leqq 0.48$, this is multiplied by 4 (the tetragonal ThC_2 region extends $0.48 < x < 0.60$, tetragonal UC_2 $0.67 < x \leqq 1.00$).

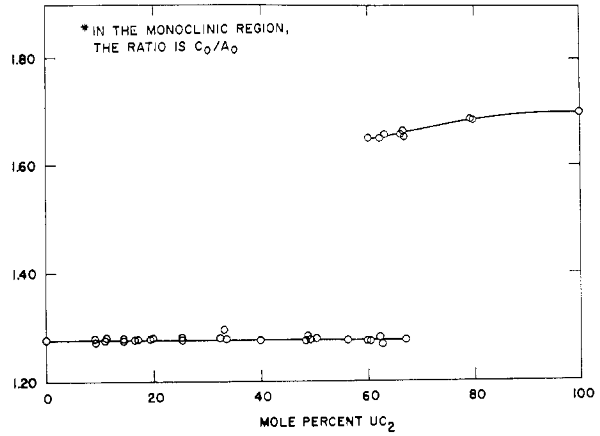

Figure 10.—C_0/A_0 ratios in the ThC_2–UC_2 system.

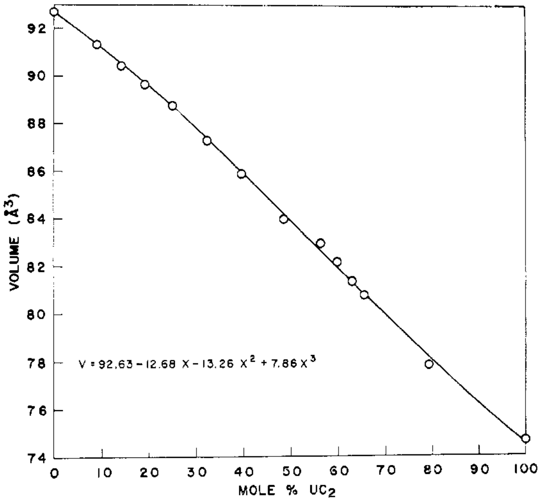

Figure 11.—Unit cell volumes in the ThC_2–UC_2 system.

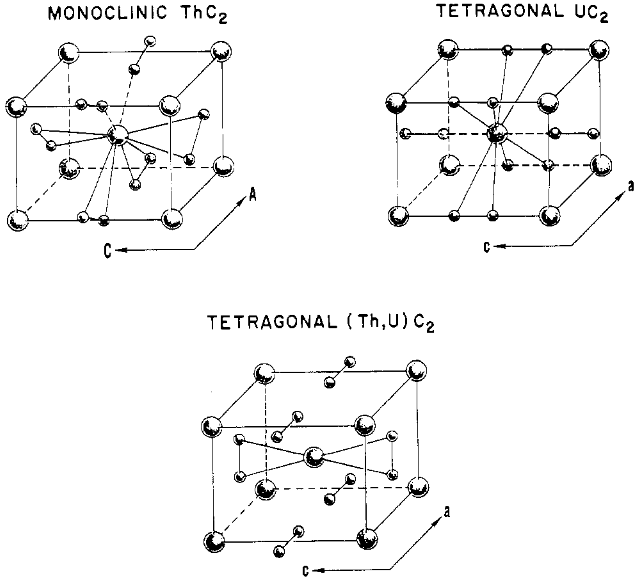

Figure 12.—Structures of monoclinic ThC_2 and tetragonal UC_2 and proposed structure of $(Th_{0.4}U_{0.6})C_2$.

coefficient of 36 × 10^{-6}/deg. The volume expansion coefficient of ThC_2 is 26 × 10^{-6}/deg,[13] while the parameters of Ferguson, Street, and Waters[22] imply 44 × 10^{-6}/deg for $UC_{1.82}$. Thus, linear interpolation between volumetric properties of ThC_2 and UC_2 describes intermediate compositions over a wide range of temperatures.

The continuous volumetric properties indicate that all compositions of $(Th_xU_y)C_2$ probably have C–C units ranging in length from the 1.5 A observed for ThC_2[23] to 1.3 A for UC_2.[24,25] The room-temperature structures of monoclinic ThC_2[23] and tetragonal UC_2[24,25] and the tetragonal structure proposed for $(Th_{0.4}U_{0.6})C_2$ are shown in Figure 12. This structure, proposed for the solid solution, is the same as that proposed for ThC_2 at 1460°.[10,26] Indeed, the ThC_2–UC_2 room-temperature results appear to establish the presence of C–C units in tetragonal ThC_2.

In Figure 2, it was shown that the lattice parameter $2b_0$ of monoclinic ThC_2 approached A_0 as the UC_2 content increased and the structure degenerated to tetragonality. Similarly, as monoclinic ThC_2 is heated, the constant A_0 increases markedly in comparison to $2b_0$ and approaches the latter as the structure tends toward tetragonality. This behavior of the parameters of ThC_2 is shown in Figure 13. In addition to small (0.2 A) thorium atom displacements, conversion from the monoclinic to the tetragonal form would appear to be accomplished by rotational adjustments of C–C units in the plane of the monoclinic *A* and *b* axes (Figure 12). This would be consistent with the correspondence between the monoclinic *C* and tetragonal *c* axial lengths.

The transition from tetragonal UC_2 to tetragonal ThC_2 (Figure 12), by a continuous variation of C–C orientations, would require disordered orientations to maintain tetragonal symmetry. The disparity between these structures is evidenced by comparison with the ratio $c/a = \sqrt{2} = 1.414$ for cubic closest packing of metal atoms. The UC_2 structure is expanded along the *c* direction, increasing c/a from 1.414 to 1.702, while the ThC_2 structure is expanded along the *a* direction, decreasing c/a from 1.414 to 1.275. The dilitations are parallel to the C–C bonds in each structure. These structural considerations reinforce the thermal analysis and X-ray data which indicate the presence, at low temperatures, of a miscibility gap where tetragonal $(Th,U)C_2$ and $(U,Th)C_2$ coexist.

It was noted above that it has not been possible to detect the presence of a second carbide phase in compositions within the proposed miscibility gap. Recently, electron microscope and electron microprobe analyses of these two phase samples were undertaken in an additional attempt to detect the presence of a second phase. No evidence of a second phase was detected in surface replicas studied in the electron microscope. The electron microprobe analyzer found some variation in the Th/U ratio from grain to grain,

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[22] I. F. Ferguson, R. S. Street, and T. N. Waters, "High Temperature X-ray Diffraction Studies, Part 2, Uranium Monocarbide and Uranium Dicarbide," United Kingdom Atomic Energy Authority Report AERE-M-819, Jan 1961.

[23] E. B. Hunt and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4777 (1951).

[24] A. E. Austin, *Acta Cryst.*, **12**, 159 (1959).

[25] M. Atoji and R. C. Medrud, *J. Chem. Phys.*, **31**, 332 (1959).

[26] Unit cell dimensions of tetragonal ThC_2 exclude a UC_2-type arrangement of C–C units because of the improbably-short Th–C distances that would result.

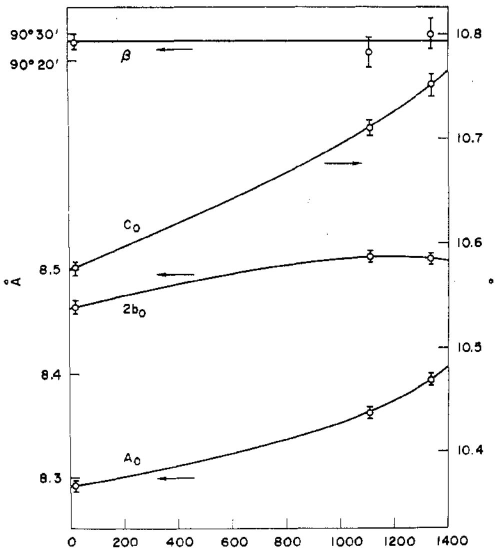

Figure 13.—Temperature dependence of the lattice parameters of monoclinic ThC_2.

but the results lack the statistical validity necessary to establish the presence of a second phase. Finally, Hill and Cavin[27] have also recently reported the probable presence of a two-phase region in UC_2–ThC_2 alloys at about 60 to 70 wt % UC_2.

The data discussed above do not point conclusively to a given construction for the quasi-binary phase diagram. However, several bits of evidence are quite concrete. First, there is a narrow region of immiscibility at low temperatures in the region 60 to 67 mole % UC_2. Second, the system at high temperature (at least above 1600°) is a continuous series of solid solutions of cubic symmetry.

These data point toward a pseudo-binary phase diagram of the type shown in Figure 14. This is similar to the diagram recently proposed by Hill and Cavin.[27] The differences, however, concern the interpretation of the X-ray and thermal analysis data on pure ThC_2 and the solid solutions with less than 20 mole % UC_2. The interpretation presented below also takes into account the diffusionless character of the phase transitions.

Martensitic transitions are distinguished by being diffusionless; that is, the compositions of the high- and low-temperature forms are identical, but differ in crystal structure. In the conventional phase diagram of a binary system, the two-phase region is an area of coexistence of two phases. At a given temperature, a point within the region represents the over-all composition of the mixture of the two phases whose compositions are given by the intersection of the isothermal tie line with the boundaries of the region. No single phase with a temperature and composition corresponding to points within the region can exist. In contrast, the "two-phase" (or coexistence) region in a binary system exhibiting martensitic polymorphism represents the temperature interval over which two phases of identical composition may coexist. Within this region, only the relative amounts of the polymorphs vary with temperature.

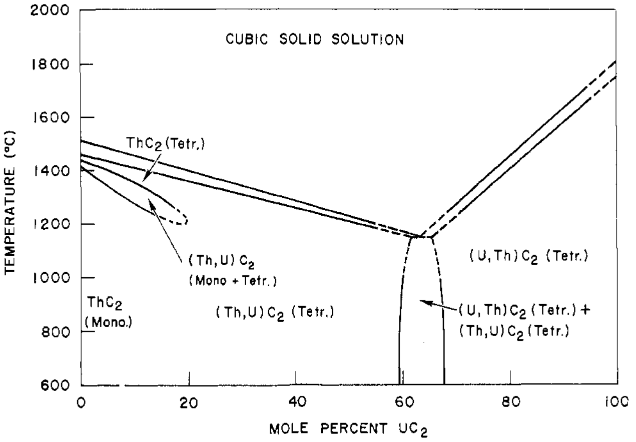

Figure 14.—Proposed phase diagram of the quasi-binary UC_2–ThC_2 system.

It should be made quite clear that the existence of two different phases, with identical compositions at the same temperature and pressure, is not a violation of the phase rule. Rather, it is an example of the more general application of the phase rule, since an intensive variable other than pressure and temperature must be considered. This variable, for martensitic transformations, is the "strain energy." The phase rule must, therefore, be written as $F = C - P + 3$. Thus, for a two-component system, the temperature, pressure, and strain energy must be specified to fully define the system in a two-phase region. The application of the phase rule, the diagnosis of martensitic transformations in unary and binary systems, and their inclusions in phase diagrams is discussed in more detail by Wolten.[28,29] In a binary system, the two-phase region associated with a martensitic transformation is manifested by the observed hysteresis loop which indicates the temperature range over which one polymorph is transformed into another of identical composition. The varying widths of these hysteresis loops for the monoclinic–tetragonal transformations of HfO_2 (25°) and ZrO_2 (200°) have been reported by Wolten.[30]

In ThC_2, the average transition temperatures have been reported as 1427 ± 21° and 1481 ± 28°.[13] However, the hysteresis range is represented by the values observed on heating and cooling, which are given in Table III.

In ThC_2–UC_2 alloys the width of the hysteresis loop changes with composition, although this effect is somewhat masked by the limited precision of the data. The width of the hysteresis loop for the tetragonal-to-cubic transition for these alloys apparently increases as the region of the miscibility gap is ap-

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(27) N. A. Hill and O. B. Cavin, "Phase Equilibrium Studies in the System UC_2–ThC_2," Oak Ridge National Laboratory Report ORNL-3668, Sept 1964.

(28) G. M. Wolten, "Martensitic Phase Transformation: Application of High-Temperature Diffractometry," in Encyclopedia of X-rays and Gamma Rays, G. L. Clark, Ed., Reinhold Publishing Corp., New York, N. Y., 1963.

(29) G. M. Wolten, *J. Chem. Educ.*, **37**, 237 (1960).

(30) G. M. Wolten, *J. Am. Ceram. Soc.*, **46**, 418 (1963).