URANIUM-CARBON



The Constitutional Diagram

The constitutional diagram for uranium-carbon shown in the accompanying figure(1) has been revised to show the allotropic transformation of UC2 from tetragonal to face-centered cubic at $1820 \pm 20 \text{ C}(2)$. Two additional compounds, UC and U₂C₃, are found in the system. Early investigators⁽³⁾ did not discover U₂C₃ by X-ray examination but had indirect indications that U₂C₃ might exist at high temperatures and decompose during cooling. Later, Mallett and co-workers⁽⁴⁾ obtained the sesquicarbide by heating the proper uranium-carbon composition in the range 1250 to 1800 C and then subjecting it to a slight stress. The requirement of residual stress for the formation of U₂C₃ has since been confirmed⁽²⁾. The sesquicarbide formed by this technique is stable from room temperature to 1840 ± 20 C.

UC and UC₂ are reported to be mutually soluble in the region above the sesquicarbid $e^{(1,2)}$.

Solubilities of carbon in gamma uranium have been reported by Blumenthal⁽⁵⁾ as follows:

Temperature, C	Solubility, ppm				
800	65				
950	70				
975	80				
1000	90				
1020	110				
1050	115				

Crystallography

The crystallography of the uranium carbides is summarized in the tabulation below. The data for UC are from Rundle⁽⁶⁾. Wilson⁽²⁾ gives values of 4.9614 and 4.9597 \pm 0.0005 A for UC at room temperature, and Litz⁽⁷⁾ reports a value of a = 4.955 A. The data for U₂C₃ are from Mallett⁽⁴⁾; a value of 0.8070 \pm 0.0005 A is given by Wilson⁽²⁾. The data for the tetragonal and face-centered cubic forms of UC₂ are from Wilson. Similar data are reported by Rundle⁽⁶⁾, who reports values of a = 3.524 and c = 5.999, and by Litz⁽⁷⁾ who gives lattice constants of a = 3.54 and c = 5.99 A.

Discussion of this system can also be found in The Chemistry of $Uranium^{(8)}$.

		Unit Cell					
		Dimonsions	Number	Densi	ity,	Spage	
Phase	Type	A A	OI Molecules	X-Ray	Other	Group	Remarks
Delta ₁ (UC)	Fcc	a = 4.961	4	13.63			NaCl-type structure
Epsilon (U ₂ C ₃)	Cubic	a = 8.088	8	12,88		143d	
Zeta (UC2)	Bc tetrag- onal	a = 3.516 c = 5.972	2	11,68		I4/mmm	CaC ₂ -type structure
Delta ₂ (UC ₂)	Fcc	a = 5.472	4				CaF2-type structure; data for 1820 C

References

- Mallett, M. W., Gerds, A. F., and Nelson, H. R., "The Uranium-Carbon System", Trans. Electrochem. Soc., <u>99</u>, 197-204 (1952).
- (2) Wilson, W. B., private communication (1957).
- (3) Wilhelm, H. A., Chiotti, P., Snow, A. I., and Daane, A. H., "The Carbides of Uranium and Thorium", J. Chem. Soc. (Supplementary Issue 2), 318-321 (1949).
- (4) Mallett, M. W., Gerds, A. F., and Vaughan, D. A., "Uranium Sesquicarbide" (AECD-3060); Trans. Electrochem. Soc., <u>98</u>, 505-509 (1951).
- (5) Blumenthal, B., "Uranium Alloy Newsletter", WASH-296, 10 (March, 1956).
- (6) Rundle, R. E., Baenziger, N. C., Wilson, A. S., and McDonald, R. A., "The Structures of the Carbides, Nitrides, and Oxides of Uranium", J. Am. Chem. Soc., <u>70</u>, 99-05 (1948).
- (7) Litz, L., Garrett, A. B., and Croxton, F. C., "Preparation and Structure of the Carbides of Uranium", J. Am. Chem. Soc., 70, 1718 (1948).
- (8) Katz, J. J., and Rabinowitch, Eugene, The Chemistry of Uranium, Part I, McGraw-Hill Book Company, Inc. (1951), p 217.

URANIUM-CERIUM

Only limited data exist for the uranium-cerium system.

Uranium and cerium are only partially miscible in the liquid state. (1, 2, 3, 4) There is evidence of a eutectic at the uranium end of the system, perhaps at about 1000 C. (2, 3) The solubility of cerium in liquid uranium is reported to increase from 1.0 w/o at 1150 C to 1.5 w/o at 1250 C, while the solubility of uranium in cerium increases from 1.3 w/o at 1000 C to 3.5 w/o at 1250 C. (4)

Crystallography

There are no compounds in the uranium-cerium system.

References

- (1) National Physical Laboratory, United Kingdom, unpublished information (May, 1949).
- (2) Neher, M., Cullity, B. D., and Kauffman, A. R., unpublished information (January, 1945).
- (3) Greninger, A. B., and Foote, F., unpublished information (May, 1945).
- (4) Wilhelm, H. A., Nuclear Fuels Newsletter, WASH-704 (December, 1952). Classified.

URANIUM-CHROMIUM



The Constitutional Diagram

Chromium is one of the few elements which forms a eutectic with uranium, without intervening intermetallic compounds. The diagram which is shown here is based largely on the work of Daane and Wilson⁽¹⁾, who studied the system by X-ray, thermal, and metallographic techniques. The eutectoid isotherms were revised by Saller, on the basis of both thermal and dilatometric measurements. The eutectic composition appears to be slightly less than 20 a/o chromium, or about 19.4 a/o chromium⁽²⁾. This composition was determined by using a series of low-carbon cast samples. The work of Mott and Haines⁽³⁾ confirms the diagram presented here.

The solubility of uranium in chromium is slight, and the solubility of chromium in uranium is limited (1). In the gamma uranium, the solubility of chomium is variously re-

ported to be 4 a/o(1) and greater than 5 a/o(3). On the basis of the behavior of beta-treated alloys during isothermal transformation in the alpha region⁽⁴⁾, the solubility in beta-uranium is estimated to be about 1.5 a/o chromium. The solubility of chromium in alpha-uranium is somewhat less than in the beta, but is not known^(1,3).

Bloom and $Grant^{(5)}$ have reported that an allotropic change occurs in chromium just below its melting point, but this change is not confirmed by McCaldin and Duwez⁽⁶⁾. In either case, this portion of the diagram would be relatively unimportant for working with these alloys.

Crystallography

There is no compound in the uranium-chromium system.

References

- (1) Daane, A. H., and Wilson, A. S., "Uranium-Chromium System", J. Metals, 7, 1219 (1955).
- (2) Saller, H. A., Rough, F. A., and Dickerson, R. F., "Preparation and Properties of the Eutectic Uranium-Chromium Alloy", BMI-884 (November, 1953).
- (3) Mott, B. W., and Haines, H. R., "A Metallographic Study of the Transformation of Beta, etc." (Appendix I: Note on the Constitution of U-Cr Alloys), AERE M/R 1211 (June 19, 1953).
- (4) White, D. W., Knolls Atomic Power Laboratory, unpublished information (1952).
- (5) Bloom, D. S., and Grant, N. J., "Chromium-Nickel Phase Diagram", J. Metals, (11), 1009 (1951).
- McCaldin, J. A., and Duwez, Pol, "Allotropic Transformations at High Temperature", J. Metals, (5), 619-20 (1954).

URANIUM-COBALT



The Constitutional Diagram

The diagram shown is that of Waldron and Browne⁽¹⁾ and is in agreement with the earlier work of Noyce and Daane⁽²⁾ except at the cobalt-rich end, where Waldron and Browne report a larger solubility range for UCo₂ and three additional compounds with compositions UCo₃, UCo₄, and U₂Co₁₁.

Crystallography

The crystal structures are known for three of the six compounds⁽³⁾. The compound U_6Co is isomorphous with U_6Mn , U_6Fe , and U_6Ni . The observed unit-cell volume for all these phases is nearly equal to the volume calculated by addition of atomic volumes, or about 550 A³. The atomic positions can be described on the basis of space group I4/mcm, although a possible variation from their positions in space groups I42 and I4c2 has not been eliminated.

The structure of UCo₂ has been reported by both $Baenziger^{(3)}$ and Waldron and Browne, the latter claiming a large variation of unit cell size with composition. UCo₂ has the C15, MgCu₂ structure and is isomorphous with UFe₂ and UMn₂ but not with UNi₂, which has the C14, MgZn₂ structure. Ternary alloys involving these phases are reported in the section devoted to ternary alloys.

		Unit Cell	Number			
Phase	Туре	Dimensions, A	of Molecules	$\frac{\text{Density, } g/\text{cm}^3}{\text{X-Ray}} \frac{\text{Other}}{\text{Other}}$	Space Group	Remarks
Delta (U ₆ Co)	Bc tetragonal	10.36 ± 0.02 5.21 ± 0.02	4	17.7	I4/mcm I42 or I4c2	Isomorphous with U ₆ Mn, U ₆ Fe, and U ₆ Mn
Epsilon (UCo)	Bcc	6.3557 ± 0.0004	8	15.37	I43m or I2,3	
Zeta (UCo ₂)	Fcc	6.929 to 7.000	8	13.83	Fd3m	C15, MgCu ₂ structure; isomorphous with UFe ₂ and UMn ₂

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Crystal structures have not yet been reported for the remaining phases.

References

- (1) Waldron, M. B., and Browne, J. D., United Kingdom, unpublished information (1956).
- (2) Noyce, W. K., and Daane, A. H., "The Uranium-Cobalt System", AECD-2826, (March 1, 1946).
- (3) Baenziger, N. C., et al., "Compounds of Uranium With the Transition Metals of the First Long Period" (AECD-2598), Acta Cryst., <u>3</u>, 34-40 (1950).

URANIUM-COPPER



The Constitutional Diagram

The system uranium-copper has been studied and a diagram has been constructed on the basis of information obtained by X-ray diffraction, thermal analysis, and metallography⁽¹⁾. The diagram is self explanatory. The region of immiscibility above 1080 C is reported to extend from 1.5 to 48 w/o copper. The immiscibility was found to exist in 5 and 45 w/o copper alloys at 1550 C and in a 25 w/o copper alloy at 1850 to 1900 C⁽¹⁾.

Data from the United Kingdom^(2,3) indicate that an additional compound, or compounds, may occur in this system. This indication is not supported by the work of Wilhelm and Carlson⁽¹⁾, although a small thermal break was observed at 860 C in the uranium-rich portion of the system. This break conceivably could be related to the presence of an additional compound, although it was considered to be the result of contamination at the time of the study. If an additional compound is present in the system, it is surely in the high-uranium region, since X-ray studies showed that UCu₅ and copper exist together in copper-rich alloys⁽¹⁾.

There is evidence of slight solubility of uranium in UCu₅. There is no evidence of appreciable solubility of uranium in copper, or of copper in uranium(1).

Crystallography

The structure of UCu₅ has been determined by Baenziger⁽⁴⁾. The data on this compound are tabulated below. The dimensions of the face-centered cubic unit cell vary from 7.033 \pm 0.002 to 7.038 \pm 0.001 A, indicating a slight solubility of uranium in UCu₅.

Wilhelm and Carlson⁽¹⁾ have reported a lattice constant of $a = 7.0208 \pm 0.002 A$. The calculated and observed densities are 10.60 ± 0.02 and 10.6 g/cm³, respectively.

	Unit Cell						
		Dimensions,	Number of	Den g/c	sity, cm ³	Space	
Phase	Type	A	Molecules	<u>X-Ray</u>	Other	Group	Remarks
Delta (UCu5)	Fcc	7.033 ± 0.002 to 7.038 ± 0.001	4			F43m or F23	Isomorphous with UNi5, PdBe5, and AuBe5

References

- Wilhelm, H. A., and Carlson, O. N., "The Uranium-Manganese and Uranium-Copper Alloy Systems" (AECD-2717), Trans. Am. Soc. Metals, 42, 1311 (1950).
- (2) Fulmer Research Institute, United Kingdom, unpublished information (1952-1953).
- (3) Swansea University College, United Kingdom, unpublished information (May, 1951).
- (4) Baenziger, N. C., Rundle, R. E., Snow, A. I., and Wilson, A. S., "Compounds of Uranium With the Transition Metals of the First Long Period" (AECD-2598), Acta Cryst., <u>3</u>, 34-40 (1950).

URANIUM-DYSPROSIUM

Uranium and dysprosium exhibit an immiscibility gap in the liquid state. Solubility of dysprosium in liquid uranium is reported to increase from 0.15 w/o at 1150 C to 0.2 w/o at 1250 $C^{(1)}$.

Crystallography

Nothing is known concerning the possibility of compounds in this system.

Reference

(1) Wilhelm, H. A., "Nuclear Fuels Newsletter", WASH-704 (December, 1957). Classified.

URANIUM-ERBIUM

Uranium and erbium exhibit an immiscibility gap in the liquid state. Solubility of erbium in liquid uranium is reported to increase from 0.15 w/o at 1150 C to 0.2 w/o at 1250 C. (1)

Crystallography

Nothing is known concerning the possibility of compounds in this system.

Reference

(1) Wilhelm, H. A., "Nuclear Fuels Newsletter", WASH-704 (December, 1957). Classified.

URANIUM-EUROPIUM

Uranium and europium show little miscibility in the liquid state. The solubility of europium in liquid uranium is reported to be 0.15 w/o at 1150 C and 0.2 w/o at 1250 C, while uranium solubility in europium is given as 0.5 w/o at 1000 C and 1.3 w/o at 1250 C. (1)

Crystallography

Data concerning the possibility of compounds in this system are not available.

Reference

(1) Wilhelm, H. A., "Nuclear Fuels Newsletter", WASH-704 (December, 1957). Classified.

URANIUM-GADOLINIUM

Uranium and gadolinium exhibit an immiscibility gap in the liquid state. Solubility of gadolinium in liquid uranium is reported to increase from 0.075 w/o at 1150 C to 0.15 w/o at 1250 C. (1)

Crystallography

Nothing is known concerning the possibility of compounds in this system.

Reference

(1) Wilhelm, H. A., "Nuclear Fuels Newsletter", WASH-704 (December, 1957). Classified.

URANIUM-GALLIUM



The Constitutional Diagram

The liquidus of the system has been determined by Jaffee. (1) In addition, evidence of two compounds has been reported. Maskrey and Frost⁽²⁾ reported UGa₃, while Dempster⁽³⁾ reported UGa₂. Because work in the United Kingdom⁽⁴⁾ tends to support the presence of the second compound, it is included with the other data to give a tentative diagram.

Judging from the liquidus and a reported melting point of about 1300 C for $UGa_3^{(4)}$, it seems likely that UGa_3 melts congruently. The compound UGa_2 , if present, may be stable to some lower temperature.

There appears to be a eutectic at the high-uranium end of the system where a dip in the liquidus occurs. Jaffee⁽¹⁾ found little solubility of uranium in solid gallium. He found the melting point of gallium virtually unaffected by small additions of uranium. On the other hand, it was reported from the United Kingdom that a eutectic occurs at 14 a/o uranium and about 28 C⁽⁴⁾. This report is in serious disagreement with the liquidus as shown. Since complete information is not available, a full evaluation cannot be made.

Jaffee's method for determining the liquidus was rather simple; he determined solubility by feeling with a stirring rod to determine whether uranium was present in the bottom of a crucible of gallium⁽¹⁾. In spite of the simplicity of his method, the resulting data connect nicely with filtration data obtained by Hayes⁽⁵⁾ and Wilkinson⁽⁶⁾ for temperatures of 700 and 500 C at the gallium end of the system.

The solid solubility of gallium in uranium is reported to be very low(6).

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Crystallography

The data for UGa₃ shown in the tabulation below are from the work of Frost and Maskrey⁽²⁾. Iandelli has also reported UGa₃, giving a lattice constant $a = 4.249 A^{(7)} UGa_2$ data reported by Dempster⁽³⁾ were not available.

	Unit Cell								
Phase	Туре	Dimensions, A	Number of Molecules	Densi g/cr X-Ray	ty, n ³ Other	Space <u>Group</u>	Remarks		
UGa ₂	No data	available			·				
UGa ₃	Simple cubic	a = 4.2475	1	9.686		Pm3m	L12-type, AuCu ₃ ordered structure; isomorphous with UA1 ₃ USn ₃ , UIn ₃ , USi ₃ , UGe ₃ , UPb ₃		

References

- Jaffee, R. I., Evans, R. M., Fromm, E. O., and Gonser, B. W., "Gallium in Nuclear Reactors; Considerations for Use in Liquid Fuel Rods", BMI-T-20 (January, 1950). Classified.
- Maskrey, J. T., and Frost, B.R.T., "The System Uranium-Lead" (AERE M/R 1027), J. Inst. Metals, (12), 171-80 (1953).
- (3) Dempster, A. J., Progress Report, AL-4120, (March, 1948).
- (4) Atomic Energy Research Establishment, United Kingdom, unpublished information, (May, 1951).
- (5) Hayes, E. E., and Gordon, P., J. Met. and Cer., TID-65, 130-141 (July, 1948). Classified.
- (6) Wilkinson, unpublished information (March, 1948).
- (7) Iandelli, A., and Ferro, R., Ann. chim. (Rome), <u>42</u>, 598-606 (1952).

URANIUM-GERMANIUM

No information is available on the constitution of the uranium-germanium alloys, except that a compound, UGe₃, has been identified (1, 2).

Crystallography

The crystallography of UGe₃, as reported by Maskrey and Frost⁽²⁾, is shown below. Iandelli⁽¹⁾ reports a value of a = 4. 198 A for UGe₃, and reports UGa₃, UIn₃, UTl₃, USi₃, and UPb₃ to have similar structures.

		Unit Cell			
Phase	Type	Dimensions, A	Number of Molecules	Space Group	Remarks
UGe ₃	Simple cubic	a = 4.2062	1	Pm3m	Ll2-type structure, isomorphous with UAl3, USn3, USi3, ÜGa3, UIn3, UPb3