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A COMPILATION OF THORIUM BINARY PHASE DIAGRAMS

By
O. N. Carlson
E. R. Stevens

January 1968

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A COMPILATION OF THORIUM BINARY PHASE DIAGRAMS

O. N. Carlson and E. R. Stevens

ABSTRACT

The known phase diagrams and crystallographic data for the intermediate phases for 63 binary systems of thorium have been compiled in this report. A brief discussion together with a complete bibliography for each system is included. The compilation is based on a literature survey through 1967 and supplements the more selective and condensed version summarized in a section of the forthcoming third edition of the Reactor Handbook on Materials.

INTRODUCTION

Thorium metal and its alloys have received a considerable amount of attention in recent years, particularly by organizations engaged in research on nuclear materials. The major interest in thorium derives from its potential usefulness as a breeder material in advanced atomic reactors. Principal emphasis of the alloy studies has been on improving the corrosion resistance and strength properties of thorium metal and in determining its compatibility with other materials such as fuel claddings or structural components. Inasmuch as the phase diagram provides valuable and necessary information for use in the development of a particular alloy, many of the binary systems of thorium have been investigated. Sixty-three of these systems are summarized in this report.

The authors of this compilation have exhaustively surveyed the published literature on the subject and have attempted to keep abreast of work currently in progress. Some of the earlier work which was either rather preliminary in nature or was carried out on poor quality thorium metal has been omitted entirely where these results have obviously been superseded by more complete and accurate work. However, where there are conflicting results of interpretations the authors have not tried to resolve the points of disagreement but rather to present the evidence in question as objectively and concisely as possible. In instances where it was possible to do so, the results of two or more investigations have been combined into a composite diagram. A bibliography of the pertinent work is provided should the reader wish more detailed information on a specific system.

Thorium exhibits two allotropic modifications; a face-centered cubic form, alpha, stable at room temperature and a high temperature body-centered cubic form, beta. The transition temperature between these two forms has been reported anywhere from 1350° to 1400°C depending upon the purity of the metal. This variation should be kept in mind when analyzing this collection of diagrams. The most recent value as determined at the Ames Laboratory on high purity thorium is $1350^{\circ} \pm 10^{\circ}\text{C}$ and the generally accepted value for the melting point is $1755^{\circ} \pm 5^{\circ}\text{C}$. The atomic diameter of thorium is a relatively large $3.59 \text{ \AA}$ and its electronegativity is 1.3 on the Pauling scale.

Many of the phase diagrams presented in this compilation are quite tentative and need further investigation. As higher purity thorium becomes available and experimental techniques for determining phase diagrams are improved, more complete information will undoubtedly be forthcoming.

The phase relationships for those systems of importance to fuel element fabrication and other reactor application have been summarized by the authors of this report in a section of the forthcoming third edition of the Reactor Handbook on Materials. The authors would like to acknowledge the encouragement and support of Dr. David H. Gurinsky of the Brookhaven National Laboratory, editor of the chapter in which that section will appear. His suggestion led to the preparation of this report which supplements the more selective and condensed handbook version.

Thanks are expressed to those colleagues at the Ames Laboratory whose helpful suggestions and discussions contributed a great deal to this manuscript. A special note of thanks is due Mr. Robert Lichtenberg for his assistance in searching the literature, preparing the diagrams and compiling the crystallographic data.

THE THORIUM - ALUMINUM SYSTEM

The Phase Diagram

While various investigators have studied this system, Murray¹ has carried out the most detailed investigation and has proposed the diagram presented in Fig. 1. The system is characterized by six intermetallic compounds and three eutectics. The compounds Th_2Al , Th_3Al_2 and ThAl_2 all melt congruently while ThAl , " Th_2Al_3 " and ThAl_3 are formed by peritectic reactions. A unique feature of this diagram is the eutectoidal decomposition of Th_3Al_2 and " Th_2Al_3 " at 1075° and 1100°C , respectively. Van Vucht² agrees with the diagram of Murray¹ with the exception of the composition of " Th_2Al_3 " which he prefers to designate as ThAl_x with the possible stoichiometry of $\text{Th}_{12}\text{Al}_{19}$.

Murray¹ reports the solid solubility of aluminum in thorium at 1300° and 1000°C as 0.85 at. % and 0.4 at. %, respectively, and Bannister and Thomson³ have shown that aluminum depresses the transformation temperature of thorium by an inverse peritectic reaction to 1382°C .

Fig. 1.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₂ Al	Tetragonal	a = 7.614 c = 5.857	4	C16 CuAl ₂	I4/mcm	4
Th ₃ Al ₂	Tetragonal	a = 8.125 c = 4.217	2	D5 _a U ₃ Si ₂	P4/mbm	4
ThAl	Orthorhombic	a = 4.42 b = 11.45 c = 4.19	4	B _f CrB	Cmcm	5, 2
"Th ₂ Al ₃ "	Tetragonal	a = 9.870 c = 7.837	-	-	-	1
ThAl ₂	Hexagonal	a = 4.388 c = 4.162	1	C32 AlB ₂	P6/mmm	4
ThAl ₃	Hexagonal	a = 6.500 c = 4.626	2	DO ₁₉ Ni ₃ Sn	P6 ₃ /mmc	4

References

1. J. R. Murray, The Thorium-Aluminum System, J. Inst. Metals 87 349 (1959).
2. J. H. N. van Vucht, Ternary System Th-Ce-Al, Phillips Res. Rept. 16 (1961).
3. G. H. Bannister and J. R. Thomson, The Body-Centered Cubic to Face-Centered Cubic Phase Transformation in Thorium and Some Thorium-Rich Alloys, British Rept. AERE-R-4428 (1963).
4. J. R. Murray, The Crystal Structures of Some Thorium Compounds, J. Inst. Metals 84 91 (1955).

5. P. B. Braun and J. H. N. van Vucht, Al-Th Intermetallic Compounds. II., Acta Cryst. 8 246 (1955).

THE THORIUM - ANTIMONY SYSTEM

The Phase Diagram

Hayes and Gordon¹ have determined the solubility of thorium in liquid antimony at several temperatures and report values as follows:

<u>Temp. °C</u>	<u>Solubility</u>	
	<u>wt % Th</u>	<u>at. % Th</u>
900	1.0	0.53
850	0.5	0.26
800	0.3	0.16
750	0.1	0.05
700	< 0.05	< 0.03
650	< 0.05	< 0.03

Ferro² reports three compounds, ThSb, Th₃Sb₄ and ThSb₂.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThSb	Cubic	a = 6.318	4	B1 NaCl	Fm3m	2
Th ₃ Sb ₄	Cubic	a = 9.374	4	D7 ₃ Th ₃ P ₄	I43d	2
ThSb ₂	Tetragonal	a = 4.353 c = 9.172	2	C38 Cu ₂ Sb	P4/nmm	2

References

1. E. E. Hayes and P. Gordon, The Solubility of Uranium and Thorium in Liquid Metals and Alloys, USAEC Rept. TID-2501-Del. 115 (1957).
2. R. Ferro, Crystal Structures of the Thorium Antimonides, Acta Cryst. 9 817 (1956).

THE THORIUM - ARSENIC SYSTEM

The Phase Diagram

No diagram has been reported for the phase equilibria in the thorium-arsenic system; however, three compounds, ThAs, Th₃As₄ and ThAs₂, with two crystallographic forms have been identified.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThAs	Cubic	a = 5.972	4	B1 NaCl	Fm3m	1
Th ₃ As ₄	Cubic	a = 8.843	4	D7 ₃ Th ₃ P ₄	I43d	1
β-ThAs ₂	Tetragonal	a = 4.086 c = 8.575	2	C38 Cu ₂ Sb	P4/nmm	1
α-ThAs ₂	Orthorhombic	a = 7.287 b = 9.784 c = 4.002	4	C23 PbCl ₂	Pmnb	2

References

1. R. Ferro, The Crystal Structures of Thorium Arsenides, Acta Cryst. 8 360 (1955).
2. F. Hullizer, A C23-Type Modification of ThAs_2 , Nature 209 499 (1966).

THE THORIUM - BERYLLIUM SYSTEM

The Phase Diagram

The somewhat tentative phase diagram of Badaeva and Kuznetsova¹ is shown in Fig. 2. The compound, ThBe_{13} , melts congruently at about 1930°C and has the composition, 92.86 at. % beryllium. A eutectic occurs at 38.5 at. % beryllium and 1240°C , and the peritectic point is near 0.03 at. % thorium and 1330°C . The solubility of thorium in beryllium is less than 0.01 at. % from 1250°C to room temperature. Thorium dissolves less than 1 at. % beryllium at 1150°C and this decreases to a room temperature value of near zero.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThBe_{13}	Cubic	$a = 10.395$	8	D_{23} NaZn_{13}	Fm3c	2, 3

Fig. 2.

References

1. T. A. Badaeva and R. I. Kuznetsova, Structure of Thorium - Beryllium Alloys, AEC-tr-5834, translated from Stroenie Splavov Nekotorykh Sistem s Uranom i Thoriem 358 Gosatomizdat, Moscow (1961).
2. N. C. Baenziger and R. E. Rundle, The MBe_{13} Compounds, Acta Cryst. 2 258 (1949).
3. W. C. Koehler, J. Singer and A. S. Coffinberry, X-ray and Neutron Diffraction Studies of MBe_{13} Intermetallic Compounds, Acta Cryst. 5 394 (1952).

THE THORIUM - BISMUTH SYSTEM

The Phase Diagram

A previously reported phase diagram¹ is so tentative and inconsistent with the crystallographic data that it is not presented herein. Two compounds, Th_3Bi_4 and $ThBi_2$, have been identified by Ferro,² who also reports the possible existence of two additional compounds in the vicinity of $ThBi$. No evidence was found for the Th_2Bi phase which earlier investigators¹ had reported. Other features of the system that have been fairly well established are a eutectic at $1350^\circ C$ and approximately 21 at. % bismuth, a horizontal at about $1230^\circ C$, probably associated with the Th_3Bi_4 phase, and a horizontal at $271^\circ C$ extending from 67 at. % bismuth to pure bismuth.

The solubility of thorium in liquid bismuth has been studied extensively and the data of Hayes and Gordon³ are presented below:

<u>Temp. °C</u>	<u>Solubility</u>	
	<u>wt %</u>	<u>at. %</u>
900	3.6	3.2
850	2.6	2.3
800	1.7	1.5
750	1.2	1.1
700	0.8	0.7
650	0.5	0.5
600	0.3	0.3
550	0.2	0.2
500	0.1	0.1

Crystallography

<u>Compound</u>	<u>Crystal lattice</u>	<u>Unit cell dimensions, Å</u>	<u>Z</u>	<u>Type</u>	<u>Space group</u>	<u>Ref.</u>
Th ₃ Bi ₄	Cubic	a = 9.559	4	D7 ₃ Th ₃ P ₄	I4 ₃ d	2
ThBi ₂	Tetragonal	a = 4.492 c = 9.298	2	C38 Cu ₂ Sb	P4/nmm	2

References

1. F. A. Rough and A. A. Bauer, Constitution of Uranium and Thorium Alloys, USAEC Rept. BMI-1300, Battelle Memorial Institute (1958).

2. R. Ferro, The Crystal Structures of Thorium Bismuthides, Acta Cryst. 10 476 (1957).
3. E. E. Hayes and P. Gordon, The Solubility of Uranium and Thorium in Liquid Metals and Alloys, USAEC Rept. TID-2501-Del. 115 (1957).

THE THORIUM - BORON SYSTEM

The Phase Diagram

Brewer et al.¹ have reported a few features of the thorium-boron system but a phase diagram is not available. A eutectic reaction, occurring at 1550°C, lies between thorium and a compound, ThB₄. Thorium tetraboride has a narrow range of homogeneity and melts somewhere above 2500°C. Lafferty² reports that the melting point of a second compound, ThB₆, is 2195°C.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThB ₄	Tetragonal	a = 7.256 c = 4.113 or a = 7.257 c = 4.097	4	----	P4/mbm	3, 4
ThB ₆	Cubic	a = 4.110 or a = 4.113 ₂	1	D ₂ ₁ CaB ₆	Pm3m	5, 6

References

1. L. Brewer, D. L. Sawyer, D. H. Templeton and C. H. Dauben, The Borides of Thorium and Uranium, USAEC Rept. AECD-2823 (1950).
2. J. M. Lafferty, Boron Cathodes, J. Appl. Phys. 22 299 (1951).
3. A. Zalkin and D. H. Templeton, The Crystal Structure of CeB_4 , ThB_4 and VB_4 , Acta Cryst. 6 269 (1953).
4. K. J. Matterson and H. Jones, A Study of the Tetraborides of Uranium and Thorium, Trans. Brit. Ceram. Soc. 60 475 (1961).
5. B. Post, D. Moskowitz and F. W. Glaser, Borides of Rare Earth Metals, J. Am. Chem. Soc. 78 1800 (1956).
6. P. Blum and F. Bertaut, Contribution to the Studies of Borides with a High Content of Boron, Acta Cryst. 7 81 (1954).

THE THORIUM - CADMIUM SYSTEM

The Phase Diagram

Brown¹ has identified one compound, ThCd_2 , in this system but a phase diagram has not been proposed.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThCd ₂	Hexagonal	a = 5.005 c = 3.514	1	C32 AlB ₂	P6/mmm	1

References

1. A. Brown, MX₂ Compounds of Thorium and the Polymorphism of Thorium Disilicide, *Acta Cryst.* **14** 860 (1961).

THE THORIUM - CARBON SYSTEM

The Phase Diagram

A phase diagram for the thorium-carbon system was first proposed by Wilhelm and Chiotti.¹ Modifications and variations suggested by later investigators have tended to produce a rather confusing picture of the phase equilibria for this system. Recently, Chiotti et al.² have proposed a composite diagram as shown in Fig. 3.

The effect of carbon on the solid state transformation of thorium was established by Chiotti and Dooley,³ while the solidus-liquidus data are from the earlier work of Wilhelm and Chiotti.¹ A miscibility gap lying between the thorium and ThC phase fields is based on the data of Chiotti and White.⁴

The congruently melting compound, ThC₂, exists in three different crystalline modifications although there are discrepancies in the reported transformation temperatures. Langer et al.,⁵ Henny and

Fig. 3.

Jones,⁶ and Hill and Cavin⁷ have studied the allotropic transformations in thorium dicarbide. Langer et al. reported the transformations temperatures as 1427° and 1481°C; Henny and Jones reported the two transformation temperatures to be 1410° and 1500°C. These values differ from those given by Chiotti et al.² and shown in Fig. 3. Substoichiometric composition lowers both solid state transformations of thorium dicarbide.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThC	Cubic	a = 5.346	4	B1 NaCl	Fm3m	1, 8
α -ThC ₂	Monoclinic	a = 6.691 b = 4.231 c = 6.744 β = 103°50'	4	-	C2/c	9, 10
β -ThC ₂	Tetragonal	a = 4.235 c = 5.408 @ 1460°C	-	-	-	5
γ -ThC ₂	Cubic	a = 5.807 @ 1540°C	-	-	-	5

References

1. H. A. Wilhelm and P. Chiotti, Thorium-Carbon System, Trans. ASM 42 1295 (1950).
2. P. Chiotti, F. W. Korbitz and G. J. Dooley, III, Electrical Resistivity and Phase Relations for the Thorium-Carbon System, J. Nucl. Mater. 23 55 (1967).

3. P. Chiotti and G. J. Dooley, III, Effect of Carbon on The Electrical Resistivity and Allotropic Transformation of Thorium, J. Nucl. Mater. 23 45 (1967).
4. P. Chiotti and R. W. White, Miscibility Gap in the Th-ThC System from High-Temperature X-ray Data, J. Nucl. Mater. 23 37 (1967).
5. S. Langer, N. Baldwin, P. Gantzel, F. Kester and C. Hancock, Studies in the Thorium-Carbon Binary System, in Symposium on Compounds of Interest in Nuclear Reactor Technology, Nuclear Metallurgy (Metallurgical Society of AIME, 1964) Vol. X, 359.
6. J. Henny and J. W. S. Jones, Phase Equilibria in the Thorium-Carbon System, British Rept. AERE-R-4993 (1965).
7. N. A. Hill and O. B. Cavin, A Monoclinic-Cubic Transformation in Thorium Dicarbide, J. Am. Ceram. Soc. 47 360 (1964).
8. C. P. Kempter and N. H. Krikorian, Some Properties of Thorium Monocarbide and Dicarbide, J. Less-Common Metals 4 244 (1962).
9. E. B. Hunt and R. E. Rundle, The Structure of Thorium Dicarbide by X-ray and Neutron Diffraction, J. Am. Chem. Soc. 73 4777 (1951).
10. P. K. Gantzel and N. L. Baldwin, Powder Indexing and Lattice Constants of ThC₂, Acta Cryst. 17 772 (1964).

THE THORIUM - CERIUM SYSTEM

The Phase Diagram

The diagram shown in Fig. 4 combines the data of Bannister and Thomson¹ and Weiner et al.² Bannister and Thomson have shown that cerium lowers the transformation temperature of thorium and proposed an inverse peritectic reaction at approximately 1300°C and 30 at. % cerium. This is in agreement with the solidus data of Weiner et al. who postulated a peritectic reaction near the cerium-rich end of the system, thus stabilizing the face-centered cubic form of cerium. The result is the continuous series of solid solutions between α -thorium and γ -cerium shown in the diagram.

Van Vucht³ suggested the possibility of continuous solid solubility between the bcc δ -cerium and β -thorium forms. Gschneidner⁴ also questions the existence of the peritectic reaction.

Crystallography

No compounds are found in the system.

References

1. G. H. Bannister and J. R. Thomson, The Body-Centered Cubic to Face-Centered Cubic Phase Transformation in Thorium and Some Thorium-Rich Alloys, British Rept. AERE-R-4428 (1963).
2. R. T. Weiner, W. E. Freeth, and G. V. Raynor, Lattice Spacings and Melting Points in the Thorium-Cerium System, J. Inst. Metals 86 185 (1957).

Fig. 4.

3. J. H. N. van Vucht, The Thorium-Cerium System, Bull. Inst. Metals 4 94 (1958).
4. K. A. Gschneidner, Jr., Rare Earth Alloys (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1961) p. 305.

THE THORIUM - CHROMIUM SYSTEM

The Phase Diagram

Wilhelm et al.¹ report a simple eutectic diagram for this system as is shown in Fig. 5. The eutectic reaction occurs at 1235°C and 25 at. % chromium. The terminal solid solubilities were not determined.

Crystallography

X-ray diffraction studies indicate the absence of compounds between thorium and chromium.

References

1. H. A. Wilhelm, A. S. Newton, A. H. Daane and C. Nehrer, Thorium Metallurgy, CT-3714 (1946).

THE THORIUM - COBALT SYSTEM

The Phase Diagram

The phase diagram for the thorium-cobalt system proposed by Thomson¹ is shown in Fig. 6. The existence of five compounds was confirmed. Four of these Th_7Co_3 , ThCo , ThCo_5 and $\text{Th}_2\text{Co}_{17}$, melt congruently at 1188°, 1137°, 1437° and 1462°C, respectively, while

Fig. 5.

Fig. 6.

the fifth compound, designated as "ThCo₃", melts incongruently at 1125°C. Eutectic reactions occur at 20 at. % cobalt and 1100°C, 40 at. % cobalt and 1037°C, 62 at. % cobalt and 975°C, 88.5 at. % cobalt and 1300°C, and 95 at. % cobalt and 1387°C.

The compound ThCo₅ is of variable composition with a maximum range of 4 at. % at 1300°C, decreasing to about 2 at. % at 1100°C.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₇ Co ₃	Hexagonal	a = 9.883 c = 6.200	2	D1O ₂ Th ₇ Fe ₃	P6 ₃ mc	2, 3
ThCo	Orthorhombic	a = 3.74 b = 10.88 c = 4.16	4	B _f CrB	Cmcm	2, 1
"ThCo ₃ "	Hexagonal	a = 5.038 c = 24.64	-	-	-	2, 1
ThCo ₅	Hexagonal	a = 5.01 c = 3.97	1	D2 _d CaZn ₅	P6/mmm	2
Th ₂ Co ₁₇	Monoclinic	a = 9.62 b = 8.46 c = 6.32 β = 99°06'	2	-	C2/m	2

References

1. J. R. Thomson, Alloys of Thorium with Certain Transition Metals. IV. The Systems Thorium-Iron and Thorium-Cobalt, J. Less-Common Metals 10 432 (1966).

2. J. V. Florio, N. C. Baenziger and R. E. Rundle, Compounds of Thorium with Transition Metals. II. Systems with Iron, Cobalt and Nickel, *Acta Cryst.* 9 367 (1956).
3. B. T. Matthias, V. B. Compton and E. Corenzwit, Some New Superconducting Compounds, *J. Phys. Chem. Solids* 19 130 (1961).

THE THORIUM - COPPER SYSTEM

The Phase Diagram

The tentative thorium-copper phase diagram reported by Elliott¹ is shown in Fig. 7. This work is based primarily on the data of Wilhelm et al.,² Murray,³ and Grube and Botzenhardt.⁴ Recent investigations by Thomson⁵ confirm the thorium-rich eutectic at about 27 at. % copper but indicate that the eutectic temperature of 1037°C is about 100°C higher than shown in Fig. 7. The discrepancies in the data are ascribed to differences in the purity of the thorium used in the various investigations.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₂ Cu	Tetragonal	a = 7.28 c = 5.74	4	C16 CuAl ₂	I4/mcm	6
ThCu ₂	Hexagonal	a = 4.35 c = 3.47	1	C32 AlB ₂	P6/mmm	6

Fig. 7.

References

1. R. P. Elliott, Constitution of Binary Alloys, First Supplement (McGraw-Hill Book Company, New York, N. Y., 1965) p. 386.
2. H. A. Wilhelm, A. S. Newton, A. H. Daane and C. Neher, Thorium Metallurgy, CT-3714 (1946).
3. J. R. Murray, The Crystal Structure of Some Thorium Compounds, J. Inst. Metals 84 91 (1955-56).
4. G. Grube and L. Botzenhardt, Alloys of Thorium with Copper, Aluminum and Sodium (in German) Z. Elektrochemie 48 418 (1942).
5. J. R. Thomson, Melting and Structural Correlation of Some Thorium-Rich Eutectics, J. Nucl. Mater. 15 88 (1965).
6. N. C. Baenziger, R. E. Rundle and A. I. Snow, Structures of the Compounds Th_2Cu , ThCu_2 , Th_2Zn and ThHg_3 , Acta Cryst. 9 93 (1956).

THE THORIUM - ERBIUM SYSTEM

The Phase Diagram

Uy and Burr¹ have reported that additions of erbium raise the allotropic transformation temperature of thorium. At about 2.5 at. % erbium this effect reaches a maximum.

Norman et al.² indicate that the solid solubility boundary for erbium in thorium is between 50 and 60 at. % at 900°C.

Crystallography

No compounds have been reported for this system.

References

1. J. C. Uy and A. A. Burr, The Effect of Certain Rare-Earth Solutes upon the F.C.C./B.C.C. Transformation Temperature of Thorium, J. Less-Common Metals 11 149 (1966).
2. M. Norman, I. R. Harris and G. V. Raynor, The Lattice Spacings of Thorium-Rich Solid Solutions with Praseodymium, Samarium, Gadolinium and Erbium, J. Less-Common Metals 11 395 (1966).

THE THORIUM - GADOLINIUM SYSTEM

The Phase Diagram

The results of Uy and Burr¹ have shown that additions of gadolinium raise the transformation temperature of thorium to a maximum at about 5 at. % gadolinium; further additions reverse this effect.

Investigations of Norman et al.² indicate that gadolinium is soluble to about 60 at. % at 900°C.

Crystallography

No compounds have been reported for this system.

References

1. J. C. Uy and A. A. Burr, The Effect of Certain Rare-Earth Solutes Upon the F.C.C./B.C.C. Transformation Temperature of Thorium, J. Less-Common Metals 11 149 (1966).
2. M. Norman, I. R. Harris and G. V. Raynor, The Lattice Spacings of Thorium-Rich Solid Solutions with Praseodymium, Samarium, Gadolinium and Erbium, J. Less-Common Metals 11 395 (1966).

THE THORIUM - GALLIUM SYSTEM

The Phase Diagram

A compound, ThGa_2 , has been identified by Brown¹ and confirmed by Holleck et al.² The latter report an additional compound in the gallium-rich portion of the system but this phase has not been characterized.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThGa_2	Tetragonal	a = 4.243 c = 14.690	4	C_c $\alpha\text{-ThSi}_2$	$I4_1/amd$	1

References

1. A. Brown, MX_2 Compounds of Thorium and the Polymorphism of Thorium Disilicide, Acta Cryst. 14 860 (1961).

2. H. Holleck, H. Nowotny and F. Benesovsky, The Crystal Structure of ThGa_2 and RuIn_3 (in German) Monatsh. Chem. 95 1386, (1964).

THE THORIUM - GERMANIUM SYSTEM

The Phase Diagram

The number and exact stoichiometry of compounds in the thorium-germanium system have not been clearly established, but phase diagrams for this system have been proposed by Stecher et al.¹ and Brown and Norreys.² The tentative diagram of Brown and Norreys, containing seven intermediate phases and three eutectics, is shown in Fig. 8.

They have determined the structures of six of these phases and assigned formulae corresponding to their approximate stoichiometries. Tharp et al.,³ Stecher et al.¹ and Brown^{4, 5} report compounds in this system having different stoichiometries and compositions from those listed in the table of crystallographic data below. However, the crystallographic data of Brown and Norreys only are presented here because of their compatibility with the phase diagram. It is apparent that additional work is needed on the phases and phase relationships in this system.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₃ Ge	-	-(unsolved)	-	-	-	-
Th ₃ Ge ₂	Tetragonal	a = 7.951 c = 4.194	-	D5a U ₃ Si ₂	P ₄ /mbm	2
ThGe	Cubic	a = 6.046	4	B1 NaCl	Fm3m	2
ThGe _{1.5}	Orthorhombic	a = 6.989 b = 8.432 c = 8.136	-	AlB ₂ C32(defect)	Pccm or Pcc2	2
ThGe _{1.6}	Orthorhombic	a = 5.913 b = 5.889 c = 14.219	-	C _c (defect)	Fddd	2
ThGe ₂	Orthorhombic	a = 4.223 b = 16.911 c = 4.052	4	C49 ZrSi ₂	Cmcm	2
Th _{0.9} Ge ₂	Orthorhombic	a = 16.642 b = 4.023 c = 4.160	-	-	Cmmm	2

References

1. P. Stecher, F. Benesovsky and H. Nowotny, Contributions to the Ternary: Thorium-Silicon - Germanium (in German), Monatsh. Chem. 94 549 (1963).
2. A. Brown and J. J. Norreys, The System Thorium - Germanium, J. Less-Common Metals 5 302 (1963).

3. A. G. Tharp, A. W. Searcy and H. Nowotny, Preparation and Identification of the Thorium Germanides, J. Elect. Chem. Soc. 105 473 (1958).
4. A. Brown, The Crystal Structures of Two Thorium Germanide Phases with Compositions Approximating to $\text{Th}_{0.9}\text{Ge}_2$ and ThGe_2 , Acta Cryst. 15 652 (1962).
5. A. Brown, MX_2 Compounds of Thorium and the Polymorphism of Thorium Disilicide, Acta Cryst. 14 860 (1961).

THE THORIUM - GOLD SYSTEM

The Phase Diagram

A composite diagram based on the work of Raub and Engel,¹ Brown² and recent results of Thomson³ is presented in Fig. 9. Three compounds, Th_2Au , ThAu_2 and ThAu_3 , have been reported although there is crystallographic evidence for the first two compounds only. Brown has shown that the compound identified by Raub and Engel as Th_3Au_5 is actually ThAu_2 . Thomson places the eutectic reaction between thorium and Th_2Au at 1100°C and 20 at. % gold and the solubility of thorium in gold at much less than 2 at. %.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₂ Au	Tetragonal	a = 7.42 c = 5.95	4	C16 CuAl ₂	I4/mcm	4
ThAu ₂	Hexagonal	a = 4.740 c = 3.402	1	C32 AlB ₂	P6/mmm	2

References

1. E. Raub and M. Engel, Alloys of Thorium with Copper, Silver and Gold, Z. Elektrochem. 49 487 (1943).
2. A. Brown, MX₂ Compounds of Thorium and the Polymorphism of Thorium Disilicide, Acta Cryst. 14 860 (1961).
3. J. R. Thomson, Melting and Structural Correlations of Some Thorium-Rich Eutectics, J. Nucl. Mater. 15 88 (1965).
4. J. R. Murray, The Crystal Structure of Some Thorium Compounds, J. Inst. Metals 84 91 (1955-56).

THE THORIUM - HAFNIUM SYSTEM

The Phase Diagram

The diagram in Fig. 10 was determined by Gibson et al.¹ The system consists of a eutectoid reaction at 11.3 at. % hafnium and 1295°C, a eutectic reaction at 31.0 at. % hafnium and 1450°C and an inverse peritectic reaction at about 96.9 at. % hafnium and 1600°C. The solubility of thorium in hafnium increases from negligible at ambient temperature to about 2.6 at. % at the eutectic and eutectoid reaction

Fig. 10.

isotherms. Maximum solubility of hafnium in thorium is about 6.4 at. % at room temperature.

Crystallography

There are no compounds in this system.

References

1. E. D. Gibson, B. A. Loomis and O. N. Carlson, Thorium-Zirconium and Thorium-Hafnium Alloy System, Trans. ASM 50 348 (1958).

THE THORIUM - HOLMIUM SYSTEM

The Phase Diagram

Uy and Burr¹ report that additions of holmium raise the transformation temperature of thorium to a maximum at about 5 at. % holmium. At greater concentrations this effect is reversed.

Kato and O'Hare² describe an unidentified phase in thorium-holmium alloys of composition 50 at. % to 70 at. % holmium at temperatures up to 1000°C.

Crystallography

No structure data are reported for this unidentified phase.

References

1. J. C. Uy and A. A. Burr, The Effect of Certain Rare-Earth Solutes upon the F.C.C./B.C.C. Transformation Temperature of Thorium, J. Less-Common Metals 11 149 (1966).

2. H. Kató and S. A. O'Hare, Thorium Alloy System, Rept.
USBM-U-1109 (Albany Metallurgy Research Center, 1964)
p. 9.

THE THORIUM - HYDROGEN SYSTEM

The Phase Diagram

The solubility of hydrogen in thorium increases rapidly from about 1 at. % at 300°C to above 20 at. % at 800°C. Peterson and Westlake¹ have studied this solubility using three grades of thorium and found that the presence of carbon greatly enhances the solubility. The results, for crystal bar thorium, which are in good agreement with data of Mallett and Campbell,² are given below:

<u>Temp. °C</u>	<u>Solubility, at. % H</u>
800	23.5
700	4.2
600	8.8
500	5.0
400	2.3
300	1.0

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThH ₂	Tetragonal	a = 4.10 c = 5.03	2	L'2b ThH ₂	I4/mmm	3
Th ₄ H ₁₅	Cubic	a = 9.11	4	-	I43d	4

References

1. D. T. Peterson and D. G. Westlake, Solubility of Thorium Dihydride in Thorium, Trans. Met. Soc. AIME 215 444 (1959).
2. M. W. Mallett and I. E. Campbell, The Dissociation Pressures of Thorium Dihydride in the Thorium-Thorium Dihydride System, J. Am. Chem. Soc. 73 4850 (1951).
3. R. E. Rundle, C. G. Skull and E. O. Wollan, The Crystal Structure of Thorium and Zirconium Dihydrides by X-ray and Neutron Diffraction, Acta Cryst. 5 22 (1952).
4. W. H. Zachariasen, Crystal Chemical Studies of the 5f-Series of Elements. XIX. The Crystal Structure of the Higher Thorium Hydride, Th_4H_{15} , Acta Cryst. 6 393 (1953).

THE THORIUM - INDIUM SYSTEM

The Phase Diagram

The partial phase diagram in Fig. 11 was established by Murray.¹ A eutectic reaction occurs between α -thorium and a congruently melting compound, Th_2In , at 1160°C and about 18 at. % indium. Two other compounds, ThIn_2 and ThIn_3 , have been reported but little is known about the phase equilibrium in this region of the system. Bannister and Thomson² observed that indium has little effect on the transformation of thorium and indicate that the solubility of indium in thorium is greater than 5 at. % at 1400°C .

Fig. 11.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₂ In	Tetragonal	a = 7.787 c = 6.113	4	C16 CuAl ₂	I4/mcm	1
ThIn ₂	Cubic	a = 7.050	-	-	-	3
ThIn ₃	Cubic	a = 4.695	1	L1 ₂ AuCu ₃	Pm3m	4

References

1. J. R. Murray, Some Observations on Thorium-rich Thorium-Indium Alloys, J. Less-Common Metals 1 314 (1959).
2. G. H. Bannister and J. R. Thomson, The Body-Centered Cubic to Face-Centered Cubic Phase Transformation in Thorium and Some Thorium-rich Alloys, British Rept. AERE-R-4428 (1953).
3. W. B. Pearson, A Handbook of Lattice Spacings of Metals and Alloys (Pergamon Press, New York, 1967).
4. R. Ferro, The Crystal Structures of ThHg₃, ThIn₃, ThTl₃, ThSn₃ and ThPb₃, Acta Cryst. 11 737 (1958).

THE THORIUM - IRIDIUM SYSTEM

The Phase Diagram

Thomson¹ has proposed the phase diagram of Fig. 12 by covering almost the entire composition range of this system. Eutectic reactions occur at about 15 at. % iridium and 1337°C and 35 at. % iridium and

Fig. 12.

1462°C and also in iridium-rich alloys at approximately 57 at. % and 90 at. % iridium. Compounds having the formulae Th_7Ir_3 , ThIr , ThIr_2 and ThIr_5 have been definitely established and evidence is given for two other compounds tentatively identified as " ThIr_3 " and ThIr_x . The peritectic compound, ThIr_x , of composition close to 40 at. % iridium is believed to decompose eutectoidally just below the 1462°C eutectic horizontal as is seen from the diagram.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th_7Ir_3	Hexagonal	$a = 10.076$ $c = 6.296$ or $a = 10.06$ $c = 6.290$	2	D_{10}^2 Th_7Fe_3	$\text{P6}_3\text{mc}$	2 3
ThIr	Orthorhombic	$a = 3.894$ $b = 11.13$ $c = 4.266$	4	B_f CrB	Cmcm	4
ThIr_2	Cubic	$a = 7.6615$ or $a = 7.664$	8	C_{15} MgCu_2	$\text{Fd}3\text{m}$	5 3
ThIr_5	Hexagonal	$a = 5.315$ $c = 4.288$	-	D_{2d} CaCu_5	-	6

References

1. J. R. Thomson, Alloys of Thorium with Certain Transition Metals, II. The Systems Thorium-Osmium, Thorium-Iridium and Thorium-Platinum, J. Less-Common Metals 6 3 (1964).

2. J. R. Thomson, Some New Intermetallic Compounds of Thorium of the Type Th_7X_3 , *Nature* 189 217 (1961).
3. B. T. Matthias, V. B. Compton and E. Corenzwit, Some New Superconducting Compounds, *J. Phys. Chem. Solids* 19 130 (1961).
4. J. R. Thomson, Crystal Structure of ThRh_2 , ThRu and ThIr , *Nature* 194 465 (1962).
5. A. E. Dwight, J. W. Downey and R. A. Conner, Jr., The Laves Phases ThOs_2 and ThIr_2 , *Trans. Met. Soc. AIME* 212 337 (1958).
6. A. E. Dwight, Factors Controlling the Occurrence of Laves Phases and AB_5 Compounds Among Transition Elements, *Trans. ASM* 53 479 (1961).

THE THORIUM - IRON SYSTEM

The Phase Diagram

The thorium-iron phase diagram shown in Fig. 13 is that of Thomson.¹ Four compounds were identified and characterized. Three of these, Th_7Fe_3 , ThFe_3 and ThFe_5 , melt incongruently at 962° , 1200° and 1212°C , respectively, while $\text{Th}_2\text{Fe}_{17}$ melts congruently at 1462°C . Eutectics are located at 45 at. % iron and 875°C and 94 at. % iron and 1412°C .

Fig. 13.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₇ Fe ₃	Hexagonal	a = 9.823 c = 6.211	2	D1O ₂ Th ₇ Fe ₃	P6 ₃ mc	2, 3
ThFe ₃	Hexagonal	a = 5.18 c = 25.2	9	NbBe ₃	R $\bar{3}$ m	4
	Rhombohedral	a = 8.98 α = 33.8°	3	-	-	
ThFe ₅	Hexagonal	a = 5.13, c = 4.02	1	D2 _d CaZn ₅	P6/mmm	2
Th ₂ Fe ₁₇	Monoclinic	a = 9.68 b = 8.56 c = 6.46 β = 99°20'	2	-	C2/m	2

References

1. J. R. Thomson, Alloys of Thorium with Certain Transition Metals. IV. The Systems Thorium-Iron and Thorium-Cobalt, J. Less-Common Metals 10 432 (1966).
2. J. V. Florio, N. C. Baenziger and R. E. Rundle, Compounds of Thorium with Transition Metals. II. Systems with Iron, Cobalt and Nickel, Acta Cryst. 9 367 (1956).
3. B. T. Matthias, V. B. Compton and E. Corenzwit, Some New Superconducting Compounds, J. Phys. Chem. Solids 19 130 (1961).
4. J. F. Smith and D. A. Hansen, The Structures of YNi₃, YCo₃, ThFe₃ and GdFe₃, Acta Cryst. 19 1019 (1965).

THE THORIUM - LANTHANUM SYSTEM

The Phase Diagram

A diagram has not been proposed for this system. Evans et al.¹ have determined the lattice spacings for the thorium-lanthanum system and conclude that α -thorium and β -lanthanum form a continuous series of solid solutions.

Crystallography

No compounds have been observed in this system.

Reference

1. D. S. Evans, G. V. Raynor and R. T. Weiner, The Lattice Spacings of Thorium-Lanthanum Alloys, J. Nucl. Mater. 2 121 (1960).

THE THORIUM - LEAD SYSTEM

The Phase Diagram

The partial phase diagram for the thorium-lead system shown in Fig. 14 is from the compilation of Rough and Bauer¹ but, in addition, includes the identified compound, ThPb, reported by Brown.² The compound, ThPb₂, has not been confirmed.

Fig. 14.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThPb	Tetragonal	a = 4.545 c = 5.644	4	C _c α -ThSi ₂	I4 ₁ /amd	2
ThPb ₃	Cubic	a = 4.855	1	L ₁ ₂	Pm3m	2
		or a = 4.856		AuCu ₃		3

References

1. F. A. Rough and A. A. Bauer, Constitution of Uranium and Thorium Alloys, USAEC Rept. BMI-1300 (1958).
2. A. Brown, The Crystal Structures of ThPb₃, UPb₃, ThPb and UPb, Acta Cryst. 14 856 (1961).
3. R. Ferro, The Crystal Structures of ThHg₃, ThIn₃, ThTl₃, ThSn₃ and ThPb₃, Acta Cryst. 11 737 (1958).

THE THORIUM - LUTETIUM SYSTEM

The Phase Diagram

Uy and Burr¹ have found that small concentrations of lutetium raise the transformation temperature of thorium attaining a temperature maximum at about 5 at. %.

Crystallography

No compounds have been reported for this system.

References

1. J. C. Uy and A. A. Burr, The Effect of Certain Rare-Earth Solutes upon the F.C.C./B.C.C. Transformation Temperature of Thorium, J. Less-Common Metals 11 149 (1966).

THE THORIUM - MAGNESIUM SYSTEM

The Phase Diagram

Two intermetallic compounds have been observed for this system. Peterson et al.¹ identified a hexagonal Laves phase, ThMg_2 , (MgNi_2 type) which transforms to the cubic form between 700° and 800°C . Peterson and Sundaram² report that this phase decomposes peritectically at 780°C . Based on the d-spacing and intensity data of Yamamoto and Rostoker,³ for the phase " ThMg_5 ", Gladyshevskii et al.⁴ have determined its structure to be cubic $\text{Th}_6\text{Mg}_{23}$, isomorphous with $\text{Th}_6\text{Mn}_{23}$. Peterson et al.⁵ and Peterson and Sundaram² confirmed the latter results and observed that this compound decomposes peritectically at $560^\circ \pm 10^\circ\text{C}$.

Yamamoto and Rostoker located a eutectic at 92.9 at. % magnesium and 582°C and determined the solid solubility of thorium in magnesium at the eutectic temperature to be 0.49 at. % thorium.

A composite phase diagram based on the above information and other published data is presented in Fig. 15.

Fig. 15.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
α -ThMg ₂ (low temp.)	Hexagonal	a = 6.086 c = 19.64	8	C36 MgNi ₂	P6 ₃ /mmc	1
β -ThMg ₂ (high temp.)	Cubic	a = 8.570	8	C15 MgCu ₂	Fd3m	1
Th ₆ Mg ₂₃	Cubic	a = 14.24	4	D8 _a Th ₆ Mn ₂₃	Fm3m	4, 5

References

1. D. T. Peterson, P. F. Diljak and C. L. Vold, The Structure of Thorium-Magnesium Intermetallic Compounds, Acta Cryst. 9 1036 (1956).
2. D. T. Peterson and C. V. Sundaram, Thorium-Magnesium System, USAEC Rept. IS-700, Section M, p. 33 (1963).
3. A. S. Yamamoto and W. Rostoker, Partial Phase Diagram of the Systems Mg-Th and Mg-Th-Zn, Trans. ASM 50 1090 (1958).
4. E. I. Gladyshevskii, P. I. Kripyakevich, Yu. B. Kuz'ma and M. Yu. Teslyuk, New Representatives of Structures of Mg₆Cu₁₆Si₇ and Th₆Mn₂₃ Types, Soviet Phys. - Cryst. 615 (1962).
5. D. T. Peterson, C. V. Sundaram and V. L. Schneider, Thorium-Magnesium Alloy Studies, USAEC Rept. IS-900, Section M, p. 35 (1964).

THE THORIUM - MANGANESE SYSTEM

The Phase Diagram

Three compounds, ThMn_2 , $\text{Th}_6\text{Mn}_{23}$ and ThMn_{12} , have been identified. Wilhelm et al.¹ report a eutectic at 911°C at a composition greater than 20 at. % manganese but a phase diagram has not been proposed.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThMn_2	Hexagonal	$a = 5.476$ $c = 8.931$	4	C14 MgZn_2	$\text{P6}_3/\text{mmc}$	2
$\text{Th}_6\text{Mn}_{23}$	Cubic	$a = 12.523$	4	D8_a $\text{Th}_6\text{Mn}_{23}$	$\text{Fm}3\text{m}$	3
ThMn_{12}	Tetragonal	$a = 8.74$ $c = 4.95$	2	D2_b ThMn_{12}	$\text{I4}/\text{mmm}$	3

References

1. H. A. Wilhelm, A. S. Newton, A. H. Daane and C. Neher, Thorium Metallurgy, CT-3714 (1946).
2. Argonne National Laboratory, Annual Report for 1960, Metallurgy Division, USAEC Rept. ANL-6330, 156 (1960).
3. J. V. Florio, R. E. Rundle and A. I. Snow, Compounds of Thorium with Transition Metals. I. The Thorium-Manganese System, Acta Cryst. 5 449 (1952).

THE THORIUM - MERCURY SYSTEM

The Phase Diagram

Further investigation is needed to clarify some discrepancies in the phase relationships; therefore, no phase diagram is presented in this report. Three compounds with formulas, ThHg, ThHg₂, and ThHg₃, have been identified, but data by Ettmayer¹ and Messing and Dean² do not support the proposed diagram of Domagala et al.³

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThHg	Cubic	a = 4.80	2	-	Fm3m	3, 4
ThHg ₂	Hexagonal	a = 4.82 c = 7.49	1	C32 AlB ₂	P6/mmm	1
ThHg ₃	Hexagonal	a = 3.364 c = 4.907	$\frac{1}{2}$	A ₃ Mg	P6 ₃ /mmc	5, 4

References

1. P. Ettmayer, Contributions to the System Mercury-Thorium, Monatsh. Chem. 96 441 (1965).
2. A. F. Messing and O. C. Dean, Solubilities of Selected Metals in Mercury: Hermex Process, USAEC Rept. ORNL-2871 June (1960).
3. R. F. Domagala, R. P. Elliott and W. Rostoker, The System Mercury-Thorium, Trans. Met. Soc. AIME 212 393 (1958).

4. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys (Pergamon Press, New York, 1967).
5. R. Ferro, The Crystal Structures of ThHg_3 , ThIn_3 , ThTl_3 , ThSn_3 and ThPb_3 , Acta Cryst. 11 737 (1958).

THE THORIUM - MOLYBDENUM SYSTEM

The Phase Diagram

McMasters et al.¹ have proposed the phase diagram presented in Fig. 16. A eutectic occurs at 15.4 at. % molybdenum and 1380°C and a eutectoid at less than 0.24 at. % molybdenum and 1358°C. The terminal solid solubilities are negligible.

Crystallography

No compounds exist in this system.

References

1. O. D. McMasters, P. E. Palmer and W. L. Larsen, Thorium-Molybdenum Phase Diagram, J. Nucl. Mater. 7 151 (1962).

THE THORIUM - NEODYMIUM SYSTEM

The Phase Diagram

Uy and Burr¹ report that neodymium raises the transformation temperature of thorium to a maximum at about 5 at. % neodymium. Kato and Copeland² report that the transformation temperature of thorium

Fig. 16.

is decreased to 1160°C by the addition of 50 at. % neodymium but make no mention of the maximum in the temperature-composition curve.

Kato and O'Hare³ found a continuous decrease in the solidus from the melting point of thorium to that of neodymium indicative of a series of solid solutions across the entire composition range at elevated temperatures.

Crystallography

There are no compounds in the thorium-neodymium system.

References

1. J. C. Uy and A. A. Burr, The Effect of Certain Rare-Earth Solutes upon the F.C.C./B.C.C. Transformation of Thorium, J. Less-Common Metals 11 149 (1966).
2. H. Kato and M. I. Copeland, Thorium Alloys, Report USBM-U-921, p. 15, Albany Metallurgy Research Center (1962).
3. H. Kato and S. A. O'Hare, Thorium Alloy Systems, Report USBM-U-1122, p. 20, Albany Metallurgy Research Center, (1964).

THE THORIUM - NICKEL SYSTEM

The Phase Diagram

The diagram shown in Fig. 17 is essentially that of Horn and Basserman¹ incorporating the later results of Thomson.² Five compounds have been identified in this system; ThNi and ThNi₅ which melt congruently at 1200° and 1530°C, respectively, and the peritectic

Fig. 17.

compounds Th_7Ni_3 , ThNi_2 and $\text{Th}_2\text{Ni}_{17}$. The eutectic temperatures and compositions are fairly well established although Thomson's value for the thorium-rich eutectic is 1062°C as compared to the earlier value of 1000°C . The peritectic horizontal associated with Th_7Ni_3 is also shown as 1112°C , as determined by Thomson rather than 1050°C as was previously reported.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th_7Ni_3	Hexagonal	$a = 9.885$ $c = 6.225$	2	D_{10}^2 Th_7Fe_3	$\text{P6}_3\text{mc}$	3, 4
ThNi	Orthorhombic	$a = 14.51$ $b = 4.31$ $c = 5.73$	8	-	Pnma	3
ThNi_2	Hexagonal	$a = 3.960$ $c = 3.844$	1	C_{32} AlB_2	$\text{P6}/\text{mmm}$	3, 5
ThNi_5	Hexagonal	$a = 4.97$ $c = 4.01$	1	D_{2d} CaZn_5	$\text{P6}/\text{mmm}$	3
$\text{Th}_2\text{Ni}_{17}$	Hexagonal	$a = 8.37$ $c = 8.14$	2	-	$\text{P6}_3/\text{mmc}$	3

References

1. L. Horn and C. Basserman, The System Nickel-Thorium (in German), Z. Metallkunde 39 272 (1948).
2. J. R. Thomson, Melting and Structural Correlations of Some Thorium-Rich Eutectics, J. Nucl. Mater. 15 88 (1965).
3. J. V. Florio, N. C. Baenziger and R. E. Rundle, Compounds of Thorium with Transition Metals. II. Systems with Iron, Cobalt and Nickel, Acta Cryst. 9 367 (1956).

4. B. T. Matthias, V. B. Compton and E. Corenzwit, Some New Superconducting Compounds, J. Phys. Chem. Solids 19 130 (1961).
5. A. Brown, MX_2 Compounds of Thorium and the Polymorphism of Thorium Disilicide, Acta Cryst. 14 860 (1961).

THE THORIUM - NIOBIUM SYSTEM

The Phase Diagram

The diagram presented in Fig. 18 combines the data of Carlson et al.¹ and of Bannister and Thomson.² The former established that the system consists of a single eutectic at 17.8 at. % niobium and 1435°C but merely indicated some lowering of the α - β transformation temperature of thorium by the addition of niobium. The latter investigators observed a significant lowering of this transformation by niobium and postulated the eutectoid reaction at 1367°C incorporated into the diagram. The solubility of niobium in α -thorium is estimated at 1 to 2 at. % at this temperature.

Crystallography

No compounds were found in this system.

References

1. O. N. Carlson, J. M. Dickinson, H. E. Lunt, and H. A. Wilhelm, Thorium-Columbium and Thorium-Titanium Alloy Systems, Trans. AIME 206 132 (1956).

Fig. 18.

2. G. H. Bannister and J. R. Thomson, The Body-Centered Cubic to Face-Centered Cubic Phase Transformation in Thorium and Some Thorium Alloys, British Rept. AERE-R-4428 (1963).

THE THORIUM - NITROGEN SYSTEM

The Phase Diagram

The partial phase diagram shown in Fig. 19 was proposed by Benz et al.¹ The thorium-rich end of the system is characterized by a peritectic at about 8.2 at. % nitrogen and 1605°C. Two compounds, ThN and Th₃N₄, have been unambiguously established, and the structure of a third compound identified as Th₂N₃ has been determined. Benz et al.¹ question the existence of the latter compound since its structure and lattice constants are identical to that of Th₂N₂O. Chiotti² determined the melting point of ThN to be 2630°C.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThN	Cubic	a = 5.144	4	B1 NaCl	Fm3m	2, 3
Th ₂ N ₃	Hexagonal	a = 3.883 c = 6.187	1	D5 ₂ La ₂ O ₃	P3̄ml	4
Th ₃ N ₄	Rhombohedral	a = 9.398 α = 23.78°	1	D7 ₁ Al ₄ C ₃	R3̄m	5

Fig. 19.

References

1. R. Benz, C. G. Hoffman and G. N. Rupert, Some Phase Equilibria in the Thorium-Nitrogen System, J. Am. Chem. Soc. 89 191 (1967).
2. P. Chiotti, Experimental Refractory Bodies of High Melting Nitrides and Uranium Dioxide, J. Am. Ceram. Soc. 35 123 (1952).
3. R. E. Rundle, A New Interpretation of Interstitial Compounds - Metallic Carbides, Nitrides and Oxides of Composition MX, Acta Cryst. 1 180 (1948).
4. W. H. Zachariasen, Crystal Chemical Studies of 5f-Series of Elements. XII. New Compounds Representing Known Structure Types, Acta Cryst. 2 388 (1949).
5. R. Benz and W. H. Zachariasen, Th_3N_4 Crystal Structure and Comparison with $\text{Th}_2\text{N}_2\text{O}$, Acta Cryst. 21 838 (1966).

THE THORIUM - OSMIUM SYSTEM

The Phase Diagram

Thomson¹ proposed the phase diagram of Fig. 20 for this system. There are two compounds, Th_7Os_3 and ThOs_2 , with melting points in excess of 1500°C and a third, designated as ThOs_x , decomposing peritectically also above 1500°C . The composition of the latter is estimated as approximately 40 at. % osmium. Eutectic reactions occur at 13 at. % osmium and 1287°C , 36 at. % osmium and 1487°C , and 85 at. % osmium and greater than 1500°C .

Fig. 20.

There is very little solubility of osmium in thorium at temperatures up to 1000°C.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₇ Os ₃	Hexagonal	a = 10.031 c = 6.296	2	D1O ₂ Th ₇ Fe ₃	P6 ₃ mc	2
		or a = 10.02 c = 6.285				3
ThOs ₂	Cubic	a = 7.7050	8	C15 MgCu ₂	Fd3m	4

References

1. J. R. Thomson, Alloys of Thorium with Certain Transition Metals, II. The Systems Thorium-Osmium, Thorium-Iridium and Thorium-Platinum, J. Less-Common Metals 6 3 (1964).
2. J. R. Thomson, Some New Intermetallic Compounds of Thorium of the Type Th₇X₃, Nature 189 217 (1961).
3. B. T. Matthias, V. B. Compton and E. Corenzwit, Some New Superconducting Compounds, J. Phys. Chem. Solids 19 130 (1961).
4. A. E. Dwight, J. W. Downey and R. A. Conner, Jr., The Laves Phases ThOs₂ and ThIr₂, Trans. Met. Soc. AIME 212 337 (1958).

THE THORIUM - OXYGEN SYSTEM

The Phase Diagram

Very little is known about the thorium-oxygen phase system and no phase diagram has been proposed. It is generally recognized that there is only one compound in the system having the formula ThO_2 and melting at $3300 \pm 100^\circ\text{C}$.¹ Rundle² reported a monoxide having the B1, NaCl - type structure but this has not been verified by other investigators.

Peterson³ has determined the solid solubility of oxygen in thorium to be quite low and gives values in parts per million at three temperatures as $1000^\circ - 35$, $1100^\circ - 52$, $1200^\circ\text{C} - 90$.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThO_2	Cubic	$a = 5.5953$	4	Cl CaF_2	$\text{Fm}\bar{3}\text{m}$	4

References

1. W. A. Lambertson, M. H. Mueller, F. H. Guntzel, Jr., Uranium Oxide Phase Equilibrium Systems, IV, $\text{UO}_2 - \text{ThO}_2$, J. Am. Ceram. Soc. 36 397 (1953).
2. R. E. Rundle, A New Interpretation of Interstitial Compounds - Metallic Carbides, Nitrides and Oxides of Composition MX, Acta Cryst. 1 180 (1948).

3. D. T. Peterson, Thermodynamics and Kinetics of the Deoxidation of Thorium by Calcium, Trans. Met. Soc. AIME 221 924 (1961).
4. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys (Pergamon Press, New York, 1967).

THE THORIUM - PALLADIUM SYSTEM

The Phase Diagram

Thomson¹ has investigated this system in rather complete detail and has proposed the phase diagram presented in Fig. 21. There are three congruently melting compounds in this system, Th_2Pd , " ThPd " and ThPd_3 melting at 1162°C , 1412°C and $>1500^\circ\text{C}$, respectively. Another compound, Th_3Pd_5 decomposes peritectically at 1387°C while a fifth phase, tentatively identified as " Th_3Pd_4 " melts incongruently at 1325°C . At 1000°C ThPd_3 , ThPd_4 and ThPd_x exhibit narrow ranges of homogeneity.

Three eutectic reactions occur, one at 23 at. % palladium and 1112°C , another at 36 at. % palladium and 1137°C , and the third at 62 at. % palladium and 1217°C . There is a minimum in the liquidus and solidus at 88 at. % palladium and 1125°C , indicative of a wide range of solid solubility of thorium in palladium.

Fig. 21.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₂ Pd	Tetragonal	a = 7.330 c = 5.930 or a = 7.308 c = 5.960	4	C16 CuAl ₂	I4/mcm	2 1
"ThPd"	Orthorhombic	a = 7.25 b = 4.57 c = 5.86	-	-	-	1
Th ₃ Pd ₅	Hexagonal	a = 7.149 c = 3.899	1	ThPd ₅	P $\overline{6}$ 2m	3
ThPd ₃	Hexagonal	a = 5.856 c = 9.826	4	DO ₂₄ TiNi ₃	P6 ₃ /mmc	4
ThPd ₄	Cubic	a = 4.110	1	Ll ₂ Cu ₃ Au	Pm3m	5

References

1. J. R. Thomson, Alloys of Thorium with Certain Transition Metals. III. The System Thorium-Palladium, J. Less-Common Metals 6 94 (1964).
2. R. Ferro and R. Capelli, The Phase C16 Type in the Thorium-Palladium Alloy System, Acta Cryst. 14 1095 (1961).
3. J. R. Thomson, The Crystal Structure of Th₃Pd₅ and Th₃Pt₅, Acta Cryst. 16 320 (1963).
4. A. E. Dwight, J. W. Downey and R. A. Conner, Jr., Some AB₃ Compounds of the Transition Metals, Acta Cryst. 14 75 (1961).

5. J. R. Thomson, The Crystal Structure of ThPd_4 , Advan. X-ray Anal. 6 91 (1963).

THE THORIUM - PHOSPHORUS SYSTEM

The Phase Diagram

Early work on this system by Meisel¹ and Strotzer et al.² indicated the existence of two compounds, Th_3P_4 and substoichiometric ThP. According to Meisel, ThP, crystallizing with the NaCl-type structure is always deficient in phosphorus.

Recently, a partial phase diagram has been proposed by Javorsky and Benz,³ as is shown in Fig. 22. A eutectic occurs at $1608 \pm 20^\circ\text{C}$ and about 9.9 at. % phosphorus. The monophosphide melts congruently at 2990°C and is stable over a composition range at elevated temperatures with a minimum phosphorus content of 49.5 at. % at 1600°C and above. Earlier work by Gingerich and Wilson⁴ had indicated that the homogeneity range of the monophosphide, ThP_{1-x} , extends from the $\text{ThP}_{0.55}$ (~ 33.6 at. % phosphorus) to $\text{ThP}_{0.96}$ (~ 49 at. % phosphorus) at 1000°C . This disparity in results was explained by Javorsky and Benz as due either to ThO_2 contamination or incomplete reaction encountered by Gingerich and Wilson in preparation of their specimens.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThP	Cubic	$a = 5.818$	4	B1 NaCl	Fm3m	1
Th_3P_4	Cubic	$a = 8.600$	4	D_{7h}^{32} Th_3P_4	$I\bar{4}3d$	1

Fig. 22.

References

1. K. Meisel, The Structure of Thorium Phosphides, *Z. anorg. allgem. Chem.* 240 300 (1939).
2. E. F. Strotzer, W. Biltz and K. Meisel, Thorium Phosphide, *Z. anorg. allgem. Chem.* 238 69 (1938).
3. C. A. Javorsky and R. Benz, Phase Equilibria in the Thorium-Thorium Monophosphide System, *J. Nucl. Mater.* 23 192 (1967).
4. K. A. Gingerich and D. W. Wilson, Preparation and Properties of Thorium Monophosphide, ThP_{1-x} , and Phase Studies of the Partial System Th-ThP, *Inorg. Chem.* 4 987 (1965).

THE THORIUM - PLATINUM SYSTEM

The Phase Diagram

A phase diagram has been proposed for this system by Thomson¹ as is shown in Fig. 23. It consists of at least three congruently melting compounds, ThPt , Th_3Pt_5 and " ThPt_3 ", adjoined by eutectics at 17, 52, 69 and 90 at. % platinum. There are also the following peritectic compounds: Th_7Pt_3 , " Th_3Pt_4 ", " ThPt_2 ", " ThPt_4 " and " ThPt_5 ." The terminal solid solubility in each component is negligible. The identified compounds include Th_7Pt_3 , ThPt and Th_3Pt .

Fig. 23.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₇ Pt ₃	Hexagonal	a = 10.126 c = 6.346	2	D1O ₂ Th ₇ Fe ₃	P6 ₃ mc	2
ThPt	Orthorhombic	a = 3.900 b = 11.09 c = 4.454	4	B _f CrB	Cmcm	3
Th ₃ Pt ₅	Hexagonal	a = 7.162 c = 3.908	1	Th ₃ Pd ₅	P6 ₂ m	4

References

1. J. R. Thomson, Alloys of Thorium with Certain Transition Metals; II. The Systems Thorium-Osmium, Thorium - Iridium and Thorium-Platinum, J. Less-Common Metals 6 3 (1964).
2. J. R. Thomson, Some New Intermetallic Compounds of Thorium of the Type Th₇X₃, Nature 189 217 (1961).
3. J. R. Thomson, The Crystal Structure of ThPt and Some Related Compounds, Acta Cryst. 15 1308 (1962).
4. J. R. Thomson, The Crystal Structure of Th₃Pd₅ and Th₃Pt₅, Acta Cryst. 16 320 (1963).

THE THORIUM - PLUTONIUM SYSTEM

The Phase Diagram

A composite diagram for the thorium-plutonium system is shown in Fig. 24. The plutonium-rich end is from Schonfeld¹ and the thorium-rich end, including the liquidus, is from Bochvar et al.² The plutonium-rich

Fig. 24.

portion of this diagram is in general agreement with the earlier results of Poole et al.³ The drastic lowering of the transformation temperature of thorium as shown in Fig. 24 has not been confirmed⁴ by investigators at Harwell or Los Alamos and there are discrepancies in the reported solubility limits of plutonium in thorium. There are still unresolved differences in the shape of the thorium-liquidus, the temperatures of the peritectic and eutectic horizontals and of the various phase transformations in plutonium.

Crystallography

Only one compound, tentatively identified as ThPu_2 , occurs in this system. Poole et al.³ indexed it on the basis of an orthorhombic cell with $a = 9.820 \text{ \AA}$, $b = 8.164 \text{ \AA}$ and $c = 6.681 \text{ \AA}$ and preferred the formula $\text{Th}_6\text{Pu}_{13}$.

References

1. F. W. Schoenfeld, Plutonium Phase Diagrams Studied at Los Alamos, in *The Metal Plutonium*, p. 240 (The University of Chicago Press, Chicago, Illinois, 1961).
2. A. A. Bochvar, S. T. Konobeevskii, V. I. Kutaitsev, T. S. Men'shikova and N. T. Chebotarey, Interaction between Plutonium and Other Metals in Connection with their Arrangement in Mendeleev's Periodic Table, *The Soviet Journal of Atomic Energy* 5 1177 (1958).

3. D. M. Poole, G. K. Williamson and J. A. C. Marples, A Preliminary Investigation of the Plutonium-Thorium System, J. Inst. Metals 86 172 (1957-58).
4. F. W. Schonfeld, Plutonium Phase Diagrams Published By The Russians, in The Metal Plutonium, p. 255 (The University of Chicago Press, Chicago, Illinois, 1961).

THE THORIUM - PRASEODYMIUM SYSTEM

The Phase Diagram

Norman et al.¹ determined lattice spacings of thorium-praseodymium alloys and found that the solid solubility exceeds 90 at. % praseodymium in thorium at 900°C.

Preliminary investigations by Kato and Copeland² revealed that additions of praseodymium lowers the transformation temperature and melting point of thorium.

Crystallography

No compounds have been found in this system.

References

1. M. Norman, I. R. Harris and G. V. Raynor, The Lattice Spacings of Thorium-Rich Solid Solutions with Praseodymium, Samarium, Gadolinium and Erbium, J. Less-Common Metals 11 395 (1966).
2. H. Kato and M. I. Copeland, Thorium Alloys, Report USBM-U-921, p. 15, Albany Metallurgy Research Center (1962).

THE THORIUM - RHENIUM SYSTEM

The Phase Diagram

A diagram has not been proposed for this system although one compound, ThRe_2 , has been identified. Niemiec¹ reports finding no solubility in either component.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThRe_2	Hexagonal	$a = 5.498$	4	C14 MgZn ₂	$P6_3/mmc$	1
		$c = 9.116$				
		or				
		$a = 5.492$				2
		$c = 9.097$				

References

1. J. Niemiec, X-ray Analysis of the Rhenium-Thorium System, Bull. acad. polon. sci., Ser. sci., chim. 9 501 (1961).
2. A. E. Dwight, Factors Controlling the Occurrence of Laves Phases and AB_5 Compounds Among Transition Elements, Trans. ASM 53 479 (1961).

THE THORIUM - RHODIUM SYSTEM

The Phase Diagram

The phase diagram shown in Fig. 25 was proposed by Thomson.¹ Four eutectics and seven compounds compose the principal features of the system. Eutectic points have been established at 20 at. % rhodium

Fig. 25.

and 1237°C, 34 at. % rhodium and 1312°C, 64 at. % rhodium and 1425°C and 87 at. % rhodium and 1450°C. The compounds, Th_7Rh_3 , ThRh and ThRh_3 melt congruently at 1362°, >1500° and >1500°C, respectively, while ThRh_2 decomposes peritectically at >1500°C and has a solid state transformation in the temperature range of 1200°-1300°C. The structure of the high temperature modification, β - ThRh_2 , has been determined but the low temperature form is still unknown. Three other compounds, tentatively identified as " Th_3Rh_4 ", " Th_3Rh_5 " and " ThRh_5 ", were detected in this system but their crystal structures have not been determined. They form by peritectic reactions at 1487°, 1450° and >1500°C, respectively.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th_7Rh_3	Hexagonal	$a = 10.031$ $c = 6.287$	2	DlO_2 Th_7Fe_3	$\text{P6}_3\text{mc}$	2
		or $a = 10.028$ $c = 6.293$				3
ThRh	Orthorhombic	$a = 3.866$ $b = 11.24$ $c = 4.220$	4	Bf CrB	Cmcm	4
β - ThRh_2	Hexagonal	$a = 4.629$ $c = 5.849$	2	B8_2 Ni_2In	$\text{P6}_3/\text{mmc}$	1, 5

References

1. J. R. Thomson, Alloys of Thorium with Certain Transition Metals. I. The Systems Thorium - Ruthenium and Thorium-Rhodium, J. Less-Common Metals 5 437 (1963).

2. J. R. Thomson, Some New Intermetallic Compounds of Thorium of the Type Th_7X_3 , *Nature* 189 217 (1961).
3. R. Ferro and G. Rambaldi, The Phase DlO_2 Type in the Thorium-Rhodium System, *Acta Cryst.* 14 1094 (1961).
4. J. R. Thomson, The Crystal Structure of ThPt and Some Related Compounds, *Acta Cryst.* 15 1308 (1962).
5. J. R. Thomson, Crystal Structures of ThRh_2 , ThRu and ThIr , *Nature* 194 465 (1962).

THE THORIUM - RUTHENIUM SYSTEM

The Phase Diagram

Thomson's¹ proposed diagram for the thorium-ruthenium system is shown in Fig. 26. Three compounds, Th_7Ru_3 , ThRu , and ThRu_2 , have been identified and a fourth compound was tentatively designated as " Th_3Ru_2 ". These four compounds melt congruently at temperatures of 1412° , 1462° , $>1500^\circ$ and 1425°C , respectively, and are adjoined by five eutectic reactions.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th_7Ru_3	Hexagonal	a = 9.969 c = 6.302	2	DlO_2 Th_7Fe_3	$\text{P6}_3\text{mc}$	2
ThRu	Orthorhombic	a = 3.878 b = 11.29 c = 4.071	4	B_f CrB	Cmcm	3
ThRu_2	Cubic	a = 7.649	8	Cl5 MgCu_2	Fd3m	4

Fig. 26.

References

1. J. R. Thomson, Alloys of Thorium with Certain Transition Metals, I. The Systems Thorium-Ruthenium and Thorium-Rhodium, J. Less-Common Metals 5 437 (1963).
2. J. R. Thomson, Some New Intermetallic Compounds of Thorium of the Type Th_7X_3 , Nature 189 217 (1961).
3. J. R. Thomson, Crystal Structures of ThRh_2 , ThRu and ThIr , Nature 194 465 (1962).
4. A. E. Dwight, Factors Controlling the Occurrence of Laves Phases and AB_5 Compounds Among Transition Elements, Trans. ASM 53 479 (1961).

THE THORIUM - SAMARIUM SYSTEM

The Phase Diagram

Lattice spacing measurements by Norman et al.¹ indicate that the solid solubility limit of samarium in thorium is between 50-60 at. % at 900°C.

Crystallography

No compounds have been reported for this system.

References

1. M. Norman, I. R. Harris and G. V. Raynor, The Lattice Spacings of Thorium-Rich Solid Solutions with Praseodymium, Samarium, Gadolinium and Erbium, J. Less-Common Metals 11 395 (1966).

THE THORIUM - SELENIUM SYSTEM

The Phase Diagram

D'Eye et al.¹ proposed a tentative diagram for the thorium-selenium system which included five compounds, ThSe, Th₂Se₃, Th₇Se₁₂, ThSe₂ and Th₃Se₇. However, in re-examining this system, Graham and McTaggart² confirmed the presence of ThSe₂ only while attempts to prepare ThSe, Th₇Se₁₂ and Th₂Se₃ were unsuccessful. They suggest that these latter three compounds may be oxygen stabilized which could account for their failure to reproduce them. Graham and McTaggart also identified a new compound which they assigned the formula ThSe_{2.5}.

In view of the ambiguities in the information thus far available, a phase diagram has not been presented for this system.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThSe ₂	Orthorhombic	a = 4.435 b = 7.629 c = 9.085	4	C23 PbCl ₂	Pmnb	2, 3
ThSe _{2.5}	Tetragonal	a = 5.629 c = 10.764	4	ThSe _{2.5}	P4 ₂ /n or P4 ₂ /nmc	2

References

1. R. W. M. D'Eye, P. G. Sellman and J. R. Murray, The Thorium-Selenium System, J. Chem. Soc. 2555 (1952).

2. J. Graham and F. K. McTaggart, Observations on the Systems Th-S, Th-Se and Th-Te, Aust. J. Chem. 13 67 (1960).
3. R. W. M. D'Eye, The Crystal Structures of ThSe_2 and $\text{Th}_7\text{Se}_{12}$, J. Chem. Soc. 1670 (1953).

THE THORIUM - SILICON SYSTEM

The Phase Diagram

The phase diagram proposed by Brown and Norreys¹ for this system is presented in Fig. 27. There are six compounds represented in the diagram, five of which have been fairly well established by x-ray diffraction data. These compounds are a congruently melting phase ThSi and four peritectic compounds, Th_3Si_2 , Th_3Si_5 , $\text{Th}_6\text{Si}_{11}$ and ThSi_2 .

The nomenclature of Brown and Norreys¹ has been preserved in illustrating the high temperature alpha forms and low temperature beta forms of the compounds $\text{Th}_6\text{Si}_{11}$ and ThSi_2 . Another phase, X, has been suggested to eutectoidally decompose to $\alpha\text{-Th}_6\text{Si}_{11}$ and $\alpha\text{-ThSi}_2$. Eutectics are located at 10 at. % silicon and about 1350°-1400°C and 82 at. % silicon and 1350°C.

Stecher et al.² have presented data that differs from this diagram in several respects such as the polymorphism of ThSi_2 , the number of compounds and other general features of the system. It is apparent that additional work is needed in order to resolve some of the areas of disagreement.

Fig. 27.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th_3Si_2	Tetragonal	a = 7.835 c = 4.154	2	U_3Si_2	P4/mbm	3
ThSi	Orthorhombic	a = 5.896 b = 7.88 c = 4.148	4	B27 FeB	Pbnm	2, 3
Th_3Si_5	Hexagonal	a = 3.985 c = 4.228	1	C32 AlB_2	P6/mmm	4, 5
$\beta\text{-Th}_6\text{Si}_{11}$ (low temp.)	Hexagonal	a = 4.013 c = 4.258	1	C32 AlB_2	P6/mmm	1
$\alpha\text{-Th}_6\text{Si}_{11}$ (high temp.)	Tetragonal	a = 4.01 c = 13.89	-	-	I4/amd	1
$\beta\text{-ThSi}_2$ (low temp.)	Hexagonal	a = 4.136 c = 4.126	1	C32 AlB_2	P6/mmm	4, 5
$\alpha\text{-ThSi}_2$ (high temp.)	Tetragonal	a = 4.135 c = 14.375	4	C_c ThSi_2	I4/amd	5

References

1. A. Brown and J. J. Norreys, The System Thorium-Silicon, J. Inst. Metals 89 238 (1960-61).
2. P. Stecher, F. Benesovsky and H. Nowotny, A Contribution to the Ternary System: Thorium-Silicon - Germanium (in German), Monatsh. Chem. 94 549 (1963).
3. E. L. Jacobson, R. D. Freeman, A. G. Tharp and A. W. Searcy, Preparation, Identification and Chemical Properties of the Thorium Silicides, J. Am. Chem. Soc. 78 4850 (1956).

4. A. Brown and J. J. Norreys, Beta-Polymorphs of Uranium and Thorium Disilicides, *Nature* 183 673 (1959).
5. A. Brown, MX_2 Compounds of Thorium and the Polymorphism of Thorium Disilicide, *Acta Cryst.* 14 860 (1961).

THE THORIUM - SILVER SYSTEM

The Phase Diagram

Raub and Engel¹ studied the silver-rich end of the system and proposed a partial phase diagram showing the compounds Th_3Ag_5 and $ThAg_3$, although the crystal structures of these compounds were not reported; Brown² has shown that the phase, Th_3Ag_5 , actually corresponds to $ThAg_2$, the structure of which was determined.

Recently, Thomson³ observed a eutectic between thorium and a third compound, Th_2Ag , at 30 at. % silver and 1012°C. At the eutectic temperature the solubility of silver in thorium is much less than 2 at. %. The work of these various investigators has been incorporated into the phase diagram of Fig. 28.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th_2Ag	Tetragonal	a = 7.56 c = 5.84	4	C16 $CuAl_2$	I4/mcm	4
$ThAg_2$	Hexagonal	a = 4.837 c = 3.353	1	C32 AlB_2	P6/mmm	2

Fig. 28.

References

1. E. Raub and M. Engel, Alloys of Thorium with Copper, Silver and Gold, Z. Electrochem. 49 487 (1943).
2. A. Brown, MX_2 Compounds of Thorium and the Polymorphism of Thorium Disilicide, Acta Cryst. 14 860 (1961).
3. J. R. Thomson, Melting and Structural Correlation of Some Thorium-Rich Eutectics, J. Nucl. Mater. 15 88 (1965).
4. J. R. Murray, The Crystal Structure of Some Thorium Compounds, J. Inst. Metals 84 91 (1955-56).

THE THORIUM - SODIUM SYSTEM

The Phase Diagram

A partial diagram showing the presence of an intermetallic compound, ThNa_4 , has been reported by Grube and Botzenhardt.¹ According to the compilation of Rough and Bauer,² however, this work has been disputed.

Crystallography

The presence of compounds in this system is not well established.

References

1. G. Grube and L. Botzenhardt, Alloys of Thorium with Copper, Aluminum and Sodium (in German), Z. Elektrochemie 48 418 (1942).
2. F. A. Rough and A. A. Bauer, Constitution of Uranium and Thorium Alloys, USAEC Rept. BMI-1300 (1958).

THE THORIUM - SULFUR SYSTEM

The Phase Diagram

The disagreement among the early work of Zachariasen,^{1, 2} Eastman et al.³ and Strotzer and Zumbusch⁴ prompted Graham and McTaggart⁵ to reinvestigate the thorium-sulfur system. They confirmed the existence of ThS_2 and found a new phase, $\text{ThS}_{2.5}$. Unsuccessful attempts to form Th_7S_{12} , Th_2S_3 and ThS reported by the previous investigators were attributed to the absence of oxygen in the alloys which may have had a stabilizing effect on the formation of these three phases. Additional work on the phase equilibria of this system is needed before a phase diagram can be presented.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThS_2	Orthorhombic	a = 4.283 b = 7.275 c = 8.617	4	C23 PbCl ₂	Pmnb	2, 5
$\text{ThS}_{2.5}$	Tetragonal	a = 5.43 c = 10.15	4	-	P4 ₂ /n or P4 ₂ /nmc	5

References

1. W. H. Zachariasen, Crystal Chemical Studies of the 5f-Series of Elements. IX. The Crystal Structure of Th_7S_{12} , Acta Cryst. 2 288 (1949).

2. W. H. Zachariasen, Crystal Chemical Studies of the 5f-Series of Elements. X. Sulfides and Oxy-Sulfides, *Acta Cryst.* 2 291 (1949).
3. E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, Preparation and Properties of the Sulfides of Thorium and Uranium, *J. Am. Chem. Soc.* 72 4019 (1950).
4. E. F. Strotzer and M. Zumbusch, Thorium-Sulfide, *Z. anorg. allgem. Chem.* 247 415 (1941).
5. J. Graham and F. K. McTaggart, Observations on the Systems Th-S, Th-Se and Th-Te; *Aust. J. Chem.* 13 67 (1960).

THE THORIUM - TANTALUM SYSTEM

The Phase Diagram

A phase diagram for the thorium-tantalum system is of the simple eutectic type as shown in Fig. 29. McMasters and Larsen¹ reported a eutectic at 5.1 at. % tantalum and 1565°C with a eutectoid (see inset) at approximately 1338°C. The terminal solid solubilities are quite limited and are estimated as less than 0.26 at. % thorium and 0.52 at. % tantalum at the eutectic temperature.

Crystallography

There is no evidence of compounds in this system.

References

1. O. D. McMasters and W. L. Larsen, Phase Equilibria in the Thorium-Tantalum System, *J. Less-Common Metals* 3 312 (1961).

Fig. 29.

THE THORIUM - TECHNETIUM SYSTEM

The Phase Diagram

While a phase diagram has not been proposed for this system, Darby et al.¹ have identified one compound, ThTc_2 .

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThTc_2	Hexagonal	a = 5.394 c = 9.222	4	C14 MgZn ₂	P6 ₃ /mmc	1

References

1. J. B. Darby, Jr., A. F. Berndt and J. W. Downey, Some Intermediate Phases in the Thorium-Techneium and Uranium-Techneium Systems, J. Less-Common Metals 9 466 (1965).

THE THORIUM - TELLURIUM SYSTEM

The Phase Diagram

Like the other thorium-chalcogenide systems, the thorium-tellurium system needs more study before a phase diagram can be presented. Graham and McTaggart¹ have investigated this system and identified three compounds, Th_2Te_3 , ThTe_2 and ThTe_3 . High purity thorium was used in this work and care was taken to avoid contamination of the reacted materials. Deliberate addition of oxygen yielded a phase with the monotelluride structure previously reported by D'Eye and Sellman.²

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₂ Te ₃	Hexagonal	a = 12.49 c = 4.354	-	-	-	1
ThTe ₂	Hexagonal	a = 8.49 c = 9.01	-	-	-	1
ThTe ₃	Monoclinic	a = 6.14 b = 4.31 c = 10.44 $\beta = 98.4^\circ$	-	-	-	1

References

1. J. Graham and F. K. McTaggart, Observations on the Systems Th-S, Th-Se and Th-Te, Aust. J. Chem. 13 67 (1960).
2. R. W. M. D'Eye and P. G. Sellman, The Thorium-Tellurium System, J. Chem. Soc. 3760 (1954).

THE THORIUM - THALLIUM SYSTEM

The Phase Diagram

The solubility data for thorium in liquid thallium at different temperatures reported by Hayes and Gordon¹ is summarized below:

<u>Temp. °C</u>	<u>Solubility</u>	
	<u>wt % Th</u>	<u>at. % Th</u>
900	0.33	0.29
800	0.27	0.24
450	< 0.05	< 0.04

Ferro² reports evidence of an intermetallic compound, ThTl_3 , but no details are given on the phase system.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThTl_3	Cubic	$a = 4.748$	1	Ll_2 AuCu_3	Pm3m	2

References

1. E. E. Hayes and P. Gordon, The Solubility of Uranium and Thorium in Liquid Metals and Alloys, USAEC Rept. TID-2501-Del., p. 115 (1957).
2. R. Ferro, The Crystal Structures of ThHg_3 , ThIn_3 , ThTl_3 , ThSn_3 and ThPb_3 , Acta Cryst. 11 737 (1958).

THE THORIUM - TIN SYSTEM

The Phase Diagram

Hayes and Gordon¹ have reported the solubility of thorium in liquid tin as follows:

<u>Temp. °C.</u>	<u>Solubility</u>	
	<u>wt % Th</u>	<u>at. % Th</u>
600	< 0.05	< 0.03
700	0.2	0.1
800	1.9	1.4
900	4.3	2.2

Ferro² has identified an intermetallic compound, ThSn_3 , but a phase diagram has not been proposed.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
ThSn_3	Cubic	$a = 4.718$	1	Ll_2 AuCu_3	$\text{Pm}3\text{m}$	2

References

1. E. E. Hayes and P. Gordon, The Solubility of Uranium and Thorium in Liquid Metals and Alloys, USAEC Rept. TID-2501-Del., p. 115 (1957).
2. R. Ferro, The Crystal Structures of ThHg_3 , ThIn_3 , ThTl_3 , ThSn_3 and ThPb_3 , Acta Cryst. 11 737 (1958).

THE THORIUM - TITANIUM SYSTEM

The Phase Diagram

The thorium-titanium phase diagram of Carlson et al.¹ is shown in Fig. 30. The system consists of a single eutectic, with limited terminal solid solubility and no compounds. The eutectic lies at 12 at. % titanium and 1190°C . The transformation temperatures are relatively unaffected by the addition of the other component.

Crystallography

No compounds are present in the thorium-titanium system.

Fig. 30.

References

1. O. N. Carlson, J. M. Dickinson, H. E. Lunt and H. A. Wilhelm, Thorium-Columbium and Thorium-Titanium Alloy Systems, Trans. AIME 206 132 (1956).

THE THORIUM - TUNGSTEN SYSTEM

The Phase Diagram

The diagram in Fig. 31 is taken from the compilation of Rough and Bauer.¹ A eutectic point at about 8 at. % tungsten and 1380°C is indicated in contrast to an earlier value of 1475°C reported by Wilhelm et al.²

Crystallography

No compounds occur in the thorium-tungsten system.

References

1. F. A. Rough and A. A. Bauer, Constitution of Uranium and Thorium Alloys, USAEC Rept. BMI-1300 (1958).
2. H. A. Wilhelm, A. S. Newton, A. H. Daane and C. Neher, Thorium Metallurgy, CT-3714 (1946).

THE THORIUM - URANIUM SYSTEM

The Phase Diagram

The contributions of various investigators are incorporated in the diagram shown in Fig. 32. The main features are those of Carlson¹ who first proposed a diagram for this system. It consists of a liquid

Fig. 31.

Fig. 32.

immiscibility loop and an uranium-rich eutectic at 1086°C. Murray² established the region of immiscibility extending from 51 to 94 at. % uranium at the monotectic temperature. Bentle³ observed extensive terminal solid solubility in thorium at elevated temperature and proposed the inverse peritectic reaction associated with the transformation in thorium. The thorium solvus data of Bentle and of Wilson et al.⁴ are included in the diagram.

Cryatallography

There are no compounds in this system.

References

1. O. N. Carlson, Some Studies on the Uranium-Thorium-Zirconium Ternary Alloy System, USAEC Rept. ISC-102 (1950).
2. J. R. Murray, The Uranium-Thorium System and Some Aspects of the Uranium-Thorium-Zirconium System, J. Inst. Metals 87 94 (1958).
3. G. G. Bentle, A Physical Metallurgical Study of Thorium-Rich, Thorium-Uranium Alloys, USAEC Rept. NAA-SR-2069 (1958).
4. W. B. Wilson, A. E. Austin and C. M. Schwartz, Solid Solubility of Uranium in Thorium and the Allotropic Transformation of Th-U Alloys, Trans. Met. Soc. AIME 212 52 (1958).

THE THORIUM - VANADIUM SYSTEM

The Phase Diagram

The thorium-vanadium phase diagram shown in Fig. 33 was determined by Palmer et al.¹ The system is characterized by a eutectic at 19.3 at. % vanadium and 1435°C and a eutectoid at 0.15 at. % vanadium and 1345°C (see inset). The maximum solubility of thorium in vanadium at 1390°C is 0.1 at. %.

Crystallography

There are no compounds in this system.

References

1. P. E. Palmer, O. D. McMasters and W. L. Larsen, Thorium-Vanadium Phase Diagram, Trans. Quart. ASM 55 301, (1962).

THE THORIUM - YTTERBIUM SYSTEM

The Phase Diagram

The thorium-ytterbium system has been examined by Evans and Raynor.¹ The pure metals are essentially immiscible in the liquid state even at the melting point of thorium. Changes in the lattice parameters of a specimen annealed at 660°C indicate that the limits of terminal solid solubility are 0.4 at. % ytterbium in thorium and 0.25 at. % thorium in ytterbium. Gschneidner² pointed out that the experimental observations of Evans and Raynor are consistent with predictions.

Fig. 33.

Crystallography

No compounds are found in the thorium-ytterbium system.

References

1. D. S. Evans and G. V. Raynor, The System Thorium-Ytterbium: Its Alloy Properties, J. Less-Common Metals 3 179 (1961).
2. K. A. Gschneidner, Some Comments on the Ytterbium-Thorium System, J. Less-Common Metals 4 107 (1962).

THE THORIUM - YTTRIUM SYSTEM

The Phase Diagram

Eash and Carlson's¹ phase diagram for the thorium-yttrium system is shown in Fig. 34. A continuous series of solid solutions exists between the high temperature modifications of thorium and yttrium. The β -phase decomposes by a eutectoid reaction at 46.5 at. % yttrium and 1375°C. Additions of yttrium effect a maximum in the α to β transformation at 14.3 at. % yttrium and 1435°C. Evans and Raynor² place the boundaries of the two phase region between the cubic and hexagonal solid solutions at 49 and 69 at. % yttrium at 750°C and ascribe this discrepancy in results to differences in metal purity.

Crystallography

There is an absence of compounds in the thorium-yttrium system.

Fig. 34.

References

1. D. T. Eash and O. N. Carlson, Investigation of the Thorium-Yttrium System, Trans. ASM 52 1097 (1960).
2. D. S. Evans and G. V. Raynor, Lattice Spacings in Thorium-Yttrium Alloys, J. Nucl. Mater. 2 209 (1960).

THE THORIUM - ZINC SYSTEM

The Phase Diagram

Chiotti and Gill¹ have established the diagram shown in Fig. 35. The system is characterized by four congruently melting compounds, adjoined by eutectics. The solubility of thorium in zinc decreases from 3.41 at. % at 900°C to 0.0007 at. % at 419°C and has been shown to follow the relation, $\log (\text{at. \% Th}) = -6230/T + 5.850$.

Crystallography

Compound	Crystal lattice	Unit cell dimensions, Å	Z	Type	Space group	Ref.
Th ₂ Zn	Tetragonal	a = 7.60 c = 5.64	4	C16 Al ₂ Cu	I4/mcm	2
ThZn ₂ *	Hexagonal	a = 4.497 c = 3.718	1	C32 AlB ₂	P6/mmm	3
ThZn ₄	Tetragonal	a = 4.273 c = 10.359	2	D1 ₃ BaAl ₄	I4/mmm	1, 5
Th ₂ Zn ₁₇	Hexagonal	a = 9.03 c = 13.20	3	-	R $\bar{3}$ m	6

* May also exist as CeCu₂-type structure.⁴

Fig. 35.

References

1. P. Chiotti and K. J. Gill, Phase Diagram and Thermodynamic Properties of the Thorium-Zinc System, Trans. Met. Soc. AIME 221 573 (1961).
2. N. C. Baenziger, R. E. Rundle and A. I. Snow, Structures of the Compounds Th_2Cu , ThCu_2 , Th_2Zn and ThHg_3 , Acta Cryst. 2 93 (1956).
3. A Brown, MX_2 Compounds of Thorium and the Polymorphism of Thorium Disilicide, Acta Cryst. 14 860 (1961).
4. E. R. Ryba and M. E. Bell, Fundamental Studies in High Temperature Materials Phenomena. Scope III. Transformation in AB_2 Intermetallic Compounds, USAEC Rept., TID-18412 (1963).
5. E. S. Makarov and L. S. Gudkov, X-ray Diffraction Study of Thorium-Zinc Alloys, Soviet Phys. -Cryst. 1 511 (1956).
6. E. S. Makarov and S. I. Vinogradov, Crystal Structure of the $\text{Th}_2\text{Zn}_{17}$ and U_2Zn_{17} , Soviet Phys. -Cryst. 1 499 (1956).

THE THORIUM - ZIRCONIUM SYSTEM

The Phase Diagram

The phase diagram for the thorium-zirconium system proposed by Gibson et al.¹ is shown in Fig. 36. The thorium-rich portion of this system has been investigated extensively by others also and, while there is general agreement about the main features of the diagram, there are differences in some of the details. The results of the various investigations are summarized in the table below.

Fig. 36.

SUMMARY OF RESULTS OF DIFFERENT INVESTIGATIONS ON Th-Zr

<u>Region of diagram</u>	<u>SYSTEM</u>		
	<u>Gibson et al.¹</u>	<u>Murray²</u>	<u>Badaeva and Alekseenko³</u>
Minimum in liquidus - solidus	45.9 at. % Zr and 1350°C	46 at. % Zr and 1290°C	-
Monotectoid	45.9 at. % Zr and 910°C	46 at. % Zr and 917.5°C	40 at. % Zr and 920°C
Maximum of immiscibility loop	~ 52.2 at. % Zr and ~ 955°C	52.5 at. % Zr and 950°C	54 at. % Zr and 945°C
Extent of immiscibility gap at monotectoid temperature	45.9-59.9 at. % Zr	46-58 at. % Zr	40-69.5 at. % Zr
Eutectoid	85 at. % Zr and 650°C	~ 88 at. % Zr and 650°C	86 at. % Zr and 650°C

Another point of disagreement is the thorium-rich solvus which Johnson and Honeycombe⁴ and Evans and Raynor⁵ place at 9.9 at. % zirconium at 920°C decreasing to about 5.0 at. % at 650°C. Gibson's solvus boundary lies at much higher zirconium concentration as is seen from the diagram, a position which is supported by the data of Badaeva and Alekscenko.³

Crystallography

No compounds occur in this system.

References

1. E. D. Gibson, B. A. Loomis and O. N. Carlson, Thorium-Zirconium and Thorium-Hafnium Alloy Systems, Trans. ASM 50 348 (1958).

2. J. R. Murray, The Constitution of Thorium-Zirconium Alloys Containing more than 15 at. % Zirconium and the Effect of Some Third Elements on the Stability of the Body-Centered Cubic Phase in these Alloys, J. Less-Common Metals 2 1 (1960).
3. T. A. Badaeva and G. K. Aleksoenko, Phase Diagram of the Thorium-Zirconium System, USAEC Translation AEC-tr-5834, p. 348 (1963).
4. R. H. Johnson and R. W. K. Honeycombe, The Solid Solubility of Zirconium in α -Thorium, J. Nucl. Mater. 4 59 (1961).
5. D. S. Evans and G. V. Raynor, The Solubility of Zirconium in α -Thorium, J. Nucl. Mater. 4 66 (1961).

SUMMARY

As of the date of this compilation some information was found on the phase relationships for all but a few of the possible binary systems of thorium. In summarizing this information the authors have divided the systems, perhaps somewhat arbitrarily into the four categories listed below:

1. Completed Systems

In an absolute sense of course no alloy system is really ever complete, but from an analysis of the data available approximately one-third of the systems of thorium are well enough established that additional work does not appear to be warranted at this time. Predominant in this category are those systems having possible reactor interest such as Th-U, Th-Be, Th-Zr, Th-Hf, Th-C, Th-Al, Th-Mg, Th-Zn and Th-Pu. Likewise those systems involving the groups VA and VIA elements which form simple eutectic systems with thorium and the transition metals iron, cobalt and nickel are rather well established as are the Th-Y and Th-Ti systems.

2. Nearly Completed Systems

This group includes a number of systems on which a considerable amount of work has been done and the general features of the diagrams are fairly well established. However, there are either conflicting results that still need to be resolved or regions of the diagram that are still somewhat tentative in nature. Included are the Th-Ag, Th-Au and Th-Cu systems about which some uncertainty exists over the middle

composition ranges. Some excellent work has been done on the difficult Th-N and Th-P systems for the thorium-rich end of the diagrams. The analogous systems of Th-Ge and Th-Si have also been investigated quite extensively but still have need for additional work particularly on the identity and structure of the compounds. The Th-Ce system has also been studied in considerable detail but uncertainty still exists over the equilibrium between the high temperature phases. The compounds and phase reactions for all of the platinum group elements have been determined to an impressive degree thanks to the efforts of J. R. Thomson of Harwell. The only regions of uncertainty in any of these systems occur at the higher temperatures.

3. Systems For Which Limited Data Are Available

Rather complete crystallographic data are available on the compounds of thorium with As, Bi, B, Cd, Ga, H, Hg, In, Pb, Mn, Na, O, Re, S, Sb, Se, Sn, Tc, Te and Tl. However, information related to the phase relationships for these systems is quite limited and tentative. The binary systems of thorium with many of the rare earth metals have been studied in a rather cursory manner. They all appear to form extensive or complete solid solutions with thorium but, with the possible exception of holmium, do not form intermetallic compounds.

4. Systems For Which No Data Are Available

As far as the authors have been able to ascertain no work has been reported for the systems of thorium with most of the alkali and alkaline earth metals, specifically Li, K, Rb, Cs, Ca, Sr and Ba.

Likewise among the rare earth group of elements no data are available for the systems with Dy, Eu, Pm, Sc, Tb and Tm.

A cursory survey of the literature indicated that some work has been done on a few ternary systems such as Th-U-Zr, Th-U-Pu, Th-U-Al, Th-Ce-Al, Th-Si-Ge and Th-Mg-Zn; however the paucity of information available led to the decision to limit this compilation to two component systems.