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A THERMODYNAMIC STUDY OF PHASE STABILITY IN THE TRANSITION-METAL RICH PHASES OF THE THORIUM-IRON, THORIUM-COBALT, AND THORIUM-NICKEL SYSTEMS AND THE COPPER RICH PHASES OF THE THORIUM-COPPER SYSTEMS

by

Nicholas J. Magnani

Ph.D. Thesis, November 1968

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ABSTRACT

Solid electrolyte electromotive force cells have been used to determine the free energies, entropies and enthalpies of formation of several thorium-poor phases in the binary systems of thorium with iron, cobalt, nickel and copper. These phases were $\text{Th}_2\text{Fe}_{17}$, $\text{Th}_2\text{Co}_{17}$, ThCo_5 , $\text{Th}_2\text{Ni}_{17}$, ThNi_5 , ThNi_2 and ThCu_4 . The electrolyte which was used in the cells was CaF_2 which is an ionic conductor over the temperature range of the measurements (600-850°C) and over the range of partial pressures of fluorine encountered in this investigation. The cells were of the type:

where M equals iron, cobalt, nickel and copper for Equation 1, cobalt and nickel for Equation 2, and nickel for Equation 3. The data indicate a decreasing stability of equivalent intermediate phases in the Th-M systems from nickel to cobalt to iron. The data also suggest there is a correlation between crystallographic data and thermodynamic data for these phases and that interactions between thorium and the nearest neighbor transition metals are the dominant interactions stabilizing these phases.

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INTRODUCTION

The purpose of this investigation was to determine the free energies, entropies, and enthalpies of formation of several intermediate phases in the thorium-poor regions in binary systems of thorium with iron, cobalt, nickel and copper. The limitation to the thorium-poor regions was due to the chemical reactivity of the more thorium-rich phases preventing the attainment of equilibrium in the more thorium-rich alloys.

This group of systems was chosen because of the crystallographic relationships both among the phases within a particular system and among the phases in adjacent systems. These relationships may make it possible to interpret the thermodynamic data in terms of the crystallographic nature of the intermediate phases. In addition to the foregoing basic consideration there is also interest in thorium alloys in connection with potential application in nuclear reactor technology. In particular, the thermodynamics of formation of thorium compounds can be useful in the design of nuclear fuel reprocessing methods and in helping one understand interactions between fuel elements and their protective claddings.

LITERATURE REVIEW

Phase Relations

The thorium-iron and thorium-cobalt phase diagrams as proposed by Thomson (1) are shown in Figures 1 and 2. The thorium-nickel phase diagram in Figure 3 and the thorium-copper phase diagram in Figure 4 are reproduced from the compilations of Hansen (2) and Elliot (3) respectively. The phase diagrams show that the solid solubility ranges are sufficiently small so that their effects on the evaluation of the thermodynamic functions can be neglected within the experimental precision of the present technique. Justification of the neglect of the effect can be made in the following way. With regard to terminal solubilities, available data for the systems are shown in Table 1. These data were used with a Raoult's law approximation to calculate $\Delta F^{\circ}(\text{ThMx})$ for the equilibrium reaction

where M = iron, cobalt, nickel or copper. The evaluation of $\Delta F^{\circ}(\text{ThMx})$ was also made by assuming unit activity for M(solid solution) in Equation 1. In all of the systems the difference between $\Delta F^{\circ}(\text{ThMx})$ that was obtained by using unit activity and by using a Raoult's law activity was negligible within the

Figure 1. The thorium-iron phase diagram

Figure 2. The thorium-cobalt phase diagram

Figure 3. The thorium-nickel phase diagram

Figure 4. The thorium-copper phase diagram

experimental precision of the measurements.

Table 1. Terminal solubilities of thorium in iron, cobalt, nickel and copper

	Terminal solubility (at%)	Temperature (°C)	References ^a
Iron	<2	1400	1
Cobalt	<2	1375	1
Nickel	<0.003	298	4
	<0.02	1000	4
Copper	~2	940	3

^aNumbers refer to the references in Bibliography.

With regard to solubilities in the intermediate phases, the only phase to have more than a very narrow solubility range is ThCo₅. This phase is stable over the composition range 83.5 to 85.0 at.% cobalt at 1100°C (1). This composition range is expected to be narrower at 700°C which is approximately the midpoint of the temperature range in which the data were taken. Because the composition range in which ThCo₅ is stable is quite narrow the error introduced in the determination of $\Delta F^\circ(\text{ThCo}_5)$ is again negligible, within the experimental precision of the measurements, if unit activity is assumed for ThCo₅.

Crystallography

Since one of the goals of this investigation was to interpret thermodynamic data in terms of the crystallography of intermediate phases, a discussion of the crystallography of the phases and of the relations among the structures is pertinent. The crystal systems, lattice parameters and crystal structures for the intermediate phases in the binary systems of thorium with manganese through zinc (atomic numbers 25-30) are shown in Table 2. The thorium-manganese and thorium-zinc systems are included in addition to the binary systems of thorium with iron, cobalt, nickel and copper because of the similarities in the crystallographic structures which occur in all of the systems and because of the relevance of the phases in the thorium-manganese and thorium-zinc systems to the establishment of systematic trends with either decreasing or increasing atomic number.

Rudman (5) has shown the relation between the elemental structures and the Laves phases. He has obtained the atomic array of the Laves phases (AB_2) by starting with close packed atomic layers of B atoms in an array analogous to the elemental structures. He has then substituted one A atom for two out of every four B atoms on selected crystallographic sites.

Table 2. Crystal systems, lattice parameters and crystal structures which have been reported for binary alloys of thorium with manganese, iron, cobalt, nickel, copper and zinc

Compound	Crystal system	Lattice parameters (Å)	Crystal structure	References ^a
ThMn ₁₂	Tetragonal	a=8.74±0.01 c=4.95±0.01	ThMn ₁₂	6
Th ₂ Fe ₁₇	Hexagonal	a=8.565±0.002 c=12.469±0.003	Th ₂ Zn ₁₇	7,8
Th ₂ Co ₁₇	Hexagonal	a=8.438±0.005 c=12.254±0.008	Th ₂ Zn ₁₇	7,8
Th ₂ Ni ₁₇	Hexagonal	a=8.37 c=8.14	Th ₂ Ni ₁₇	8
Th ₂ Zn ₁₇	Hexagonal	a=9.03 c=13.20	Th ₂ Zn ₁₇	9
ThFe ₅	Hexagonal	a=5.120±0.002 c=4.05±0.002	CaCu ₅	1,8
ThCo ₅	Hexagonal	a=4.956±0.002 c=4.029±0.002	CaCu ₅	1,8
ThNi ₅	Hexagonal	a=4.97 c=4.01	CaCu ₅	8
ThCu ₄	Structure unknown			
ThZn ₄	Tetragonal	a=4.273 c=10.359	BaAl ₄	10
Th ₆ Mn ₂₃	Cubic	a=12.523±0.001	Th ₆ Mn ₂₃	6
ThFe ₃	Hexagonal	a=5.207±0.003 c=25.18±0.02	NbBe ₃	1,8,11

^aNumbers refer to the references in the Bibliography. Cell parameters are those of the first listed reference.

Table 2. (Continued)

Compound	Crystal system	Lattice parameters (Å)	Crystal structure	References ^a
ThCo ₃	Hexagonal	a=5.038±0.002 c=24.64 ± 0.02	NbBe ₃	1,8
ThMn ₂	Hexagonal	a=5.476 c=8.931	MgZn ₂	12,6
ThNi ₂	Hexagonal	a=3.960±0.003 c=3.844±0.004	AlB ₂	13,8
ThCu ₂	Hexagonal	a=4.387±0.001 c=3.472±0.001	AlB ₂	13,14,15
ThZn ₂	Hexagonal	a=4.497±0.002 c=3.718±0.002	AlB ₂	12,13
ThCo	Ortho-rhombic	a=3.776±0.002 b=10.877±0.005 c=4.153±0.002	CrB	1,8,16
ThNi	Ortho-rhombic	a=14.15 b=4.31 c=5.73	ThNi	8
Th ₂ Cu	Tetragonal	a=7.28 c=5.74	Al ₂ Cu	14,15
Th ₂ Zn	Tetragonal	a=7.60 c=5.64	Al ₂ Cu	14
Th ₇ Fe ₃	Hexagonal	a=9.830±0.003 c=6.214±0.002	Th ₇ Fe ₃	1,8
Th ₇ Co ₃	Hexagonal	a=9.842±0.003 c=6.207±0.002	Th ₇ Fe ₃	1,8
Th ₇ Ni ₃	Hexagonal	a=8.37 c=8.14	Th ₇ Fe ₃	8

This leads to an ideal size ratio of $2V_B/V_A = 1$ which when converted to a radius ratio becomes 1.26. This is very close to the ideal radius ratio of 1.23 which has been derived by Laves (17) from crystallographic contact distances which occur in these phases.

The ThFe_5 , ThCo_5 and ThNi_5 phases were found by Florio, Baenziger and Rundle (8) to crystallize with CaCu_5 structures. Dwight (18) has shown that the CaCu_5 and UNi_5 (AB_5) structures are related to the MgZn_2 and MgCu_2 (AB_2) Laves phases respectively. One can visualize the CaCu_5 structure as being obtained from the MgZn_2 structure by a substitution of B atoms for A atoms on certain sites with a translation of the same sites a short distance along the c-axis. In comparison, the UNi_5 structure could be obtained from the MgCu_2 structure by the substitution of B atoms for A atoms on appropriate lattice sites without any translation of the sites (18). The symmetry of the Laves phases are preserved in the one-five structures, but all A-A contacts are replaced by A-B contacts. If one combines Dwight's relation (18) between the one-five structures and the Laves phases with Rudman's (5) relation between the Laves phases and the elemental close packed structures, then the close relationship between the one-five structures

and the elemental close packed structures becomes evident. The value of the radius ratio, r_A/r_B , is important in determining whether the CaCu_5 structure or the UNi_5 structure forms. Dwight (18) has found the UNi_5 structure forms for ratios of 1.16 to 1.30 while the CaCu_5 structure forms for ratios of 1.29 to 1.61. Consistent with Dwight's findings the radius ratios of the thorium systems under investigation are such that the CaCu_5 structure forms.

Florio, Baenziger, and Rundle (8) determined the structures for the $\text{Th}_2\text{Fe}_{17}$, $\text{Th}_2\text{Co}_{17}$, and $\text{Th}_2\text{Ni}_{17}$ phases and showed how they, along with the ThMn_{12} structure, are related to the CaCu_5 structure. The relationship is obtained by the substitution of pairs of transition metal atoms for thorium atoms in the CaCu_5 lattice. Johnson, Smith and Wood (7) have modified the work of Florio, Baenziger and Rundle (8) and have shown that the $\text{Th}_2\text{Fe}_{17}$ and $\text{Th}_2\text{Co}_{17}$ phases are isostructural with the $\text{Th}_2\text{Zn}_{17}$ structure which was originally reported by Makarov and Vinogradov (9). Ray (19) has extended the discussion of Florio, Baenziger and Rundle (8) to include the $\text{Th}_2\text{Zn}_{17}$ structure. The same type of relationship is obtained between the $\text{Th}_2\text{Zn}_{17}$ and CaCu_5 structure as was obtained between the $\text{Th}_2\text{Ni}_{17}$ and CaCu_5 structure. The only difference

is the location of the substitution sites.

The ThFe_3 phase was found by Smith and Hansen (11) to have the NbBe_3 structure. They also found the structure was very susceptible to faulting with the stacking faults occurring normal to the c-axis. It is quite probable that ThCo_3 is isostructural with ThFe_3 , and extensive faulting could explain the magnitude of the c-axis which has been reported (8,1) as several times larger than would be expected if the two phases were isostructural. The similarities between the NbBe_3 structure and the CaCu_5 and MgCu_2 structures have been discussed by Cromer and Olsen (20). They showed that the NbBe_3 structure can be considered as a composite of the CaCu_5 structure and the MgCu_2 structure.

The most thorium-rich phase on which reproducible data were obtained was the ThNi_2 phase. ThNi_2 (8) along with ThCu_2 (14) and ThZn_2 (13) have been found to be isostructural with AlB_2 ; however, Ryba and Bell (21) have reported that ThZn_2 may also exist with the CeCu_2 structure. The AlB_2 structure is related to the Laves phases and hence to other structures which have been herein discussed only to the extent that the numerical coordination of A to B atoms and B to A atoms is the same. The coordination geometry of B atoms around A atoms and

of A atoms around B atoms is significantly different in the AlB_2 structures than in the Laves phases and neither the numerical coordination nor coordination geometry is the same for the B-B or A-A coordination.

Electromotive Force Cells

The theory of electrochemical cells is discussed in detail in several texts including those by Delahay (22), MacInnes (23), Milazzo (24) and Glasstone (25). In metallic conductors electricity passes without the transfer of matter in the material of the conductor, but in electrolytic conductors the carriers of electricity are ions so there is a transfer of matter. At the point where an electric current passes from one type of conductor to the other there will be an accumulation of atoms which have either lost or gained electrons. This is always accompanied by a chemical reaction. Concerning this reaction, Faraday stated in 1834 (23), "The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes."

Faraday's laws can be expressed by the equation

$$\frac{m}{M} = \frac{It}{n|f|} = \frac{Q}{n|f|} \quad (2)$$

where f is the amount of electricity corresponding to the

reaction of one chemical equivalent of substance,
 m is the mass of element reacted with atomic weight M ,
 and n is the number of chemical equivalents per mole.
 The work done on a charge, Q , when its potential is changed
 by E equals QE . The electrical work, W_e , done on a cell is
 given by

$$W_e = -QE, \quad (3)$$

and for one mole of element reacted

$$W_e = -|n| f E. \quad (4)$$

Under reversible conditions, the change in the work function,
 A , is defined by

$$\Delta A = W = - \sum_{\alpha} P^{\alpha} \Delta V^{\alpha} - |n| f E \quad (5)$$

where W = total work done on the system at constant pressure.

The Gibbs free energy, ΔF , at constant pressure is defined
 by

$$\Delta F = \Delta A + \sum_{\alpha} P^{\alpha} \Delta V^{\alpha} = -|n| f E. \quad (6)$$

This equation relates the Gibbs free energy of an emf cell to
 the potential of the cell.

The relation derived above holds only for emf cells
 operated under reversible conditions. Oriani (26) has dis-
 cussed the criteria of reversibility and states that the

electrolyte must exhibit only ionic conductivity, the more electropositive metal must have only one valence state with respect to the anions of the electrolyte, and the valence state must be known. Only one reaction should occur at each electrode interface and the cell must be operated at a high enough temperature, 0.3 or 0.4 of the absolute melting temperature of the alloy, to facilitate equilibrium with respect to diffusion, inside the alloy electrode. There are several conditions that will be met if the cell is operating reversibly. The emf should be time independent at constant temperature, should have the same value irrespective of whether the cell is heating or cooling, and should recover to its original value after current is passed through the cell in either direction.

The foregoing criteria and conditions of reversibility are for both solid and liquid electrolytes. If a solid electrolyte is used, there are several additional problems, and Schmalzried (27) discussed several of these. He found: (i) since the electrolyte is made by sintering, one can have molecular transport via pores or grain boundaries from one side to the other in the electrolyte; (ii) at high temperatures, reactions between the electrolyte and adjacent solid

phases are possible; and (iii) the effective charge of the charge carrier must be known. Kiukkola and Wagner (28) also mention the problem of mass transport due to capillary action through the electrolyte and surface diffusion on the electrolyte pellet surface. These authors (29) also indicate that interference due to electronic conduction is more serious with solid than with liquid electrolytes, but they also state that as a rule solubilities in solid electrolytes are lower than in liquid electrolytes.

The first and primary consideration in the choice of an electrolyte is that it must be an ionic conductor over the temperature and activity range encountered during measurements. Ure (30) has found CaF_2 to be an ionic conductor from 600 to 1000°C with anti-Frenkel defects (equal concentrations of negative ion interstitials and vacancies) responsible for the conduction. Patterson¹ has found CaF_2 to exhibit ionic conductivity from 400 to 900°C. This work plus past experience leaves little question that CaF_2 would remain an ionic conductor over the range of partial pressures of fluorine encountered in this investigation.

¹Patterson, J. W., Ames, Iowa. Ionic conductivity of CaF_2 . Private communication. 1968.

Several successful emf investigations have been done on thorium systems using CaF_2 as a solid electrolyte. Aronson and coworkers (31,32,33) have used CaF_2 to determine the thermodynamics of formation of the thorium carbides, borides and sulfides. Satow (34,35) also determined the thermodynamics of formation of the thorium carbides and obtained good agreement with Aronson (31). These values on the carbides from emf measurements compare favorably with results from gas-solid equilibrium measurements which further supports the choice of CaF_2 as a satisfactory solid electrolyte.

Thermochemical Considerations

The emf cells used in this investigation were of the type,

with all phases solid throughout the experiments. One of the criteria of reversibility for an emf cell is that only one reaction should occur at each electrode interface. This means the state of the CaF_2 should be unaffected by the cell reaction and the alloys should remain as metals and not be oxidized to fluorides.

Hamer, Malmberg and Rubin (36) have prepared an electromotive force series for solid and liquid fluorides. Of the

materials that were used in this investigation calcium was the highest in the series with thorium next and the transition metals grouped lowest. This relationship among these emf's is such that CaF_2 will be unaffected by the cell reaction, the transition metals will remain only as metals and the thorium can exist both as a metal and a fluoride with the changes in its state corresponding to the reaction within the cell.

For the potential of an emf cell reaction, Schmalzried (27) derives the equation

$$E = \frac{1}{|n|f} \int_{\mu'(F)}^{\mu''(F)} t_{\text{ion}} d\mu(F) \quad (7)$$

where $\mu(F)$ is the chemical potential of fluorine in an electrode pellet, t_{ion} is one for an ionic conductor and $|n|$ is one for fluoride ions. Since CaF_2 is an ionic conductor for the partial pressures of fluorine encountered in the cells

$$E = \frac{1}{f} [\mu''(F) - \mu'(F)] = \frac{1}{f} RT \ln \frac{a''(F)}{a'(F)} \quad (8)$$

where $a(F)$ is the activity of fluorine in an electrode pellet.

The cell reaction can be written as two half cell reactions, each corresponding to a reaction at the electrolyte-electrode interface. The half cell reactions are

Under reversible open circuit conditions the free energy change for Equation 9 is

$$\Delta F(9) = 0 = \Delta F^{\circ}(\text{ThF}_4) + RT \ln \frac{a_{\text{ThF}_4} (a_{e^-}')^4}{a_{\text{Th}} (a_{\text{F}}')^4} \quad (11)$$

and the free energy change for Equation 10 is

$$\begin{aligned} -\Delta F(10) = 0 = \Delta F^{\circ}(\text{ThF}_4) - \Delta F^{\circ}(\text{ThM}_x) \\ + RT \ln \frac{a_{\text{ThF}_4} (a_{e^-}'')^4 (a_m)^x}{a_{\text{ThM}_x} (a_{\text{F}}'')^4} \end{aligned} \quad (12)$$

Since thorium, ThF_4 and ThM_x are solid phases with negligible solubility in each other, their activities are unity. Combining Equations 11 and 12 for the half cell reactions, one gets

$$\Delta F^{\circ}(\text{ThM}_x) = -RT \ln \frac{(a_{e^-}')^4 (a_{\text{F}}'')^4}{(a_{e^-}'')^4 (a_{\text{F}}')^4} \quad (13)$$

The electrons are very mobile so the activity of the electrons is the same on each side of the cell. Equations 8 and 13 can be combined to eliminate the $\ln a''(\text{F})/a'(\text{F})$ term resulting in Equation 6, which was the result obtained from Faraday's laws. This derivation illustrates why it is important to have an ionic conductor over all fluorine potentials present in the cell if Schmalzried's relation (Equation 7) is to be integrable.

Heat capacity data are not available for any of the phases which were studied in this investigation, therefore, ΔC_p values for the reactions leading to the formation of these phases were taken as zero. This neglects any temperature variation in ΔH and ΔS and implies a linear relation between ΔF and temperature. Such an approximation usually does not introduce significant error over narrow intervals of 100-200°C (37). The entropy for the cell reaction is related to the experimental emf's through the relation

$$\Delta S = |n| f (\partial E / \partial T)_p \quad (14)$$

The enthalpy is determined by combining the free energy values and the entropy values

$$\Delta H = |n| f [T (\partial E / \partial T)_p - E] \quad (15)$$

EXPERIMENTAL PROCEDURE

Apparatus

The emf measurements that were made in this investigation were on double emf cells of the type

Ta|Th alloy, $\text{ThF}_4|\text{CaF}_2|\text{Th}$, $\text{ThF}_4|\text{Ta}|\text{Th}$, $\text{ThF}_4|\text{CaF}_2|\text{Th}'$ alloy, Th|Ta.

With this arrangement two sets of data could be obtained simultaneously by measuring the potential differences between each alloy electrode and the thorium electrode at the center. Tantalum was chosen to make the electrical contacts between the external circuit and the cell electrodes. This choice was based on initial experiences with the thorium-copper system and subsequent experience with the thorium-nickel system. In both cases the contacts performed satisfactorily and spectroscopic analysis indicated the tantalum content of the electrode pellets after a run was below the detection limit of 500 p.p.m. A cursory experiment was carried out on the thorium-nickel system using silver in place of tantalum. In this case measurements of the cell emf's were not reproducible so the use of silver was not pursued further.

A schematic diagram of the apparatus with the pellets in place is shown in Figure 5. The small quartz tube encircling

Figure 5. Electromotive force apparatus

the pellets simply facilitated loading the cell into the large tube. Electrical contact was maintained throughout the experiment by means of a spring loaded push rod. The top tantalum electrode contact was attached to the push rod by tantalum tabs pressed against the rod and the 20 mil tantalum lead wire was wrapped around the push rod and then threaded through a quartz tube in the center of the spring in such a manner that there was no electrical contact between the lead wires and the spring. A gas tight system was obtained by bonding the lead wires in quartz tubes with epoxy cement and by using Veeco vacuum seals around the tubes (see Figure 5).

A chromel-alumel thermocouple was used to determine the cell temperatures. The thermocouple wire was calibrated by the manufacturer against a National Bureau of Standards platinum wire, and it was calibrated against the melting points of aluminum, silver, and copper on a differential thermal apparatus at this laboratory. The calibration indicated that standard tables could be used for the conversion of thermocouple emf's to temperature without the introduction of significant error (less than 0.1%). The thermocouple was housed in a tantalum thermocouple well which was insulated from the brass head by a quartz tube. The thermocouple well

was joined to the quartz tube by epoxy cement.

The brass head (see Figure 5) was wrapped with copper coils through which water was passed for cooling. A vacuum-tight joint was obtained between the brass head and the outer quartz tube by using an O-ring seal.

All external positive leads were shielded at the potential of the guard circuit of the potentiometer. The negative leads were not shielded since they were grounded inside the potentiometer. The use of shielded cable prevents electrostatic interference, while the use of guarded circuiting prevents leakage between critical circuit points. The emf measurements were made with a Leeds and Northrup K-3 potentiometer and an electronic D-C null detector. The null detector was inserted between the potentiometer and the positive side of the emf cell with the side of the detector having the higher impedance attached to the emf cell. This eliminated shunting the emf cell with a 5,000 ohm resistance during the measurement, which would be detrimental to the life of the cell since the cell is a high impedance potential source. The null detector was switched to the normal position for the standardization of the slide wire by means of a Leeds and Northrup rotary selector switch with silver contacts. This

was the same type of switch which was used to change the various emf sources entering the potentiometer.

The cell was heated by a Lindberg Hevi-Duty non-inductively wound split tube furnace. The furnace was powered by a West stepless transformer which was controlled by a West set point unit with a chromel-alumel control thermocouple mounted in the center of the furnace. Temperatures could be maintained to $\pm 1^{\circ}\text{C}$ for several days with this equipment.

The experiments were run with the cell in a helium atmosphere with the pressure of helium 2" of mercury above atmospheric pressure. The helium was purified by successively passing it through copper wool at 400°C , Linde molecular sieves, and a liquid nitrogen cold trap which was situated to prevent pump vapors from reaching the cell area during the initial pump down. The molecular sieves were regenerated periodically by heating them to 300°C under a vacuum.

Sample Preparation

The results of impurity analysis for the alloying elements and ThF_4 are shown in Table 3. The iron analysis is the manufacturer's analysis for high-purity electrolytic iron while the iron which was used in this investigation was a further purified super-purity grade and should have impurity

Table 3. Impurity analyses of alloying elements and ThF₄ in ppm

Impurity	Th ^a	ThF ₄ ^b	Cu ^c	Ni ^d	Co ^e	Fe ^f
H	<1	-	-	-	6	-
B	-	<0.5	-	-	-	-
C	50	-	-	50	60	<100
N	20	-	-	20	-	-
O	80	-	-	80	100	-
Na	<10	-	-	-	-	-
Mg	<20	55-120	-	-	-	-
Al	25	<25	-	-	-	-
Si	<20	50-100	<0.1	-	10	-
P	-	-	-	-	<30	-
S	-	-	<1	76	10	<60
Ca	<20	150-500	-	-	-	-
Ti	<20	-	-	-	-	-
Cr	20	-	-	-	-	-
Mn	<20	<20	<0.5	-	30	-
Fe	<20	-	<0.7	70	80	-
Ni	<20	-	<1	-	600	-
Cu	-	-	-	10	30	-
Zn	-	-	-	-	30	-
Se	-	-	<1	-	-	-
Y	<100	-	-	-	-	-
Ag	-	-	<0.2	-	-	-
Cd	-	<0.2	-	-	-	-

^aAmes Laboratory Th, 99.98% pure, typical analysis.

^bAmes Laboratory ThF₄, typical analysis.

^cAmerican Smelting and Refining Co. Cu, 99.999+% pure, company analysis.

^dBelmont Ni shot, 99.97% pure, company analysis and Ames Laboratory typical analysis.

^eAmerican Metals Corp. Co 99.9+% pure, company analysis.

^fGlidden Company super-purity grade electrolytic iron, 99.9+% pure, company analysis.

Table 3. (Continued)

Impurity	Th ^a	ThF ₄ ^b	Cu ^c	Ni ^d	Co ^e	Fe ^f
In	-	35-45	-	-	-	-
Sn	-	-	<1	-	-	-
Sb	-	-	<1	-	-	-
Te	-	-	<2	-	-	-
Au	-	-	<2	-	-	-
Pb	-	-	<1	-	<1	-
Bi	-	-	<0.1	-	-	-

concentrations appreciably lower than those indicated in the table. The ThF₄ was also further purified from that analyzed for the table. This purification was achieved by heating the ThF₄ with ammonium bi-fluoride at 150-180°C for 12 hours and then slowly heating to 350°C while passing dry air over the fluorides. This should have reduced any residual oxides or oxi-fluorides that might have been present. The CaF₂ which was used for the electrolyte was from Electronic Space Products Incorporated and quoted as being 99.95% pure.

Alloys were prepared by arc-melting the elements in an argon atmosphere that had been purified by melting zirconium several times. The arc-melted alloys were successively inverted and remelted several times to get homogeneous samples. Alloys that passed through peritectic transformations on cooling were sealed in tantalum crucibles under a vacuum and held at 25°C below the transformation temperature for 10-14 days to

remove any non-equilibrium phases that might have formed, while alloys that passed through eutectic transformations were not heat treated.

Debye-Scherrer powder photographs of the alloys indicated in each case the presence of only the two equilibrium phases. The thorium-nickel alloys that passed through a peritectic transformation were analyzed further by the electron beam microprobe to be certain no traces of non-equilibrium phases were present. The results indicated only the two equilibrium phases were present. Because of the results in the thorium-nickel system, phase identification for the rest of the alloys was made on the basis of x-ray data only.

The alloys were very reactive and were therefore stored in a dry-box containing an argon atmosphere. For the x-ray measurements fine powders were prepared and the x-ray capillary tubes were loaded in the dry box. For the preparation of electrode pellets all of the steps were performed in the dry box except the actual pressing of the pellet which had to be done in the air. The alloys that were brittle were crushed with a diamond mortar and those that were not brittle were filed with a tungsten-carbide file. The thorium was filed with a standard file and then the filings were passed through

a group of small magnets to remove any iron present. All of the powders were passed through a 60 mesh screen to remove any large particles and then 20 wt % ThF_4 powder was added. The mixture was pressed in a $\frac{1}{2}$ " tungsten carbide die at 30,000 psi. The resultant electrode pellets were from 2 to 5 mm. thick.

The electrolyte pellets were prepared by pressing $\frac{1}{2}$ to 2 grams of CaF_2 at 7,500 psi in a $\frac{1}{2}$ " tungsten carbide die, then hydrostatically pressing the pellets at 50,000 psi, and then sintering them in an induction furnace under a vacuum at 1000°C for 15 minutes.

EMF Measurements

The system was pumped down to about 0.5 torr after being loaded with the electrode and electrolyte pellets, flushed with helium, heated at 200°C for several hours while under a vacuum to remove any adsorbed gases, filled to a positive pressure of helium, and heated. It normally took from 25-100 hours for the cells to stabilize at a particular temperature, with the lower temperature data usually taking the longer time. During a given run, the emf was measured about every half hour until the emf readings showed no significant variation with time. When this condition was met for several hours the temperature was changed and another data point was taken.

The apparatus was usually loaded with two different alloy pellets with different compositions but from the same two-phase region. In all cases the data were verified with at least two different experimental runs and with non-systematic heating and cooling of the system. A voltage was occasionally impressed across the cell to see if the potential would return, after the impressed voltage was removed, to its original value. The voltages impressed were both higher and lower than the cell potential and in both cases the emf would come back to the earlier readings which indicates the values were equilibrium values.

The absence of thermally induced emfs in the system was verified by making a dummy run in which no pellets were in the system. This allowed the spring loaded push rod to push the top tantalum contact against the tantalum plate (see Figure 5). This procedure has been used by Oriani (26). In the present case the emfs produced by this technique were approximately 0.05 mv which is completely negligible compared to the potentials generated by the cells.

RESULTS

The potentials of the emf cells were measured over the temperature range 850-1100°K. The data are summarized in Table 4.

Table 4. Electromotive force data

Comp. at %	Temp. °K	EMF mv	Comp. at %	Temp. °K	EMF mv
Fe-5Th	1055	175.86	Co-5Th	1022	322.00
			"	1100	319.08
Fe-7Th	1021	174.25			
"	975	186.64	Co-11Th	1087	320.90
"	1043	172.98	"	1039	320.85
"	1066	174.09	"	991	321.68
"	1089	174.15	"	945	352.40
"	997	187.60	"	1033	328.25
"	974	194.58	"	986	331.90
"	1055	178.62	"	940	340.90
"	1007	188.77	"	917	349.24
"	960	186.91			
"	937	189.01	Co-13Th	1078	308.70
"	984	181.31	"	1033	322.50
"	1031	178.00	"	940	346.90
"	1080	175.98			
			Ni-3Th	954	563.41
Co-3Th	1076	320.95	"	891	571.48
"	980	319.84	"	1000	563.30
"	920	336.40	"	954	569.41
"	1021	322.67	"	1045	561.33
"	974	330.90	"	1091	562.98
			"	978	566.41
Co-5Th	1084	313.27			
"	1037	317.34	Ni-11Th	1023	554.70
"	998	319.63	"	930	574.58
"	951	325.92	"	977	561.69
"	983	323.16	"	1070	549.98
"	1063	321.96	"	1119	534.85

Table 4. (Continued)

Comp. at %	Temp. °K	EMF mv	Comp. at %	Temp. °K	EMF mv
Ni-15Th	952	565.92	Cu-5Th	850	227.59
"	997	559.78	"	897	230.70
"	1047	549.17	"	946	235.93
"	1094	542.11	"	851	228.07
"	1023	563.95	"	898	231.20
"	977	571.46			
"	1070	547.49	Cu-7Th	937	234.27
"	1119	534.02	"	895	232.07
			"	884	229.25
			"	939	234.51
Ni-29Th	986	151.36			
"	1025	155.54			
"	1072	162.20			
"	1121	166.05			
"	983	166.16			
"	1052	168.18			
"	1004	166.59			
"	963	166.53			
"	939	157.66			

Three different types of cells were used in this investigation. The free energies of formation of the $\text{Th}_2\text{Fe}_{17}$, $\text{Th}_2\text{Co}_{17}$, $\text{Th}_2\text{Ni}_{17}$ and ThCu_4 phases were determined from cells of the type

where $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ and $x = 8.5$

or $\text{M} = \text{Cu}$ and $x = 4$.

The equilibrium reactions for these cells are

with

$$\Delta F^{\circ}(\text{ThM}_x) = -4 f E^{\circ}. \quad (17)$$

The free energies of formation of the ThCo_5 and ThNi_5 phases were determined from emf cells of the type

The equilibrium cell reaction for this type of cell is

with

$$\Delta F_{\text{Reaction}}^{\circ} = -4 f E^{\circ} = \frac{17}{7} \Delta F^{\circ}(\text{ThM}_5) - \frac{10}{7} \Delta F^{\circ}(\text{ThM}_{8.5}) \quad (19)$$

or

$$\Delta F^{\circ}(\text{ThM}_5) = \frac{7}{17} [-4 f E^{\circ} + \frac{10}{7} \Delta F^{\circ}(\text{ThM}_{8.5})] \quad (20)$$

Cells of the type

were used for the determinations of the free energies of formation of ThNi_2 . The equilibrium cell reaction for this type of cell is

with

$$\Delta F_{\text{Reaction}}^{\circ} = -4 f E^{\circ} = \frac{5}{3} \Delta F^{\circ}(\text{ThNi}_2) - \frac{2}{3} \Delta F^{\circ}(\text{ThNi}_5) \quad (22)$$

or

$$\Delta F^{\circ}(\text{ThNi}_2) = \frac{3}{5} \left[\frac{2}{3} \Delta F^{\circ}(\text{ThNi}_5) - 4 f E^{\circ} \right] \quad (23)$$

The free energies, entropies and enthalpies of formation which were determined in this investigation are listed in Table 5. The uncertainties in the free energies are the pre-cisional uncertainties and are related to the root mean square deviation of the fits of the experimental potentials to the linear relation

$$E = A + BT. \quad (24)$$

The fits were made by the method of least squares. The uncertainties in the entropy are related to the uncertainties of the slopes, B. The results are all reported at 973°K which is approximately the median temperature of the electromotive force measurements.

Table 5. Thermodynamic functions for the formation of selected binary alloys of thorium with iron, cobalt, nickel and copper

Phase	$-\Delta F^{\circ}_{973}$ (kcal/g-atom)	$-\Delta S^{\circ}_{973}$ (e.u./g-atom)	$-\Delta H^{\circ}_{973}$ (kcal/g-atom)
Th ₂ Ni ₁₇	5.50 ± 0.02	0.44 ± 0.15	5.93 ± 0.15
Th ₂ Co ₁₇	3.17 ± 0.04	0.79 ± 0.21	3.94 ± 0.20
Th ₂ Fe ₁₇	1.82 ± 0.04	1.21 ± 0.23	2.99 ± 0.22
ThNi ₅	8.70 ± 0.03	1.69 ± 0.18	10.35 ± 0.18
ThCo ₅	5.08 ± 0.05	2.12 ± 0.29	7.14 ± 0.32
ThCu ₄	4.38 ± 0.01	-1.49 ± 0.12	2.93 ± 0.12
ThNi ₂	9.93 ± 0.09	0.77 ± 0.70	10.68 ± 0.68

DISCUSSION

The value of several thermodynamic quantities can be estimated from the data obtained in this investigation. The free energy of formation of $\text{Th}_2\text{Cu}_{17}$ and ThCu_5 can not be measured because $\text{Th}_2\text{Cu}_{17}$ and ThCu_5 are not stable phases, but knowledge of the free energy of formation of ThCu_4 allows one to determine that $-\Delta F^\circ(\text{Th}_2\text{Cu}_{17}) < 2.3 \text{ kcal/g.atom}$ and that $-\Delta F^\circ(\text{ThCu}_5) < 3.6 \text{ kcal/g.atom}$. If $-\Delta F^\circ$ exceeded these values then the $\text{Th}_2\text{Cu}_{17}$ and ThCu_5 phases would be stable phases with respect to a mixture of copper and ThCu_4 and would appear in equilibrium alloys.

Another free energy that could not be measured was the free energy of formation of the ThFe_5 phase. ThFe_5 is an equilibrium phase, but because of the chemical reactivity of the phase reproducible data could not be obtained from alloys containing this phase. The free energy of formation of the ThFe_5 phase can be estimated because of the crystallographic relationships that exist among the phases in the systems studied in this investigation. Figure 6 shows the free energy composition diagrams for the thorium-poor side of the thorium-nickel, thorium-cobalt and thorium-iron systems. A straight line can be drawn, within experimental error, through

Figure 6. Th-M free energy composition diagrams

$\Delta F^\circ(\text{Th}_2\text{M}_{17})$, $\Delta F^\circ(\text{ThM}_5)$ and $\Delta F^\circ = 0$ at pure M for both the thorium-nickel and thorium-cobalt systems. This straight line relation should also be observed in the thorium-iron system because the $\text{Th}_2\text{Fe}_{17}$ and $\text{Th}_2\text{Co}_{17}$ phases are isostructural and very similar crystallographically to the $\text{Th}_2\text{Ni}_{17}$ phase, and the ThFe_5 , ThCo_5 and ThNi_5 phases are isostructural. An extrapolation of a straight line from $\Delta F^\circ = 0$ at pure iron through $\Delta F^\circ(\text{Th}_2\text{Fe}_{17})$ to the one-five stoichiometry yields $\Delta F^\circ(\text{ThFe}_5) = -2.9 \text{ kcal/g.atom.}$

The entropy of formation of the ThFe_5 phase can also be estimated. The entropies of formation for the Th_2M_{17} and ThM_5 phases which were determined in this investigation are shown in Figure 7. It may be noted that the shift in ΔS° from ThNi_5 to ThCo_5 is parallel to the shifts in ΔS° going from $\text{Th}_2\text{Ni}_{17}$ to $\text{Th}_2\text{Co}_{17}$ to $\text{Th}_2\text{Fe}_{17}$. Therefore, it is believed that a reliable estimation of $\Delta S^\circ(\text{ThFe}_5)$ can be made by extending the trend from ThCo_5 to ThFe_5 . The value which is obtained is $-2.5 \text{ e.u./g.atom.}$ An estimate of the enthalpy of formation of ThFe_5 can then be made. This is done by combining the estimated values of $\Delta F^\circ(\text{ThFe}_5)$ and $\Delta S^\circ(\text{ThFe}_5)$ and yields a value of $\Delta H^\circ(\text{ThFe}_5) = -5.3 \text{ kcal/g.atom.}$

Additional free energies can be estimated but with less

Figure 7. Entropies of formation of Th_2M_{17} and ThM_5 phases

reliability. The values of the free energies of formation of ThFe_3 , ThCo_3 , ThNi and ThCu_2 can be bracketed as indicated in Figure 8. The $-\Delta F^\circ$ must be less than the value obtained from a straight line extrapolation of the line joining the two most thorium-rich phases in a particular system and $-\Delta F^\circ$ must be more than a value obtained from a line joining ΔF° of the most thorium-rich phase for which ΔF° has been determined and pure thorium at $\Delta F^\circ = 0$. The limits obtained for the free energies in kcal/g.atom atoms are: $2.6 < -\Delta F^\circ(\text{ThFe}_3) < 4.4$; $4.6 < -\Delta F^\circ(\text{ThCo}_3) < 7.6$; $7.5 < -\Delta F^\circ(\text{ThNi}) < 11.1$; and $3.7 < -\Delta F^\circ(\text{ThCu}_2) < 7.3$. Because of the crystallographic similarities between the CaCu_5 structure and the NbBe_3 structure and because the free energy of formation normally peaks toward the middle of the system, it is thought $-\Delta F^\circ(\text{ThFe}_3)$ and $-\Delta F^\circ(\text{ThCo}_3)$ will be closer to the maximum allowable value than to the minimum allowable value.

There are several interesting trends occurring in the thermodynamic functions in the systems studied in this investigation. One of these trends occurs in the Th_2M_{17} phases when they are studied as a function of atomic number. Figure 9 shows the $\Delta F^\circ(\text{Th}_2\text{M}_{17})$ which were determined in this investigation and the $\Delta F^\circ(\text{Th}_2\text{Zn}_{17})$ which is equal to -3.96 kcal/

Figure 8. Conditions imposed on free energy limits for ThFe₃, ThCo₃, ThNi and ThCu₂

Figure 9. Free energies of formation of Th_2M_{17} phases

g.atom according to Chiotti and Gill (10). Manganese does not form a Th_2M_{17} phase, and chromium does not form any inter-metallic phases with thorium but instead forms a simple eutectic system. Thus the trend of decreasing stability of the Th_2M_{17} phases with decreasing atomic number from nickel to cobalt to iron appears to persist through manganese and chromium. However, this trend does not extend above nickel since the copper and zinc values are significantly lower than the value for nickel. A similar trend of decreasing stability with decreasing atomic number from nickel to cobalt to iron is observed in the ThM_5 phases if the estimated value of $\Delta F^\circ(\text{ThFe}_5)$ is used. This trend also does not extend above nickel because the maximum allowable values for $-\Delta F^\circ$ of 3.6 kcal/g.atom and 5.0 kcal/g.atom for the non-equilibrium phases ThCu_5 and ThZn_5 respectively are significantly lower than $\Delta F^\circ(\text{ThNi}_5)$. The condition that $-\Delta F^\circ(\text{ThZn}_5) < 5.0$ kcal/g.atom is obtained from the free energies of formation of the $\text{Th}_2\text{Zn}_{17}$ and ThZn_4 phases which were obtained by Chiotti and Gill (10). If $\Delta F^\circ(\text{ThZn}_5)$ were greater than 5.0 kcal/g.atom then ThZn_5 would be a stable phase with respect to a mixture of $\text{Th}_2\text{Zn}_{17}$ and ThZn_4 and would appear in equilibrium alloys.

The trend of decreasing stability of the Th_2M_{17} phases from nickel with decreasing atomic number and the discontinuation of the trend with increasing atomic number above nickel is not entirely unexpected. Chromium through nickel are transition metals with partially filled 3d electronic energy levels while copper and nickel have their 3d electronic energy levels filled. This would imply there is a contribution to the bonding in these phases from the 3d electrons.

The thermodynamic data on the Th_2M_{17} and ThM_5 phases indicate the dominant interactions which stabilize these phases are the Th-M interactions rather than the Th-Th or M-M interactions. The straight line relations in Figure 6 show within experimental precision the free energy change for the reaction

is zero. Since M atoms can be added to ThM_5 to form Th_2M_{17} with no cost in free energy the M atoms must experience an environment that is energetically quite equivalent to the environment in elemental M. Implicitly, therefore, M-M interactions are not the dominant interactions which stabilize the phases. This conclusion is supported by crystallographic data that show M atoms added to the ThM_5 lattice are primarily

supported by M atoms.

Additional numerical confirmation is shown in Table 6 where the free energies of formation per gram atom of thorium are tabulated for the ThM_5 and Th_2M_{17} phases.

Table 6. Free energies of formation in kcal per gram atom of thorium

M	Th_2M_{17}	ThM_5
Ni	-52.2 ± 0.2	-52.2 ± 0.2
Co	-30.1 ± 0.4	-30.5 ± 0.3
Fe	-17.3 ± 0.4	-17.4^a

^aEstimated value.

The fact that the free energies per thorium atom are essentially the same for the Th_2M_{17} and ThM_5 phases within a system implies the Th-M interactions are the dominant interactions in these phases. This conclusion is also supported by crystallographic data which shows the thorium atoms are surrounded primarily by M atoms and that the thorium atom surroundings are essentially the same in the ThM_5 and Th_2M_{17} phases. The crystallographic data are as follows. There are twenty M atoms surrounding a thorium atom in the first two coordination levels in the ThM_5 phases. There are two types of thorium

atom in the $\text{Th}_2\text{Ni}_{17}$ structure with twenty Ni atoms surrounding one type of thorium atom and eighteen nickel atoms around the other type of thorium atom for an average of nineteen nickel atoms in the first two coordination levels around a thorium atom. The $\text{Th}_2\text{Fe}_{17}$ and $\text{Th}_2\text{Co}_{17}$ phases have nineteen M atoms around one thorium atom again with the M atoms in two levels. In all of the phases the second coordination level is approximately $3.2\text{\AA}$ from the thorium atoms and in all of the structures there are no thorium atoms in the first two coordination levels, in fact the thorium-thorium interatomic distances are quite large ($>4\text{\AA}$).

Contractions in interatomic distances on the formation of the ThM_5 phases also supports the conclusions that Th-M interactions are the dominant interactions and M-M interactions are rather insignificant in stabilizing these phases. Normally bond contractions can be correlated to bond strengths and in the ThM_5 systems the trend of decreasing stability of the intermediate phases from nickel to cobalt to iron is similar to the trend of decreasing contractions in the Th-M interatomic distances from nickel to cobalt to iron. The thorium-nickel nearest neighbor bond distance is 5.9% less than the sum of the atomic radii, the thorium-cobalt 5.2% less and

the thorium-iron 4.5% less. The contractions in the M-M interatomic distances follow an opposite trend with atomic number than the Th-M contractions and the free energy of formation. The nickel-nickel nearest neighbor bond distance is 1% less than the sum of the atomic distances while the cobalt-cobalt distance is 2% less and the iron-iron distance is 4% less.

SUMMARY

The free energies, entropies and enthalpies of formation have been determined for several intermediate phases in the thorium poor regions of the binary alloys of thorium with iron, cobalt, nickel and copper. The data indicate a decreasing stability of equivalent intermediate phases in the Th-M systems from nickel to cobalt to iron. The data also suggest there is a correlation between crystallographic data and thermodynamic data for these phases and that interactions between thorium and the nearest neighbor transition metals are the dominant interaction stabilizing these phases.

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