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ALLOYING BEHAVIOUR OF THORIUM WITH Fe, Co AND Ni *

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ABSTRACT

The binary phase diagrams of thorium with the Group VIII transition elements have been reinvestigated. The alloying behaviour of thorium is discussed on the basis of the crystalline structures which occur.

INTRODUCTION

The physical and chemical properties of thorium and its intermetallics present several aspects of great technological and basic research interest. One point is that the crystallochemical properties of thorium can be suitably compared with those of the rare earths and the alkaline earths in order to study (ignoring the size factor) the effect of changes in valence electron concentration (VEC) on passing from 4- to 3- and 2-valent elements. This comparison can be made by checking the existence, stability and crystal structures adopted by their compounds and therefore becomes meaningful if the available data are complete and reliable. This is not the case for the thorium phases, so a systematic revision seems to be advisable.

A research programme has recently investigated the alloying properties of thorium by means of thermal, structural and thermochemical data. The binary phase diagrams of thorium with B elements of periods I, II, III and IV have been determined [1–9].

The Th–Fe, Th–Co and Th–Ni systems [10,11] have also been reinvestigated and the structural data for these systems are brought together and discussed in this paper.

RESULTS

The constitutional phase diagrams of the Th–Fe, Th–Co and Th–Ni binary systems, derived from DTA, micrographic analysis, X-ray diffraction

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and electron microprobe analysis are shown in Figs. 1–3. Table 1 contains the crystallographic data for all the intermediate phases found in this investigation and the corresponding literature data are set out in Table 2.

Remarks on the Th–M systems

The Th–Fe system

Five intermediate phases and two eutectics are found to exist. Th_2Fe_7 displays a previously unknown polymorphic transformation at 1185 °C. $ThFe_5$ probably forms by a very sluggish peritectic reaction and so is not detectable by the usual DTA techniques. Its existence is confirmed by electron microprobe analysis on samples annealed at 1100 °C for some weeks.

The Th–Co system

Five intermediate phases, of which only Th_2Co_7 is formed by peritectic reaction, and five eutectics are included in the phase diagram. Only one compound, $ThCo_5$, displays a solid solubility range in the direction of

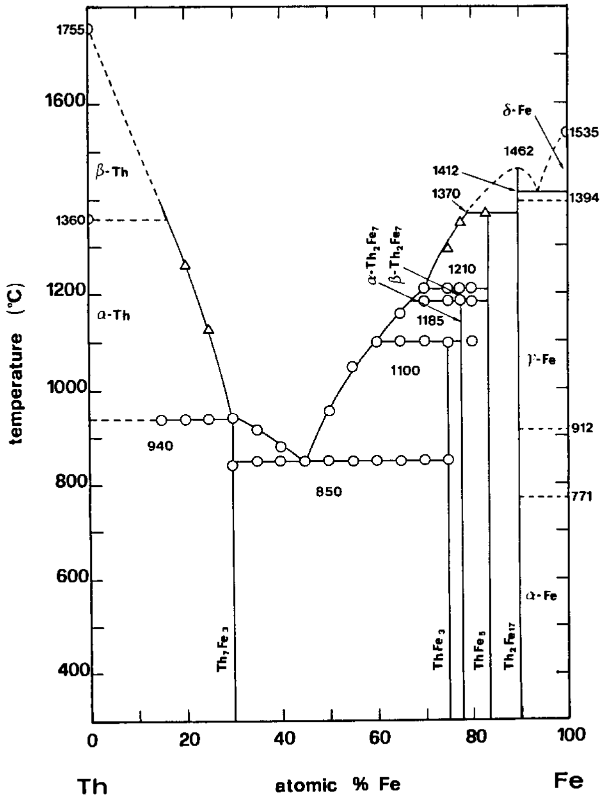

Fig. 1. Phase diagram of the Th–Fe system.

Co-rich composition. This should have its maximum width at the eutectic temperature of 1300 ° C.

The Th–Ni system

Seven intermetallic compounds and five eutectics appear. The intermediate phases show limited solid solubility with the exception of $ThNi_5$, which has a maximum existence range of 3 at.% toward Ni-rich compositions at 1310 ° C. ThNi has recently [22] been recognised as a stacking variant of the CrB–Feb-type and is isotypic with SrAg. Single crystal studies have shown that the new compound, Th_4Ni_7, crystallises with a monoclinic C-centred cell and its structure has been resolved. The Th_2Ni_7 compound replaces $ThNi_4$; this phase shows a polymorphic transformation at 1195 ° C. The high-temperature form could not be stabilised with usual quenching techniques owing to its narrow temperature existence range; it was assumed to be isomorphous with the Gd_2Co_7-type by analogy with α- and β-Th_2Fe_7 and α- and β-Th_2Co_7.

TABLE 1

Crystallographic data for the intermediate phases Th_xM_y

Compound	Structure type		a (Å)	b (Å)	c (Å)
Th_7Fe_3	Th_7Fe_3	($hP20$, $P6_3mc$)	9.830	–	6.216
$ThFe_3$	$PuNi_3$	($hR12$, $R\bar{3}m$)	5.220	–	25.147
α-Th_2Fe_7	Ce_2Ni_7	($hP36$, $P6_3/mmc$)	5.188	–	24.774
β-Th_2Fe_7	Gd_2Co_7	($hR18$, $R\bar{3}m$)	5.195	–	37.133
$ThFe_5$	$CaCu_5$	($hP6$, $P6/mmm$)	5.117	–	4.042
Th_2Fe_{17}	Th_2Zn_{17}	($hR19$, $R\bar{3}m$)	8.566	–	12.463
Th_7Co_3	Th_7Fe_3	($hP20$, $P6_3mc$)	9.843	–	6.202
ThCo	CrB	($oC8$, $Cmcm$)	3.746	10.864	4.153
α-Th_2Co_7	Ce_2Ni_7	($hP36$, $P6_3/mmc$)	5.039	–	24.676
β-Th_2Co_7	Gd_2Co_7	($hR18$, $R\bar{3}m$)	5.035	–	36.986
$ThCo_5$	$CaCu_5$	($hP6$, $P6/mmm$)	4.999	–	3.996
Th_2Co_{17}	Th_2Zn_{17}	($hR19$, $R\bar{3}m$)	8.441	–	12.260
Th_7Ni_3	Th_7Fe_3	($hP20$, $P6_3mc$)	9.887	–	6.231
ThNi	SrAg	($oP16$, $Pnma$)	14.174	4.300	5.695
Th_4Ni_7	Th_4Ni_7	($mC11$, $C2/c$)	5.509	5.510	7.445
$\beta = 111.71°$					
$ThNi_2$	AlB_2	($hP3$, $P6mmm$)	3.967	–	3.845
α-Th_2Ni_7	Ce_2Ni_7	($hP36$, $P6_3/mmc$)	4.945	–	25.80
β-Th_2Ni_7	Gd_2Co_7	($hR18$, $R\bar{3}m$)	4.945	–	38.70
$ThNi_5$	$CaCu_5$	($hP6$, $P6/mmm$)	4.926	–	3.985
Th_2Ni_{19}	Th_2Ni_{19}	($hP80$, $P6_3/mmc$)	8.36	–	8.16

TABLE 2

Previous crystallographic data for the intermediate phases of the Th–Fe, Th–Co and Th–Ni systems

Compound	Structure type	Lattice constants (Å)			References
		a	*b*	*c*	
Th_7Fe_3	Th_7Fe_3	9.85	–	6.15	12
	*hP*20, $P6_3mc$	9.830	–	6.214	13
$ThFe_3$	$PuNi_3$	5.22	–	24.96	12
	*hR*12, $R\bar{3}m$	5.18	–	25.2	14
		5.207	–	25.18	13
		5.213	–	25.11	15
α-Th_2Fe_7	Ce_2Ni_7	5.193	–	24.785	15
	*hP*36, $P6_3/mmc$				
β-Th_2Fe_7	Gd_2Co_7	5.194	–	37.19	15
	*hR*18, $R\bar{3}m$				
$ThFe_5$	$CaCu_5$	5.13	–	4.02	12
	*hP*6, $P6/mmm$	5.121	–	4.052	13
		5.116	–	4.046	16
Th_2Fe_{17}	Th_2Zn_{17}	8.565	–	12.469	17
	*hR*19, $R\bar{3}m$				
Th_7Co_3	Th_7Fe_3	9.83	–	6.17	12
	*hP*20, $P6_3mc$	9.833	–	6.200	18
		9.842	–	6.207	13
		9.840	–	6.207	16
ThCo	CrB	3.74	10.88	4.16	12
	*oC*8, *Cmcm*	3.776	10.877	4.153	13
		3.771	10.861	4.152	16
α-Th_2Co_7	Ce_2Ni_7	5.03	–	24.54	12
	*hP*36, $P6_3/mmc$	5.030	–	24.62	16, 19
		5.038	–	24.64	13
β-Th_2Co_7	Gd_2Co_7	5.030	–	36.91	19
	*hR*18, $R\bar{3}m$				
$ThCo_5$	$CaCu_5$	5.01	–	3.97	12
	*hP*6, $P6/mmm$	4.956	–	4.029	13
		5.01–4.99	–	3.99–4.00	20
Th_2Co_{17}	Th_2Zn_{17}	8.438	–	12.254	17
	*hR*19, $R\bar{3}m$	8.437	–	12.227	16
Th_7Ni_3	Th_7Fe_3	9.885	–	6.225	21
	*hP*20, $P6_3mc$				
ThNi	SrAg	14.146	4.286	5.702	22
	*oP*16, *Pnma*				
$ThNi_2$	AlB_2	3.964	–	3.852	21
	*hP*3, *P6mmm*				
$ThNi_5$	$CaCu_5$	4.92–4.97	–	3.99–4.01	21
	*hP*6, $P6/mmm$				
Th_2Ni_{19}	Th_2Ni_{19}	8.36	–	8.16	23
	*hP*80, $P6_3/mmc$				

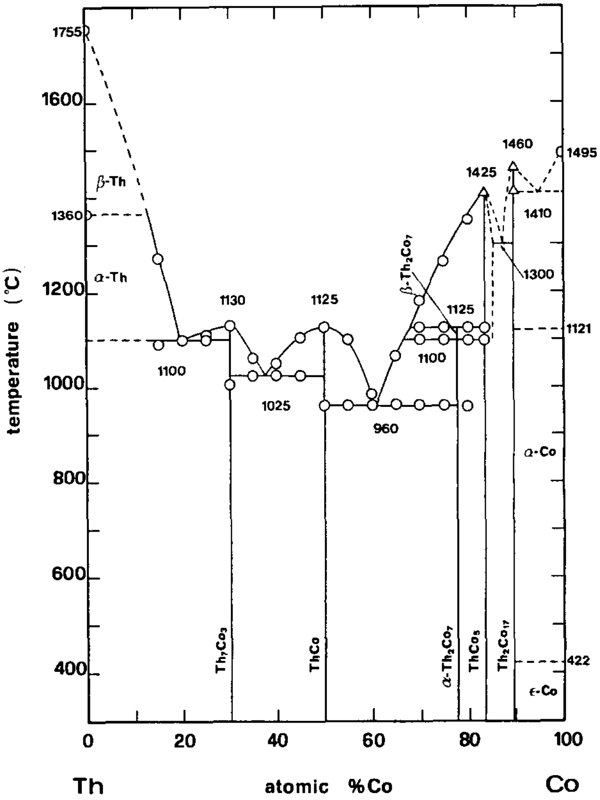

Fig. 2. Phase diagram of the Th–Co system.

The 0–15 and 85–100 at.% Fe, Co and Ni regions of these diagrams have not been investigated, due to contamination of the alloys with container material.

DISCUSSION AND CONCLUDING REMARKS

The shapes of the three diagrams formed by thorium with Fe, Co and Ni are fairly comparable. The most evident differences are the non-existence of a ThFe compound and the fact that the highest melting point in the three binary diagrams shifts from the 2 : 17 (Th–Fe) to the 1 : 5 composition (Th–Ni).

Another difference is in the number of intermetallic compounds, which increases with the atomic number of M. If we also consider the phase diagrams of Th with other elements of the same period, such as Ti, V, Cr or Mn [24], it can be seen that this rule is always observed: the number of compounds increases regularly from 0 (Ti, V, Cr) to 7 (Ni). This may be

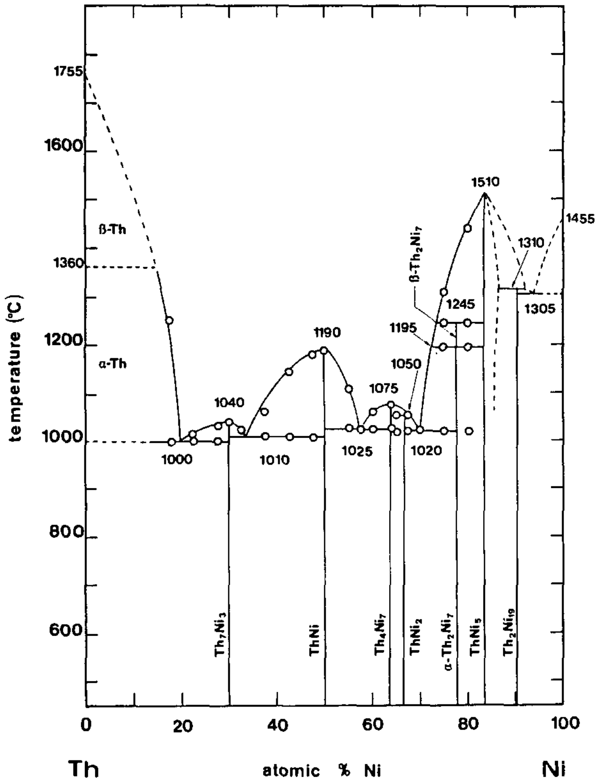

Fig. 3. Phase diagram of the Th–Ni system.

correlated with the increase in the electronegative character of the transition element partner.

An increase in the thermodynamic stability on going from Fe to Co and Ni is shown by the increase in the melting temperatures of the intermetallic compounds, as well as in their Raynor indices [25]. Those of the compositions common to the three systems are listed in Table 3: there is an evident higher stability for the M-rich compounds.

TABLE 3

Raynor index R and melting point T_m (°C) for intermetallic compounds of Th–M systems (M ≡ Fe, Co, Ni)

Compound	Fe		Co		Ni	
	T_m	R	T_m	R	T_m	R
Th_7M_3	940	65	1130	76	1040	72
Th_2M_7	1210	76	1125	71	1245	77
ThM_5	1370	83	1425	86	1510	90

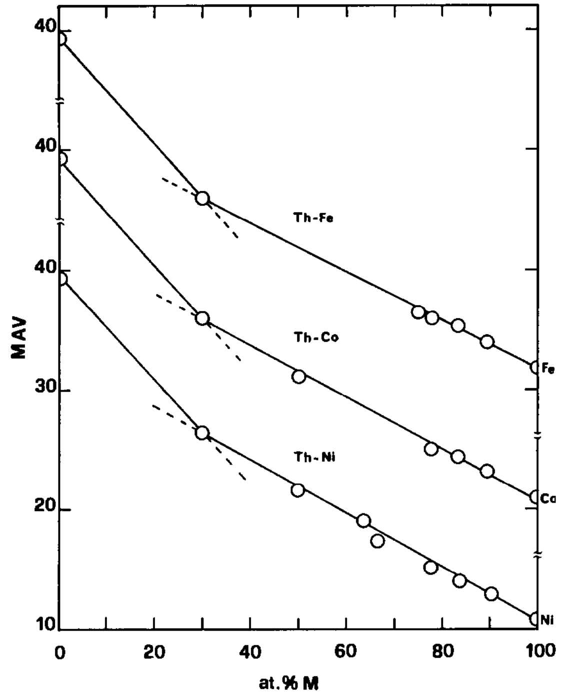

Fig. 4. Mean atomic volumes (MAV) vs. composition for Th–M systems.

It is well known [26] that formation of an intermetallic compound is accompanied by a volume contraction proportional to its stability. This contraction is different for the various compositions and, in general, the trend shows a maximum. A large contraction is related to a large decrease in the free energy of formation and corresponds to high stability. For the rare earth compounds in general, the maximum corresponds to compositions between 65 and 75 at.% M. The behaviour of thorium in the case of Th–Fe, –Co or –Ni is shown in Fig. 4, where the mean atomic volume (MAV) is plotted against the M-composition. It can be seen that the trend is very similar in all three cases, with a maximum in the contraction for the 30 at.% M, i.e. the Th_7M_3 compounds. Interestingly enough, in these systems the thermodynamic stability (Raynor index) does not agree with the structural stability (volume contraction).

The alloying behaviour of thorium with Group VIII elements is summarised in Table 4. A few similarities can be found. There are three common compositions: Th_7M_3, all crystallising with the Th_7Fe_3-type; α- and β-Th_2M_7, all crystallising with the Ce_2Ni_7-type at low temperature and the Gd_2Co_7-type at high temperature; and ThM_5, all crystallising with the $CaCu_5$-type. As regards the more common stoichiometries, 1 : 1, 1 : 2 and 1 : 3, we may note that the equiatomic composition does not exist in the iron

TABLE 4

Structure types found in the Th–M systems (M ≡ Fe, Co, Ni)

[M] (at.%)	Compound	Fe	Co	Ni
30.0	Th_7M_3	Th_7Fe_3	Th_7Fe_3	Th_7Fe_3
50.0	ThM	–	CrB	SrAg
63.6	Th_4M_7	–	–	Th_4Ni_7
66.7	ThM_2	–	–	AlB_2
75.0	ThM_3	$PuNi_3$	–	–
77.8	α-Th_2M_7	Ce_2Ni_7	Ce_2Ni_7	Ce_2Ni_7
	β-Th_2M_7	Gd_2Co_7	Gd_2Co_7	Gd_2Co_7
83.3	ThM_5	$CaCu_5$	$CaCu_5$	$CaCu_5$
89.5	Th_2M_{17}	Th_2Zn_{17}	Th_2Zn_{17}	–
90.5	Th_2M_{19}	–	–	Th_2Ni_{19}

case, the 1 : 2 composition is present only in the nickel case, and the 1 : 3 phase only exists in the iron system.

Comparison of this behaviour with an average rare earth gives rise to only some apparent similarities: the phases are often formed at the same stoichiometry, but are isostructural in only a few cases: Th_2M_7, ThM_5 and Th_2M_{17}. With divalent alkaline earth elements, there are also fewer similarities. In general, the number of compounds formed in each system seems to increase slightly on going from bivalent to trivalent to tetravalent elements. The change in VEC, together with that from light to heavy M partners, seems to play an important role in determining the existence, crystal structure and stability of the phases.

This situation has already been observed in the analysis of the alloying properties of the rare earths and thorium with Group IIIB elements [7], but is rather different from that of Group IVB elements [9], where the VEC change is not as substantial as that from Si to Pb.

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