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TERNARY INTERMETALLIC COMPOUNDS SYNTHESIZED BY MOLTEN-METAL-SOLUTION GROWTH

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Summary

Several new ternary compounds have been synthesized by growing crystals of metallic compounds in a molten-metal solution. Quantum-stability diagrams predict whether a ternary intermetallic compound, a quasi-ternary compound or a binary compound will crystallize from the solution upon slow cooling.

1. Introduction

Recently, a lot of new ternary and quaternary compounds with interesting superconducting and magnetic properties have been discovered. As a consequence, at present a lot of materials research is focussed on finding new promising compounds. In contrast to the abundance of data available on binary systems and binary compounds, very little is known about systems containing more than two components. Several semi-empirical models have been developed to predict which binary systems form intermetallic compounds and which do not. For instance Miedema *et al.* [1] developed a "macroscopic atom" model by which the heat of formation of binary intermetallic compounds can be estimated from the appropriate atomic properties of the pure components. In principle, the heat of formation for ternary intermetallic compounds may also be obtained from this model. Villars and coworkers proposed a different semi-empirical model [2]. They made use of three-dimensional stability diagrams to predict the compound formation in binary systems. By using three expressions, containing values of atomic properties, they were able to separate those binary systems which do not form compounds from those which do form intermetallic compounds. Moreover, by taking another set of expressions as selection criteria they were able to distinguish between the different crystal structures

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of the AB_x intermetallic compounds [3 - 5]. In some recent papers, Villars *et al.* [6, 7] made successful use of quantum-stability diagrams for predictions of stabilities of ternary and quaternary phases. It would be of considerable importance if such semi-empirical models could be developed further to systems with more than two components.

In our search for new ternary intermetallic compounds we restricted ourselves to the synthesis of intermetallic compounds by means of molten-metal-solution growth. Recently Remeika and coworkers published a number of papers on new ternary compounds that were synthesized by such a technique (see, for example, ref. 8). By growing crystals in a molten-metal solution of liquid tin they obtained single crystals of considerable sizes. Among these compounds several interesting ternary superconductors were obtained.

One of the aims of the present study was finding new ternary compounds, but of even more importance was the search for a phenomenological rule to predict whether binary intermetallic compounds or ternary intermetallic compounds will crystallize from the solution upon slow cooling. However, since very few ternary intermetallic systems are known at present in comparison with all possible combinations of three elements, the phenomenological rule that we will present here has a tentative character only. We used quantum-stability diagrams as proposed by Villars [5] to classify the combinations of three metals we used in our molten-metal-solution growth experiments.

2. Experimental procedures and results

A typical molten-metal-solution-growth experiment was carried out as follows. Small amounts of the metals A and B (purities, 99.9%) were weighed together with about 5 g of a metal C (purity, 99.999%). The C metal was tin, gallium, indium or lead, all of which have relatively low melting points. The mixture of about 3 at.% A, 3 at.% B and 94 at.% C was sealed into an evacuated quartz ampoule, 10 cm long and 1 cm in diameter. The ampoule was mounted in a vertical resistance furnace. After a soak time of at least 2 h at 1050 °C the melt was cooled down to a temperature about 100 °C above the melting temperature of the C metal with a cooling rate of 5 °C h^{-1}. After the growth run, the excess C was removed by centrifuging the melt. The remaining crystals were polished and the compositions of the crystals were determined by microprobe analyses. These compositional analyses were performed on a Jeol 747 Superprobe at the Technical University of Eindhoven [9, 10].

From the 48 ternary intermetallic systems we tried, 20 systems resulted in phases in which all three components were present. The crystal sizes and yields varied strongly from one system to another. Often C-rich binary crystals also occurred in the same melt. In Table 1 these systems are listed

TABLE 1

Combinations of elements forming ternary phases in a molten-metal-solution-growth experiment

Components			*Composition of the melt*			*Composition of the crystals*		
A	*B*	*C*	C_a (at.%)	C_b (at.%)	C_c (at.%)	C_a	C_b	C_c
Yb	Co	In	4.57	4.61	90.82	1.10	1.00	4.99
La	Ni	In	4.31	4.25	91.44	1.10	1.00	4.01
La	Pd	In	4.31	3.94	91.75	1.00	1.17	5.06
Zr	Mn	In	2.61	4.65	92.75	x	y	z
Ca	Pd	Sn	4.53	4.17	91.30	1.00	1.34	4.25
Yb	Pt	Sn	4.57	4.53	90.90	1.00	1.37	4.68
Mn	Ni	Sn	4.50	4.50	90.99	1.56	1.10	1.00
						4.74	1.00	12.05
Sc	Ni	Sn	4.47	4.54	90.99	1.00	1.33	2.51
Yb	Ni	Ga	2.80	3.74	93.46	1.00	2.56	6.33
Zr	Ni	Ga	2.68	3.71	93.61	1.00	1.09	4.27
Ti	Ni	Ga	2.36	3.67	93.97	1.00	1.99	5.27
Mn	Ni	Ga	2.41	3.86	93.73	4.37	1.00	16.04
Y	Co	Ga	2.41	4.36	93.23	1.07	1.00	4.43
Ca	Pd	Ga	2.80	3.74	93.46	1.00	2.64	7.99
Pr	Pd	Ga	2.62	3.75	93.63	2.13	1.00	10.62
Yb	Pd	Ga	2.81	3.74	93.46	1.00	2.40	7.36
Y	Pd	Ga	1.72	1.92	96.35	3.99	1.00	9.92
Sc	Au	Ga	3.73	3.70	92.56	5.29	1.00	12.39
Sc	Pt	Ga	3.68	3.69	92.62	1.00	1.22	3.27
						1.00	1.10	2.60
						1.13	1.00	1.91
						1.34	1.00	2.37
Sc	Pd	Ga	4.03	4.02	91.94	10.89	1.00	22.26

The starting composition of the melt is given in the second column. The C element is the major component in the melt and is the component with the lowest melting temperature. The composition of the ternary phases, obtained from the growth experiments, are given in the third column.

together with the starting melt composition and the compositions of the ternary crystals obtained after the growth run. The 28 ternary melts from which only binary intermetallic compounds were obtained are listed in Table 2. The starting melt composition is given along with the components, which were determined in the crystals resulting from the growth experiments. In several cases more than one binary phase was found. Although we did not measure the exact composition of the binaries, A–C or B–C compounds were always obtained with C the major component in these phases.

Even if three elements were found in the crystals, the real ternary character may be questionable. For the Mn–Ni–Ga and the Mn–Ni–Sn systems, low nickel concentrations were found. However, because of the strong resemblance of nickel to manganese, $Mn_5Ni_1Sn_{12}$ and $Mn_4Ni_1Ga_{16}$ are

TABLE 2

Combinations of elements forming binary phases only in a molten-metal-solution-growth experiment

Components			*Composition of the melt*			*Component in crystals*
A	*B*	*C*	C_a (at.%)	C_b (at.%)	C_c (at.%)	
Mn	Pd	In	4.57	4.53	90.91	Mn–In, Pd–In
Nd	Pd	In	6.51	2.50	91.00	Nd–In
			4.53	4.55	90.92	Nd–In
			8.66	3.33	88.00	Nd–In
			6.01	6.00	87.99	Nd–In
Ho	Zr	In	4.55	4.55	90.90	Ho–In, Zr
Yb	Fe	In	4.53	4.53	90.94	Yb–In
Yb	Ni	In	4.53	4.54	90.93	Yb–Ni, Yb–In, Ni–In
Yb	Pd	Sn	4.63	4.47	90.91	Yb–Sn, Pd–Sn, Yb
W	Pd	Sn	4.57	4.57	90.86	Pd–Sn, W
Nb	Pt	Ga	1.92	1.92	96.16	Pt–Ga
Nb	Ir	Ga	3.64	3.78	92.57	Ir–Ga
Nd	Ir	Ga	2.34	3.68	93.98	Ir–Ga
Ta	Ir	Ga	3.70	3.71	92.59	Ir–Ga
Y	Mo	Ga	2.78	3.21	94.01	Mo–Ga
			3.60	4.02	92.38	
			1.67	1.69	96.37	
Zr	Rh	Ga	2.27	1.94	95.80	—
Zr	Mo	Ga	1.77	2.21	96.02	Mo–Ga
			2.61	2.70	94.69	
Sc	Mo	Ga	1.69	1.73	96.58	Mo–Ga
Zr	Pd	Ga	1.91	1.92	96.17	Zr–Ga, Pd–Ga
Nb	Pd	Ga	2.32	3.70	93.98	Nb–Ga, Pd–Ga
Nd	Ru	Ga	3.54	3.71	92.76	Ru–Ga
Ho	Nb	Ga	2.73	3.74	93.53	Ho–Ga
Dy	Nb	Ga	2.75	3.74	93.51	Dy–Ga
Mo	Ni	Ga	2.73	3.72	93.56	Ni–Ga
Sc	Rh	Ga	2.75	3.71	93.54	Rh–Ga
V	Rh	Ga	2.81	3.71	93.48	Rh–Ga, V–Ga
			2.40	2.83	94.77	—
V	Fe	Ga	2.78	3.78	93.44	Fe–Ga, V–Ga
Ti	Pd	Ga	2.81	3.38	93.81	Pd–Ga, Ti–Ga
Y	Pt	Ga	3.81	3.21	92.97	Pt–Ga, Y–Ga
Zr	Pd	Pb	1.19	3.71	85.10	Zr–Pb, Zr–Pd
Zr	Pt	Pb	1.11	4.25	84.64	Zr–Pt, Zr

The starting composition of the melt is given in the second column. The C element is the major component in the melt and is the component with the lowest melting temperature. In the third column the binary systems obtained from the growth experiment are given.

most probably quasi-ternary phases, with 17% of the manganese sublattice occupied by nickel in the binary $MnSn_2$, and 19% of the sites occupied by nickel in the binary $MnGa_3$.

3. Discussion

By using the concept of stability diagrams proposed by Villars [2], we were able to separate the systems that do form ternary intermetallic compounds from those that do not. To make the appropriate choice of configuration coordinates we examined several combinations of expressions based on the atomic properties involved. We considered the following coordinates:

$$x = |\Delta R_{AB}| + |\Delta R_{AC}| + |\Delta R_{BC}|$$

$$y = \frac{T_A}{T_B} + \frac{T_A}{T_C} + \frac{T_B}{T_C} \qquad TA > T_B > T_C$$

$$z = |\Delta X_{AB}| + |\Delta X_{AC}| + |\Delta X_{BC}|$$

$$t = |\Delta V_{AB}| + |\Delta V_{AC}| + |\Delta V_{BC}|$$

where ΔR_{AB} is the difference between the radii of atoms A and B, T_A is the melting point of A, ΔX_{AB} is the difference in electronegativity between A and B, and ΔV_{AB} is the difference in the number of valence electrons of A and B. The C component is always the major component present in the melt. The values of the atomic properties are listed in a paper of Villars [5]. We used these data to calculate the configuration coordinates x, y, z and t.

Apart from the ternary systems we investigated ourselves, 65 ternary or quasi-ternary crystals grown in a molten metal solution have been found by Remeika *et al.* [8, 11 - 13]. Since the phases, called by them phase V and phase VII, are ternary phases with a very low concentration of the third component, we classified these phases as quasi-ternary intermetallic compounds. For the total number of 113 ternary systems, the best separation was obtained using x and y as the coordinates (x–y diagram). This means that only the atomic radii and the melting temperatures of the pure components constituting the ternary system play an important role in whether a binary or a ternary compound will be grown in the solution. A third axis, with the sums of the absolute differences of the valencies (t) as the third coordinate, hardly improves the resolving power of the diagrams. The electronegativity (z) turned out not to have a strong influence on the compound formation in molten-metal solution growth.

The quantum-stability diagram is plotted in Fig. 1. The ternary systems, from which a ternary intermetallic phase was obtained, are denoted by triangles. The crosses represent the ternary systems from which only binary phases were segregated from the melt. The open circles are used in the plot for those systems that generated quasi-ternary phases.

From the systems for which

$$\frac{T_A}{T_B} + \frac{T_A}{T_C} + \frac{T_B}{T_C} > 14$$

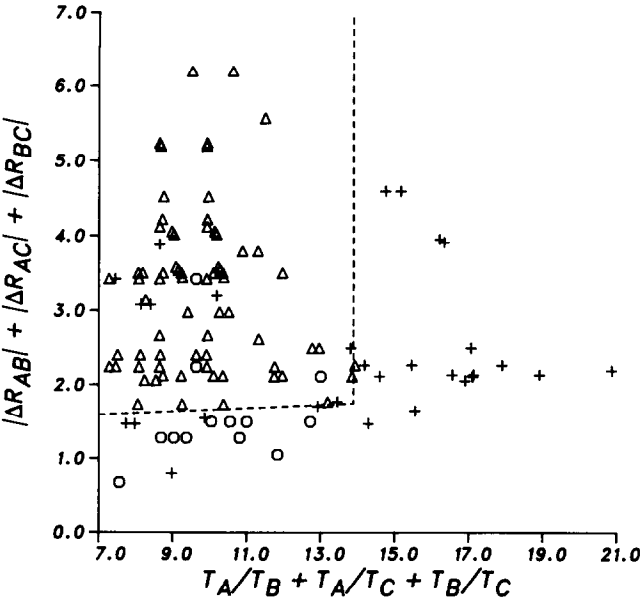

Fig. 1. Quantum-stability diagram for x *vs.* y: triangles, systems giving ternary phases; open circles, systems giving quasi-ternary phases; crosses, systems giving only binary phases.

only binary compounds were obtained from the crystal-growth experiments. For these systems the melting temperatures of the A and the B elements are considerably higher than the melting temperature of the C element. From the diagram it is shown that to obtain ternary phases we must have

$$\frac{T_A}{T_B} + \frac{T_A}{T_C} + \frac{T_B}{T_C} < 14$$

The quasi-ternary phases are mainly situated in the region for which

$$|\Delta R_{AB}| + |\Delta R_{AC}| + |\Delta R_{BC}| < 1.8$$

Thus, to obtain ternary intermetallic compounds by a molten-metal-solution growth, the melting temperatures of the pure elements constituting the ternary system should not differ too much, and, in contrast, the difference in atomic radii should not be too small. The region in the quantum-stability diagram for intermetallic compounds is given by the two inequalties:

$$\frac{T_A}{T_B} + \frac{T_A}{T_C} + \frac{T_B}{T_C} < 14$$

$$|\Delta R_{AB}| + |\Delta R_{AC}| + |\Delta R_{BC}| > 1.8$$

In this region, where the ternary intermetallic compounds are actually situated, 7 violations of the above rule occurred: the ternary systems Ho–Zr–In, Yb–Pd–In, Yb–Ni–In, Yb–Fe–In, Nd–Pd–In, Yb–Ru–In and Ca–Ru–Sn. By further investigation of component solubility and crystal-

growth conditions, ternary phases might eventually be obtained for these systems.

For those regions where no ternary phases have been encountered, it may be concluded that no ternary crystals can be grown from a molten-metal solution.

4. Conclusions

Quantum-stability diagrams, as proposed by Villars, are useful in deciding whether or not ternary compounds are formed in molten-metal-solution growth. Two quantities as diagram coordinates, containing the melting points and the differences in radii respectively of the constituent elements, turned out to be sufficient for separating regions where ternary and where binary compounds are formed.

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