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Ternary phases forming adjacent to Al_3Mn–Al_4Mn in Al–Mn–TM (TM = Fe, Co, Ni, Cu, Zn, Pd)

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ABSTRACT

The Al–Mn alloy system contains complex intermetallics in its Al-rich part, and this was the first system where quasiperiodic structures were recognized. In the present work, the solubility of TMs (TM = Fe, Co, Ni, Cu, Zn and Pd) in the stable binaries, the stabilization effect of these elements on the metastable binaries and the formation of ternary compounds are specified and compared. While the solubility of all these TMs in hexagonal μ-Al_4Mn and λ-Al_4Mn is low, the high-temperature orthorhombic T-Al_3Mn dissolves up to at least 14.5, 12, 16 and 7.5 at.% Fe, Cu, Zn and Pd, respectively. The metastable hexagonal φ-$Al_{10}Mn_3$ is stabilized by Fe, Co and Ni in wide ternary compositional regions, and in Al–Co–Mn such a region propagates up to Al_5Co_2. In alloys with Fe, Co and Ni, a ternary hexagonal phase isostructural to the Al–Cr–Ni ζ-phase ($P6_3/m$, $a \approx 1.76$, $c \approx 1.25$ nm) is formed along ~80 at.% Al, while in alloys with Cu and Pd the orthorhombic so-called R-phase ($Bbmm$, $a \approx 2.41$, $b \approx 1.25$, $c \approx 0.76$ nm) was found at similar compositions. This structure is also known in Al–Zn–Mn but at much lower-Al $Al_{68}Zn_{14.5}Mn_{17.5}$, while in the range of 75–80 at.% Al a monoclinic phase isostructural to η-$Al_{11}Cr_2$ ($C2/c$, $a \approx 1.76$, $b \approx 3.04$, $c \approx 1.76$ nm, $\beta \approx 90°$) is formed. In addition to the stable decagonal D_3-phase in Al–Fe–Mn and Al–Pd–Mn reported earlier, the stabilization of binary Al–Mn D_3-phase was revealed around $Al_{64}Cu_{20}Mn_{16}$.

1. Introduction

Investigations of binary and ternary aluminum alloys with manganese and other transition elements have been in progress since the beginning of the 20th century. Particularly, the binary Al–Mn phase diagram has been significantly revised several times. Its Al-rich part contains several complex intermetallic phases, and the formation of quasiperiodic icosahedral and decagonal structures was reported for the first time in this alloy system. First experiments with ternary alloys based on Al–Mn started long before there was good knowledge of the boundary binary phase diagrams. This primarily concerned the systems containing the elements adjacent to Mn in the periodic table such as Cr, Fe, Co, Ni, Cu and Zn. Even at the moment the information on these systems is controversial.

For the following description the relevant part of the Al–Mn phase diagram in the presently accepted form is shown in Fig. 1 [1] and the crystallographic data of the relevant phases are provided in Table 1. It should be noted that the presence of two phases close to the Al_3Mn composition, forming at higher and lower temperatures, was established only in 1960 [2], while the metastable so-called φ-$Al_{10}Mn_3$ phase was still recognized at that time as stable. The present configuration of this compositional region was specified only in 1971 [3].[1] The presently accepted positioning of the μ-Al_4Mn and λ-Al_4Mn was argued in 1987 [4], i.e. after the discovery of the

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[1] In the literature the high-temperature phase designated Al_3Mn [2] or h-$Al_{11}Mn_4$ [3] is frequently named Taylor's phase (T-phase). On the other hand, in several publications cited below, T was used to designate any ternary phase. In order to avoid confusion, the symbols of these ternary phases are supplied by subscripts indicating the third element, for example, T_{Cu} for a ternary phase in Al–Cu–Mn.

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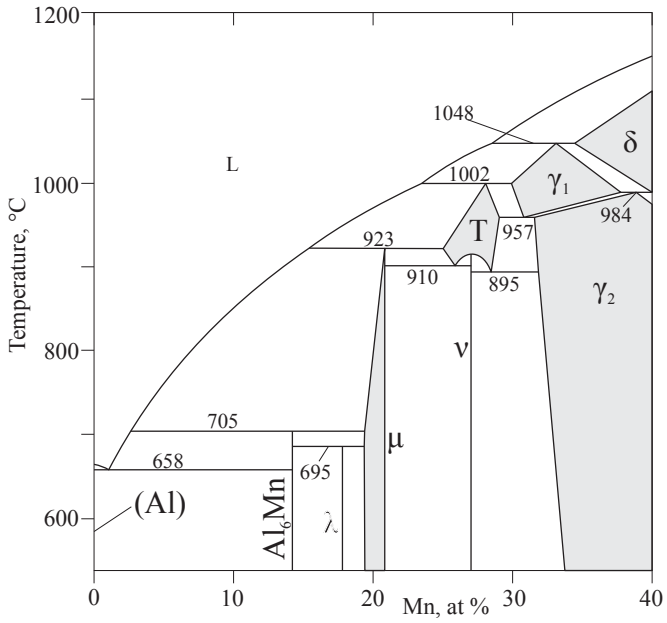

Fig. 1. Partial Al–Mn phase diagram [1]. The phases are specified in Table 1.

metastable Al–Mn quasicrystals close to these compositions. Since the first studies the structures of the binaries have also been under discussion.

The ternary Al–Cu–Mn system attracted attention much earlier. Two complex orthorhombic structures were reported there by Petri [5] on the basis of the X-ray diffraction study of needle-shaped single crystals. The phase designated T (T_{Cu} in the following, $a = 0.769$, $b = 2.406$ and $c = 1.248$ nm) was found between ~$Al_{80.1}Cu_{7.8}Mn_{12.1}$ and ~$Al_{77.7}Cu_{6.9}Mn_{15.4}$, i.e. close to the binary Al_4Mn phase. The other phase designated Y ($a = 1.479$, $b = 1.260$, $c = 1.243$ nm) was observed in a range of compositions adjacent to Al–Mn, particularly a composition ~$Al_{76.9}Cu_{3.1}Mn_{20.0}$ was reported.

In a study of Al–Cu–Mn alloys Raynor [6] cited Petri's findings without confirming or negating them. No ternaries were revealed in this work in Al–Co–Mn and Al–Fe–Mn, which dealt only with very low concentrations of the third elements. On the other hand, the same author also reported two ternary Al–Ni–Mn phases [7]. One of them, designated X, was revealed in a small compositional region around $Al_{60}Mn_{11}Ni_4$ ($\approx Al_{80}Ni_{5.3}Mn_{14.7}$), i.e. its Al and Mn concentrations were close to those of Petri's T_{Cu}-phase. The composition of the other ternary Al–Ni–Mn phase, designated Y and suggested to be metastable, was not specified. No structural information on these phases was provided in Ref. [7].

In Ref. [8] three ternary phases designated T_1, T_2 and T_3 were reported in Al–Zn–Mn (T_{Zn1}, T_{Zn2} and T_{Zn3} in the following). The composition of the T_{Zn1}-phase ~$Al_{80}Zn_{3.2}Mn_{16.8}$ was found to be "equivalent" to those of $Al_{60}Mn_{11}Ni_4$ or $Al_{20}Mn_3Cu_2$ [8], considering their very close electron-to-atom ratio e/a $\approx$ 1.85. In a later Ref. [9] by Robinson, the single crystals of both $Al_{60}Mn_{11}Ni_4$ and $Al_{20}Mn_3Cu_2$ were reported to be orthorhombic, structurally very similar between them and also similar to that of Petri's T_{Cu}-phase (*Bbmm*, $a = 2.38$, $b = 1.25$, $c = 0.755$ nm, R-phase in the following), but the structure of $Al_{80}Zn_{3.2}Mn_{16.8}$ was different. On the other hand, a great similarity to the R-phase was concluded in Ref. [10] for the T_{Zn3}-phase despite its quite different composition of $Al_{67.4}Zn_{15.7}Mn_{16.9}$ ($Al_{68.8}Zn_{13.7}Mn_{17.5}$ according to [8]). More recently, the structure of T_{Zn1} was concluded to be rather similar to that of the monoclinic ($\beta \approx 90°$) $Al_{11}Cr_2$ phase [11]. The structure of the T_{Zn2}-phase forming at intermediate composition Al_9ZnMn_2 ($Al_{74.7}Zn_{8.3}Mn_{16.7}$) was not reported. A structural model of $Al_{60}Mn_{11}Ni_4$ published in Ref. [12] was expected to be applicable to $Al_{20}Mn_3Cu_2$, while for T_{Zn3} some different cite occupancies were derived in Ref. [10] due to another ratio between the Al and TM concentrations. At that time the phase equilibria in the corresponding ternary systems were not yet established. For the following description the relevant details of the quoted ternary phase diagrams are presented in Fig. 2 according to the presently available literature data.

Table 1
Crystallographic data of the relevant phases. TW means this work.

Phase	Space group	Lattice parameters			Ref. Comment
		a, nm *α, °*	*b, nm* *β, °*	*c, nm* *γ, °*	
Al_6Mn	*Cmcm*	0.75551	0.64994	0.88724	[1]
λ-Al_4Mn	*P6₃/m*	2.8382	–	1.2389	[26]
μ-Al_4Mn	*P6₃/mmc*	2.0015	–	2.4699	[18], $Al_{79.8}Mn_{20.2}$
T-Al_3Mn	*Pnma*	1.4873	1.2420	1.2547	[46], $Al_{72.8}Mn_{27.2}$
(h-$Al_{11}Mn_4$)		1.46256(6)	1.24557(4)	1.25469(6)	TW, $Al_{70}Cu_{11.5}Mn_{18.5}$, Appen. A
		1.4782	1.2423	1.2524	[21], $Al_{73}Fe_2Mn_{25}$
		1.4726	1.2514	1.2605	[46], $Al_{72.4}Pd_{6.5}Mn_{21.1}$
		1.48447(5)	1.25024(7)	1.26359(6)	TW, $Al_{66}Zn_{16}Mn_{18}$
φ	*P6₃/mmc*	0.7543	–	0.7898	[1], $Al_{10}Mn_3$
		0.76632	–	0.78296	[18], $Al_{73.1}Ni_{7.8}Mn_{19.1}$
		0.7580(1)	–	0.7879(1)	TW, $Al_{74.7}Co_{3.7}Mn_{21.6}$
		0.7554	–	0.7872	[21], $Al_{76.1}Fe_{6.2}Mn_{17.7}$
ζ	*P6₃/m*	1.7625	–	1.2516	[18], $Al_{80.3}Ni_{2.2}Mn_{17.5}$
		1.7562(2)	–	1.2459(2)	TW, $Al_{80.0}Ni_{5.3}Mn_{14.7}$
		1.7536(3)	–	1.2444(2)	TW, $Al_{80.0}Ni_{2.7}Cu_{2.7}Mn_{14.6}$
		1.7530(3)	–	1.2440(2)	TW, $Al_{80.0}Ni_{1.9}Cu_{3.5}Mn_{14.6}$
		1.76058(7)	–	1.24638(3)	TW, $Al_{80}Co_{3.1}Mn_{16.9}$, Appen. C
		1.7630	–	1.2506	[21], $Al_{81.4}Fe_{3.6}Mn_{15.0}$
R	*Bbmm*	2.41023(15)	1.24787(8)	0.76102(7)	TW, $Al_{80}Cu_8Mn_{12}$, Appen. B
		2.4106(4)	1.2495(2)	0.7645(1)	TW, $Al_{80.0}Ni_{0.9}Cu_{4.6}Mn_{14.5}$
O	Orth.	2.3316	1.2424	3.2648	[18], $Al_{78.4}Ni_{8.3}Mn_{13.3}$
η	*C2/c*	1.7615(1)	3.0362(3)	1.7598(2)	TW, $Al_{74.4}Zn_{9.0}Mn_{16.6}$, Appen. D
		–	90.656(8)	–	