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Rational approximants to the decagonal phase in Al–Mn–M (M = Ni, Cu, Zn) systems

Alok Singh and S. Ranganathan

Centre for Advanced Study, Department of Metallurgy, Indian Institute of Science, Bangalore 560 012 (India)

Abstract

A series of alloys ($Al_{60}Mn_{11}Ni_4$, $Al_{76}Mn_{15.5}Cu_{8.5}$, $Al_{65}Mn_{15}Cu_{20}$, $Al_{24}Mn_5Zn$ and $Al_{12}Mn_{2.9}Zn$) have been prepared in as-cast and rapidly solidified conditions. The occurrence of icosahedral and decagonal quasi-crystalline phases as well as rational approximants to the decagonal phase has been established by electron microscopy. This comparative study highlights the similarities and differences among the closely related crystalline phases serving as rational approximants to the decagonal phase in the three systems Al–Mn–Ni, Al–Mn–Cu and Al–Mn–Zn. Structural features as well as the propensity for twinning of the crystals have been characterized.

1. Introduction

In 1978, Sastry *et al.* [1] reported an unknown phase in $Al_{60}Mn_{11}Ni_4$ alloy which was later to be identified as a decagonal phase [2, 3]. Owing to the presence of centred pentagons and layered structure in the crystalline $Al_{60}Mn_{11}Ni_4$ phase [4], it was regarded as a rational approximant structure of the decagonal quasi-crystal by Van Tendeloo *et al.* [5]. These investigators reported a detailed study on the $Al_{60}Mn_{11}Ni_4$ alloy in which annealing of the decagonal phase for 100 h at 400 °C gave rise to two rational approximant phases.

The $Al_{20}Mn_3Cu_2$ and the T3-(Al–Mn–Zn) phases are isostructural to the $Al_{60}Mn_1Ni_4$ phase [6], and thus can also be considered as rational approximant phases to the decagonal phase [7]. The electronic structure of the T1-(Al–Mn–Zn) phase is similar to those of the $Al_{60}Mn_{11}Ni_4$ and $Al_{20}Mn_3Cu_2$ phases [8]. Lilienfeld *et al.* [9] obtained quasi-crystals in the alloys with compositions near these isostructural $Al_{60}Mn_{11}Ni_4$, $Al_{20}Mn_3Cu_2$ and $Al_{11}Mn_3Zn_2$ phases by ion beam mixing.

The rational approximant phases in Al–Mn–Cu alloys have been studied by Li and Kuo [10] in a contemporary fashion to the current work. Although the Al–Mn–Zn system appears promising from the point of view of the quasi-crystalline and the rational approximant phase formation, it has not been studied extensively so far.

A study of quasi-crystalline phases in the three ternary systems Al–Mn–Ni, Al–Mn–Cu and Al–Mn–Zn is reported here. In all the three systems two coexisting phases appeared on the decomposition of the decagonal phase.

2. Experimental procedures

Alloys of composition $Al_{60}Mn_{11}Ni_4$, $Al_{76}Mn_{15.5}Cu_{8.5}$, $Al_{65}Mn_{15}Cu_{20}$, $Al_{24}Mn_5Zn$ and $Al_{12}Mn_{2.9}Zn$ were prepared by induction melting of high purity metals in an inert atmosphere and were rapidly solidified by either melt spinning on a copper wheel or twin rolling on stainless steel rollers. The melt-spun ribbons were thinned by ion milling and observed in a JEOL 2000FX-II transmission electron microscope.

3. Results

3.1. The Al–Mn–Ni alloy

The melt-spun $Al_{60}Mn_{11}Ni_4$ alloy formed a decagonal quasi-crystal. Figure 1 shows a tenfold diffraction pattern and a high resolution micrograph of a grain in a tenfold orientation. The diffraction spots are slightly streaked and the micrograph shows a mixture of lattice spots in a ring-like as well as linear arrangements. The linear arrangement of the spots is more or less periodic with a spacing of approximately 0.96 nm. A similar observation was reported by Van Tendeloo *et al.* [5].

The decagonal phase in the melt-spun alloy transformed to periodic structures after annealing at 600 °C for 2 h. Figure 2 shows diffraction patterns obtained from the periodic structures in the annealed alloy. The pattern in Fig. 2(a) shows streaking. The origin of this streaking can be seen in the high resolution micrograph taken along this zone axis, shown in Fig. 3. In some regions a rhombic unit mesh of 1.17 nm and 36° can be defined. This is attributed to a body-centred ortho-

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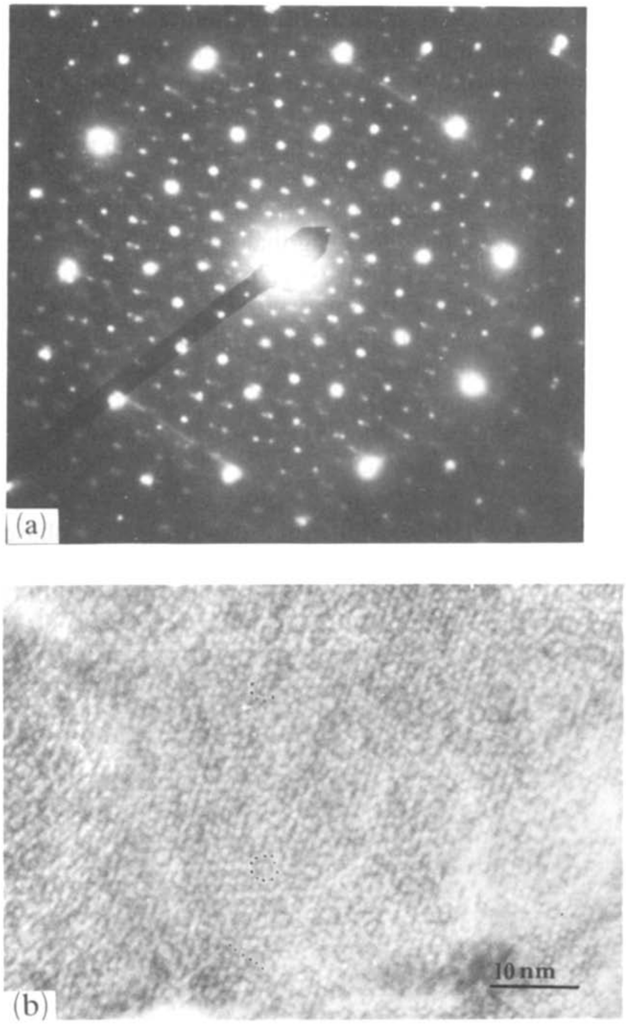

Fig. 1. (a) A tenfold symmetry diffraction pattern and (b) a high resolution micrograph showing the tenfold-oriented region of the decagonal phase in melt-spun $Al_{60}Mn_{11}Ni_4$ alloy.

rhombic structure T whose unit cell is deduced to be $a = 1.24$ nm, $b = 1.26$ nm and $c = 3.14$ nm. the diffraction patterns of Fig. 2 are thus along [100] and [001] zone axes and the high resolution micrograph of Fig. 3 is thus along the [100] zone axis of the T phase. A number of planar faults are observed, giving rise to streaked spots in the diffraction. In the regions of these faults another cell of 2.84×1.63 nm^2 is observed which is attributed to another, as yet unidentified, phase.

3.2. The Al–Mn–Cu alloys

The twin-rolled $Al_{76}Mn_{15.5}Cu_{8.5}$ and melt-spun $Al_{65}Mn_{15}Cu_{20}$ alloys showed the presence of the Al_3Mn phase. The diffraction evidence and the high resolution electron micrographs showed the presence of yet another phase coexisting with the Al_3Mn phase in the rapidly solidified alloys. This phase was first

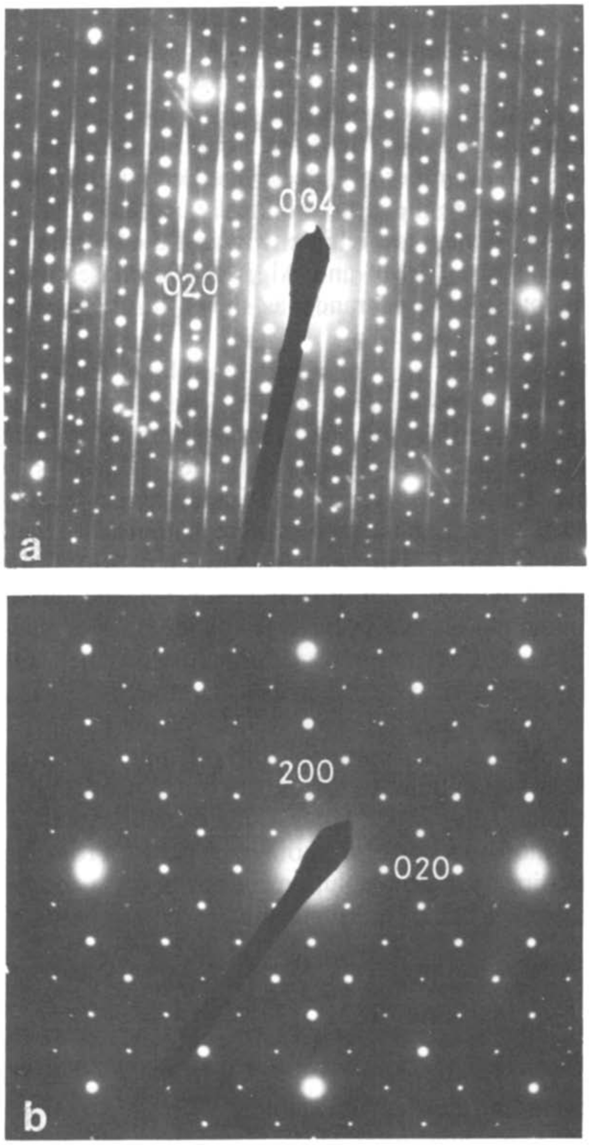

Fig. 2. (a) The [100] and (b) the [001] zone axis pattern of the T phase from the transformed regions of the decagonal phase in $Al_{60}Mn_{11}Ni_4$.

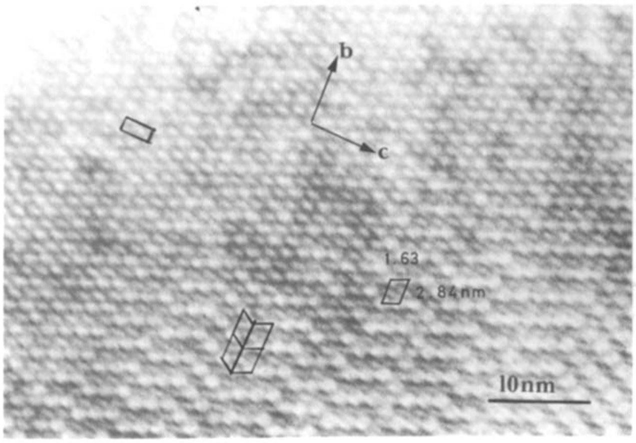

Fig. 3. A high resolution micrograph along the [100] axis of the T phase in $Al_{60}Mn_{11}Ni_4$.

reported to be an unknown monoclinic X phase [11] but was later identified to be the $Al_{20}Mn_3Cu_2$ phase with a B-centred orthorhombic structure [12]. The presence of the two phases is shown in Fig. 4. The $Al_{20}Mn_3Cu_2$ phase in [010] orientation is observed in this figure. A number of defects (marked with arrows) are visible where the structure locally becomes that of the Al_3Mn. Owing to multiple twinning, the diffraction patterns of the Al_3Mn and $Al_{20}Mn_3Cu_2$ phases have a psuedotenfold appearance, as shown in the inset in Fig. 4.

3.3. *The Al–Mn–Zn alloys*

The $Al_{24}Mn_5Zn$ ribbons consist entirely of the icosahedral quasi-crystal while the $Al_{12}Mn_{2.9}Zn$ ribbons showed the presence of a decagonal quasi-crystal. The melt-spun samples were isothermally aged at 500 and 600 °C. On aging $Al_{24}Mn_5Zn$ at 500 °C for 0.5 h and $Al_{12}Mn_{2.9}Zn$ at 600 °C for 1 h, the quasi-crystalline phases transformed to the identical crystalline phases. The major transformation product was found to be a body-centred orthorhombic (T) phase, similar to that observed in the Al–Mn–Ni alloy.

Several zone axis patterns from this phase showed streaking and extra weak spots between T-phase spots, resembling superlattice spots. This can be explained due to the copresence of another phase M. From the observation of high resolution micrographs, a monoclinic unit cell can be assigned with

$$a_M = d_{(1\bar{1}0)_T}$$

$$b_M = c_T$$

$$c_M = d_{(110)_T}$$

(d denotes the interplanar distance).

Figure 5 shows the [110] zone axis diffraction pattern of the T phase and a high resolution micrograph from a grain in [110] orientation. The high resolution micrograph features heavy planar faulting which explains the streaking of reciprocal spots. Owing to the presence of faults the unit cell in some regions has changed. The two cells present are outlined in the micrograph.

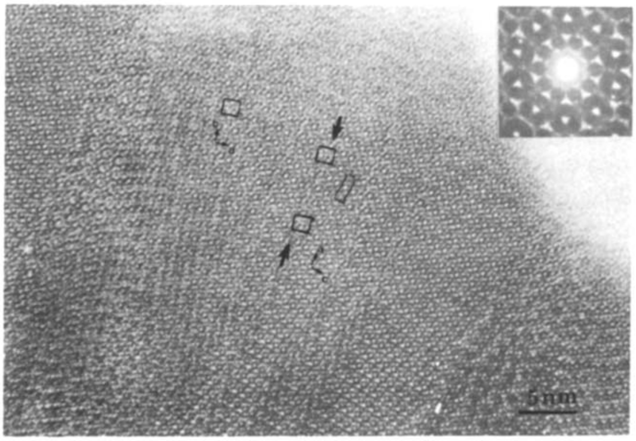

Fig. 4. A high resolution micrograph of a grain in Al_3Mn[010] orientation in twin-rolled $Al_{76}Mn_{15.5}Cu_{8.5}$ alloy.

On further annealing of the $Al_{24}Mn_5Zn$ alloy for 25.5 h at 600 °C, a hexagonal phase with lattice parameters $a = 2.84$ and $c = 1.26$ nm appeared. This phase is identical to the reported λ-Al_4Mn phase [13]. The details of the study on the Al–Mn–Zn alloys will be published elsewhere [14].

4. Discussion

It is important to note that the decagonal phase decomposes to two interrelated approximant phases in

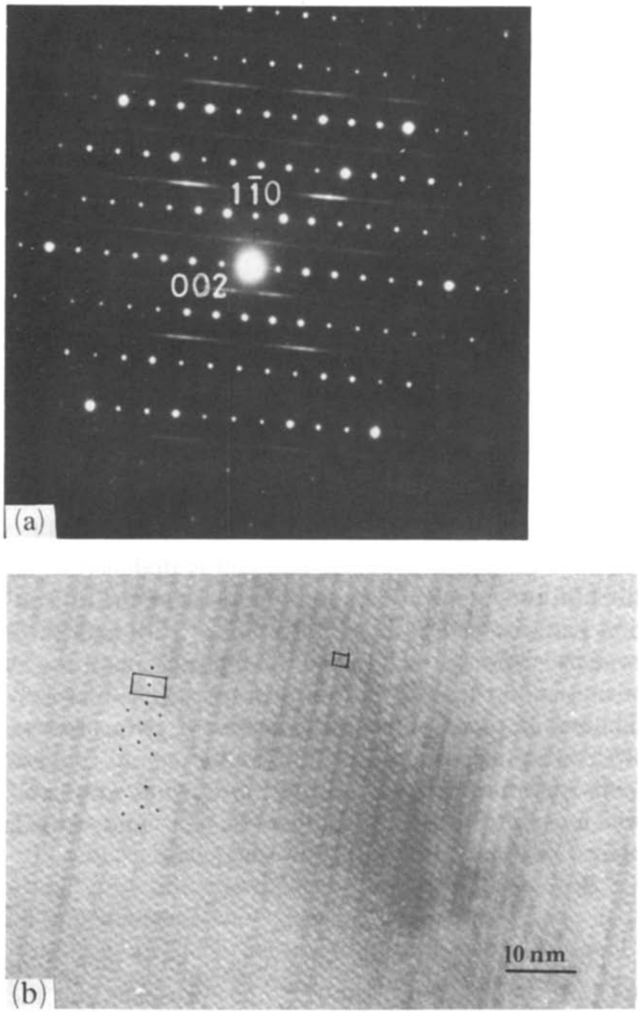

Fig. 5. (a) The [110] zone axis diffraction pattern and (b) a high resolution micrograph showing planar defects in the [110] orientation of the T phase in the melt-spun $Al_{12}Mn_{2.9}Zn$ alloy aged at 600 °C for 1 h.

Al–Mn–Cu, Al–Mn–Ni and Al–Mn–Zn alloys. All the approximants have a high density of defects initially and often the two approximants can be related through these defects. An interesting observation is that the quasi-crystalline phases in $Al_{60}Mn_{11}Ni_4$ and the Al–Mn–Zn alloys decompose to the same crystalline phase T. The relationship of the T phase to the decagonal phase will be brought out in a subsequent publication [14].

The earlier study by Van Tendeloo *et al.* [5] on the $Al_{60}Mn_{11}Ni_4$ alloy showed that the decagonal phase was fairly stable at 400 °C so that it took 100 h to transform it to crystalline phases. In the present study the transformation was complete at 600 °C in 2 h. Although the two phases obtained here at 600 °C do not appear to be quite the same as those obtained by Van Tendeloo *et al.* [5] at 400 °C, the lattice parameters of the T phase are close to their $C_{3,II}$ phase which has lattice parameters of 1.24, 1.26 and 2.68 nm.

It is clearly established that the quasi-crystal is readily formed in the composition corresponding to the T1 phase $Al_{24}Mn_5Zn$, which has an e/a ratio of 1.85 [15]. Though a similarity to the lattice cell would place T3 in the same class as $Al_{60}Mn_{11}Ni_4$ and $Al_{20}Mn_3Cu_2$, its stoichiometry ($Al_{11}Mn_{2.8}Zn_{2.2}$) is different, approximately $Al_2(Mn,Zn)$. The $Al_{60}Mn_{11}Ni_4$, $Al_{20}Mn_3Cu_2$ and T1 phases correspond to the Al_4Mn prototype structure.

The introduction of streaking in the reciprocal space by the defects in the decagonal crystalline approximants is an important observation, as the streaking of reciprocal spots is an important characteristic of the decagonal phase. The sheets of intensity perpendicular to the decagonal axis transform to lines of intensity in crystalline approximants, as observed in the T phase. This disappears on further transformation.

5. Conclusions

The quasi-crystalline phases and the rational approximant phases of the decagonal quasi-crystal have been studied in Al–Mn–Cu, Al–Mn–Zn and Al–Mn–Ni alloys. The following are the major conclusions which emerged from the study.

(1) The $Al_{60}Mn_{11}Ni_4$ decagonal phase transformed to two crystalline phases on annealing at 600 °C for 2 h. One of these phases T is a body-centred orthorhombic phase with lattice parameters $a = 1.24$ nm, $b = 1.26$ nm and $c = 3.14$ nm. The other phase, unidentified, appears to be a superstructure of the T phase.

(2) Rapid solidification of the $Al_{76}Mn_{15.5}Cu_{8.5}$ and $Al_{65}Mn_{15}Cu_{20}$ alloys results in the formation of grains which give diffraction patterns strikingly similar to those from a decagonal quasi-crystal. This effect has been shown to be due to the twinning of the Al_3Mn and $Al_{20}Mn_3Cu_2$ phases and their coexistence.

(3) The icosahedral and decagonal quasi-crystals in the Al–Mn–Zn alloys transformed on annealing at 500 and 600 °C to an orthorhombic phase T, similar to the T phase in Al–Mn–Ni alloy, and a monoclinic phase M.

(4) A prolonged annealing for 25.5 h at 600 °C gives rise to the λ-Al_4Mn type of hexagonal phase with lattice parameters $a = 2.86$ nm and $c = 1.24$ nm in $Al_{24}Mn_5Zn$.

Acknowledgments

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