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Interfacial diffusion effect on phase transitions in Al/Mn multilayered thin films

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Abstract Thin films of Al and Mn multilayers were synthesized using thermal evaporation under high vacuum conditions. The whole film thickness containing three bilayers of Al and Mn is about 120 nm. The global concentration of the samples was varied between 10 and 46.5 at.% Mn, by changing the thickness of the bilayer. The as-evaporated samples were heat treated at different temperatures (473, 623, 823 and 873 K) for 2 and 8 h to investigate the interfacial diffusion induced phase transformations in the multilayered thin films. Transmission electron microscopy (TEM) has been mainly used to characterize the crystalline structure of a variety of phases revealed on annealing, such as μ, λ and ϕ phases up to 823 K, δ phase at 823 K and T6 phase at 873 K. The occurrence of a variety of structures on annealing has been attributed to the interfacial reactions at the Al–Mn bilayers, and, therefore, the global composition of the composite films is not significant during the process of phase transformations. The crystallographic relationships of Al–Mn approximant structures of the decagonal quasicrystal are discussed to understand the evolution and stability of the T6 phase at high temperature.

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Introduction

Al–Mn system is very rich in intermetallic phases. According to its equilibrium phase diagram, the main phases are Al_6Mn, $Al_{4.2}Mn$ (μ phase), Al_4Mn (λ phase), $Al_{10}Mn_3$ (ϕ phase), and $Al_{11}Mn_4$ (δ phase) [1]. Since the discovery of the icosahedral phase [2] and the decagonal phase [3–5] in the rapidly quenched non-equilibrium Al–Mn alloys, a variety of quasiperiodic structures have been investigated and their crystallography has been examined to understand the relation with their crystalline approximants [6–11]. Among these the advent of decagonal quasicrystals, has provided further stimulation to explain the formation of various crystalline phases having intimate structural relations with the quasicrystals in the technologically important Al–Mn alloys. Subsequently, the δ-$Al_{11}Mn_4$ phase (space group Pnma; a = 14.79 Å, b = 12.42 Å, c = 12.59 Å), also named Al_3Mn phase [12], has been a subject of tremendous investigation for the crystallographers due to its pseudo-quasiperiodic characteristics [13–17]. It has been discussed in detail [13–21] that this phase is a rational approximant of 10-fold quasiperiodicity in Al–Mn alloys. All other crystalline structures exhibiting pseudo-decagonal quasiperiodicities belong to this structure.

Though the first decagonal phases have been found under the non-equilibrium conditions [3, 4], phase transition from crystalline structures to the decagonal

quasicrystal after long time annealing has been equally reported [8]. Stability aspects of decagonal phase have also been studied in Al–Pd alloys [22, 23]. In this system, two new phases (Al_3Pd-orthorhombic and Al_4Pd-hexagonal) were found to precipitate out on annealing the vapor-deposited layered Al and Pd films at around 670 K [24]. In rapidly solidified melt spun foil of Al–Pd alloy, a coexistence of decagonal phase along with a metastable cubic phase has been reported [25, 26]. In a more systematic study, a non-equilibrium decagonal quasicrystal and its related crystal structures were found to intergrow in rapidly solidified Al–Pd–Mn alloy [13]. On annealing at 1073 K, the non-equilibrium decagonal quasicrystal transforms to an equilibrium quasicrystal [13]. In the Al–Cu–Co alloy, the decagonal phases are formed without rapid solidification and are stable up to a temperature range of 823 to 1223 K [27]. Decagonal phase in a Zn–Mg–Y alloy was also reported stable [28].

In the present work, we report the formation of various phases during the annealing of the Al–Mn thin films, from two pure elements to composition-graduating crystalline phases and finally to a Mn-rich quasicrystalline phase. The thermal stability of these phases will be discussed in relationship with the interfacial diffusion induced at the Al and Mn layer interfaces.

Experimental details

A sequential deposition of alternate layers of Al and Mn was carried out on a NaCl substrate using thermal evaporation under high vacuum conditions. During the process, three bilayers of Al and Mn plus a surface coating of Al layer were synthesized. The total thickness of the whole film is about 120 nm (Fig. 1). The chemical composition of films was varied by modulating the thickness of Al and Mn, and was determined by the Rutherford back scattering spectrometry (RBS) technique, which showed a variation for sample's composition between 10 and 46.5 at.% Mn. Subsequently the as-deposited thin films were sealed in quartz tubes and annealed at different temperatures (473, 623, 823 and 873 K) for 2 and 8 h under high vacuum (10^{-8} Torr).

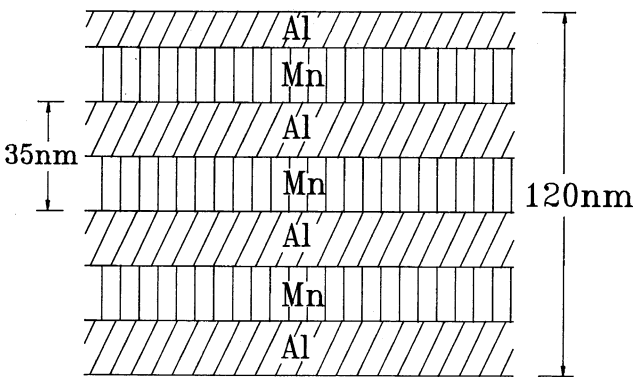

Fig. 1 A schematic of the cross sectional view of the composite multilayer thin films of Al and Mn

Microstructural characterization and phase transition of these annealed thin films were performed using a transmission electron microscope (TEM, Philips CM 30), operated at 300 kV. In order to prepare the TEM specimens, thin films were removed from the substrate by dissolving the NaCl in water, and subsequently mounted on 3 mm diameter copper grids for plain-view electron microscopy observations.

Results and discussion

Electron microscopy of as-deposited and annealed multilayered thin films

All the as-deposited Al/Mn multilayered thin films showed a set of discrete rings revealing the presence of the non-mixed Al and Mn layers. There was no indication of the formation of any intermetallic phase at this stage. After the heat treatments at different temperatures, a variety of intermetallics were revealed including the rational approximant structures and a decagonal quasicrystal.

The most interesting sample was the one with film composition of Al–18.5 at.% Mn. After first annealing at 473 K for 2 h, three intermetallic phases could already be observed in the electron diffraction patterns; these were μ-$Al_{4.12}Mn$ (19.5 at.% Mn), λ-Al_4Mn (20 at.% Mn) and ϕ-$Al_{10}Mn_3$ (23.5 at.% Mn) distributed in α-Al matrix. A sequential change noticed in the microstructure and the appearance of different phases in the matrix, encouraged a further investigation at high temperature, and accordingly the films were heat treated at 623 K for 2 h. These films no longer contained traces of α-Al. Another significant change noticed at this temperature (623 K) was the dominance of the μ-phase compared to the amount of the λ- and ϕ-phases.

On increasing the annealing temperature up to 823 K for 2 h, all the previous phases were transformed into the δ-$Al_{11}Mn_4$ (26.7 at.% Mn) phase, whose microstructure showed an avalanche morphology with dendritic growth in radial direction. A bright field electron micrograph of the δ-phase is shown in Fig. 2

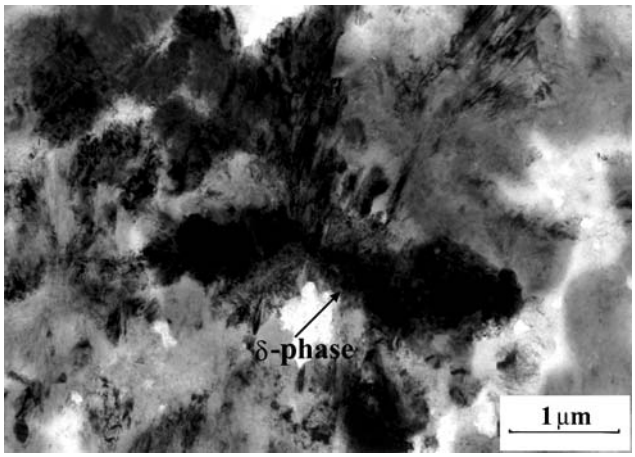

Fig. 2 Bright field electron micrograph of the δ-phase observed after the heat treatment at 823 K for 2 h

with an approximate grain size of 2 μm. The identification of δ-phase is presented in the subsequent paragraph along with the HREM image at lattice scale. A set of electron diffraction patterns recorded from this phase reveals the pseudo 5-, 3- and 2-fold rotational symmetries (Fig. 3a–c) of the quasicrystalline structure. The intensity modulations in the diffraction patterns are clearly seen in Fig. 3.

High resolution electron microscopy (HREM) investigation was also carried out to better understand the atomic structure of the δ-phase from the lattice images and to evaluate whether there is any precursor in this phase structure leading to the pseudo-rotational symmetries in the electron diffraction pattern. Figure 4 shows a HREM image containing the lattice planes of the orthorhombic structure of the δ-phase. The inset in Fig. 4 is a corresponding selected area electron diffraction pattern along the [001] zone axis which shows the strengthening of [600], [350] planes reflections in a symmetric way. However, the HREM images do not give evidence of any quasi-crystalline precursor in this crystalline structure.

The salient point of this present work is that the heat treatment at 873 K for 8 h leads to a partial phase transformation from the orthorhombic δ-phase to a decagonal T-phase. That means the quasicrystalline T-phase is thermodynamically more stable than the crystalline δ-phase at this temperature (873 K). A bright field electron micrograph (Fig. 5) shows the morphology of the T-phase, whose grains are approximately 1.2 μm. A set of corresponding electron diffraction patterns taken along the 10-fold and one of the 2-fold rotational axes of the decagonal phase are shown in Fig. 6. The 2-fold rotational symmetry reveals

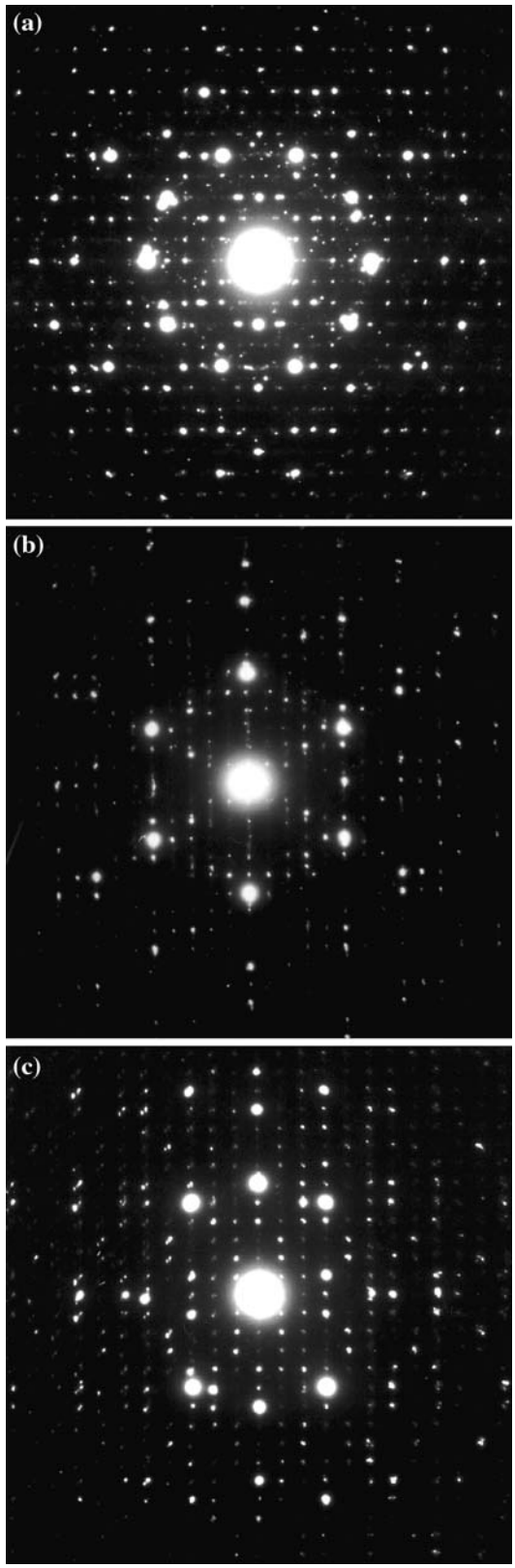

Fig. 3 Selected area electron diffraction patterns along the pseudo (a) 5-, (b) 3- and (c) 2-fold rotational zones of the δ-phase, obtained after heat treatment at 823 K for 2 h

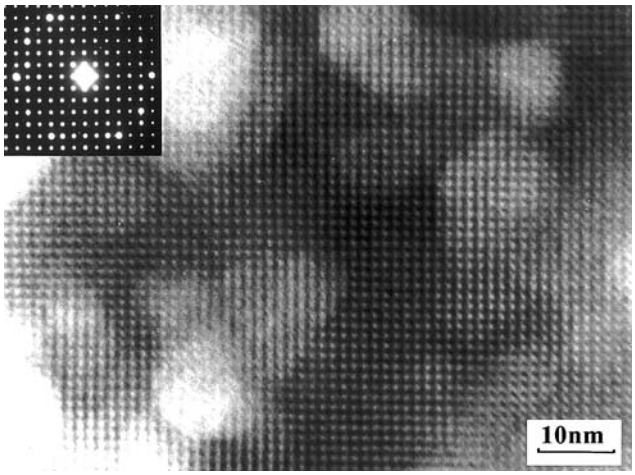

Fig. 4 High resolution electron micrograph of the δ-phase showing a perfect periodic structure, obtained after heat treatment at 823 K for 2 h. Inset shows the corresponding electron diffraction pattern along the [001] zone axis

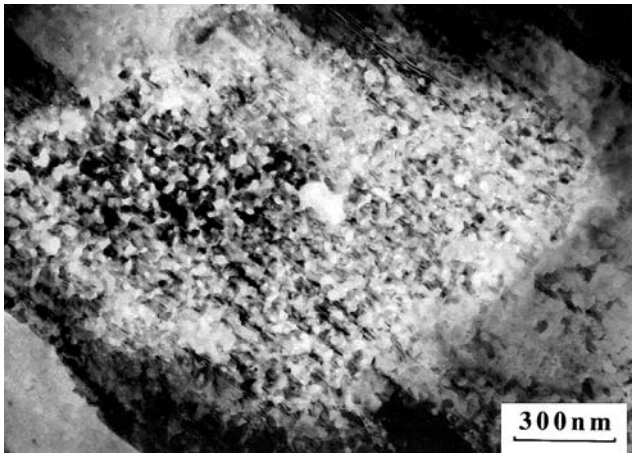

Fig. 5 Bright field electron micrograph of the decagonal quasicrystal, obtained after heat treatment at 873 K for 8 h

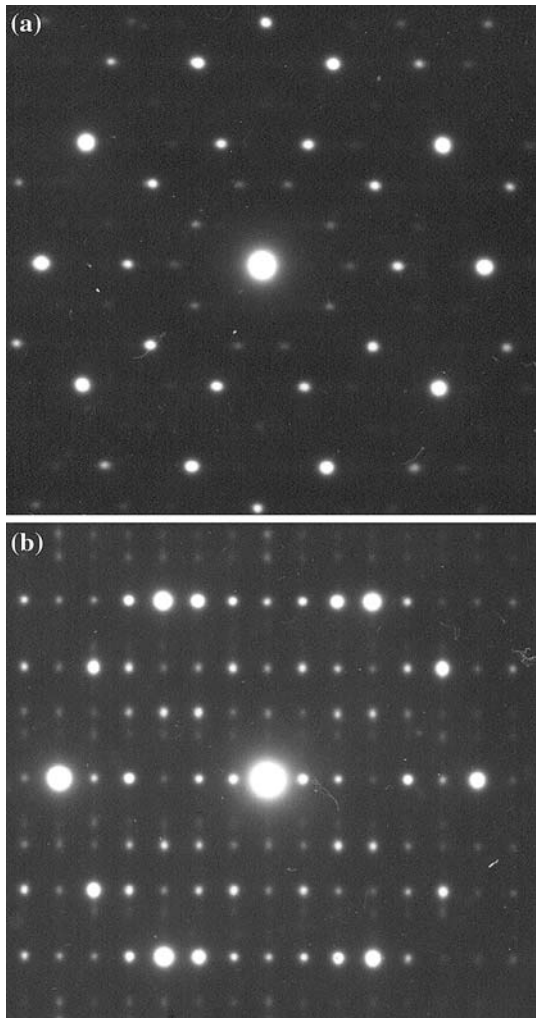

Fig. 6 Selected area electron diffraction patterns along (a) the 10- and (b) 2-fold rotational zones of the decagonal quasicrystal

(Fig. 6b) clearly that the most intense spot along the decagonal axis repeats at about 2 Å and that this reciprocal vector is divided into six parts. The periodicity along this vector is six, or about 12 Å. Therefore, the structure is referred as a T6 decagonal quasicrystal.

Thermal stability of the intermetallic phases and the role of interfacial diffusion

The details of the sequential annealing treatments and occurrence of different phases in the sample of Al–18.5 at% Mn composition are summarized in Table 1. The phase transformations observed on annealing of the multilayered Al–Mn thin films can be mainly be linked to their multilayer structure. Thus the role played by the interfacial diffusion at Al and Mn interfaces is important. As Al has a tendency to diffuse faster in Mn with increasing temperature, it is not surprising that Mn-rich phases were first formed at the vicinity of the interfaces, or rather within the Mn layers (Fig. 1). The evolution process of the phase transformation should depend on the inter-diffusion of Al and Mn layers until their whole mixing is completed. It may therefore be postulated that the occurrence of one stable phase or another depends on the type of nuclei in already existing phase, its composition and interdiffusion layer of Al into Mn. This process may start from a less-stable intermediate phase and last until the final equilibrium phase is reached. Hence the nucleation and growth of a new phase in the existing phase may be produced by excessive diffusion of Al into Mn layer.

It is also interesting to understand the formation of decagonal quasicrystals at high temperatures, particularly when it is induced in a periodic structure.

Table 1 Effect of heat treatment on evolution of crystalline and quasicrystalline phases in Al–18.5 at.%Mn multilayered thin film

Heat treatment conditions	Phases detected	Observations
As-deposited	Al, Mn	Very small particles of Al & Mn showing rings in SADP*. No inter diffusion between Al & Mn thin layers
473 K, 2h	Al, λ, μ, ϕ	Appearance of λ, μ, ϕ
623 K, 2h	λ, μ, ϕ	μ dominating phase
823 K, 2h	δ	Pseudo 5-, 3-, 2- with the ratio 1.612 ~ τ
873 K, 8h	δ, T	Coexistence of both two phases

* Selected area electron diffraction pattern

Although the discovery of decagonal phases was originally from rapidly solidified Al–Mn alloys [3, 4], it has been well known that these quasicrystalline phases could also be formed upon annealing. It was reported that even a reversible transformation is possible between the decagonal quasicrystal and the crystalline phase in the $Al_{63}Cu_{17.5}Co_{17.5}Si_2$ alloy [10]. However, the decagonal phases always found in Al-based ternary alloys were thermally stable, and those formed in $Al_{12}Mn_{2.9}Zn$ alloys could be decomposed into two crystalline phases at temperatures between 773 and 873 K [11]. In our present work, it was found that the decagonal quasicrystal nucleated in the δ-phase and formed after annealing at 873 K. The δ-phase, an orthorhombic structure, occurring at high temperatures and high Mn concentration is well known in the Al–Mn alloy phase diagram. Therefore in thin films, it probably occurred at high temperature, when the diffusion of Al is prominent at the interface, by diluting the Mn in the high Mn content phases of λ-, μ-, and ϕ-, and simultaneous rearrangement of the Al and Mn atoms. The electron diffraction patterns of the δ-phase revealed the existence of pseudo-orientations of decagonal quasicrystals in its orthorhombic structure, where the [010] orientation is parallel to the 10-fold of the decagonal quasicrystal. Although the microstructural features do not clearly resolve the phase transformations as being epitaxial in nature, a close structural correlation between the δ-phase and decagonal quasicrystal suggests that the δ-phase is indeed a precursor of the T6 phase. And the T6 phase is thermally more stable than δ-phase at 873 K. Further investigation should be done by increasing the annealing temperatures in order to see if the so-called stable quasicrystalline phase would transform into any equilibrium phases, as indicated by the phase diagram.

Conclusions

A variety of crystalline and quasicrystalline phases were observed in the multilayered Al–Mn thin films after heat treatments at different temperatures. The most interesting result is the revelation of the phase transformation from the crystalline δ-phase to the quasicrystalline T6-phase in the sample of Al–18.5% Mn composition at high temperature (873 K). The evolution of the various structures is attributed to interfacial reactions between Al and Mn layers and significant diffusion of Al in Mn at high temperatures.

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