Structural, Thermal and Electrical Properties of Al-Mn Quasicrystals Obtained by Melt Quenching

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Several kinds of melt-quenched Al-Mn alloys were prepared by a single roller method in order to investigate the structure-sensitive physical properties. By melt-quenching, a large grain size about $1\text{ }\mu\text{m}$ in diameter was obtained. An electron micrograph obtained from such a large grain showed a fivefold symmetry of a quasicrystalline structure, although these alloys contain crystalline Al in the matrix. X-ray diffraction peaks of crystalline Al become smaller with increasing Mn content and no peak was observed at 22.5 at%Mn. The peak intensity of the DTA curves decreases and the transformation temperature becomes higher with increasing Mn content. The electrical resistivity ρ of the melt-quenched alloys is extremely high, reflecting the quasicrystalline structure and the resonance state. The value of ρ increases as the Mn content increases, showing a drastic increase above 20 at%Mn. This behavior is accounted for by the disappearance of crystalline Al phase in the matrix.

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I. Introduction

For the last decade, the structures and properties of melt-quenched alloys have been very extensively studied for a large number of alloy systems and some useful nonequilibrium phases exhibiting excellent magnetic, electronic, mechanical and/or chemical properties have been found up to this date. The nonequilibrium phases are usually divided into two categories, noncrystalline (amorphous) and crystalline phases. The atomic configuration in the former phase has been considered to consist of a dense random packing of constituent atoms possessing a short-range ordering only within a several atomic distance. On the other hand, the latter phase is composed of the Bravais type lattice with regular lattice translations, even though the crystallographic feature of melt-quenched alloys is not always in agreement with that represented in their equilibrium phase diagrams.

However, Bagley⁽¹⁾⁽²⁾ has reported that fivefold symmetry without a usual lattice

translation is observed in electron diffraction patterns taken from a number of metals and nonmetallic particles. Their patterns have been identified as five tetrahedra which are bounded by $\{111\}$ planes and twin planes related to one another⁽³⁾⁽⁴⁾. Recently, Schechtman *et al.*⁽⁵⁾ have also obtained an electron diffraction pattern revealing the icosahedral symmetry with six fivefold, ten threefold and fifteen twofold axes in melt-quenched Al-14 at%Mn alloy and have claimed the existence of a nonequilibrium phase with long-range orientational order as well as icosahedral point group symmetry which can not be allowed to exist in the crystalline phases with long-range translational orders. Subsequently, Levine and Steinhardt⁽⁶⁾ have demonstrated that the arrangement and intensity of the reflection spots in the electron diffraction pattern obtained by Schechtman *et al.* can be reproduced very accurately by extending the two-dimensional Penrose tiling concept⁽⁷⁾ in which the lattice points have a quasiperiodic arrangement with icosahedral near-neighbor bond orientational order, rather than periodic and translational orders. Accordingly, the structure of the melt-quenched Al-14 at%Mn alloy can be thought to consist of an icosahedral quasicrystal which is different

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from conventional crystals or amorphous alloys.

It is important to investigate the physical properties of Al-Mn alloys for a more detailed understanding of the quasicrystal. In previous papers⁽⁸⁾⁽⁹⁾, some of the present authors have proposed a structure model using the high resolution electron microscopy, and Fukamichi *et al.* have also reported the magnetic properties measured in ac and dc magnetic fields⁽¹⁰⁾. The present paper intends to examine the structural, thermal and electrical properties of Al-Mn alloys in a wide range of composition.

II. Experimental

From pure aluminum (99.99 mass%) and manganese (99.9 mass%), several kinds of Al-Mn alloys were prepared in an argon atmosphere in an arc furnace on a water-cooled copper mould. The compositions of the alloys used in the present paper are given by the nominal values, because the weight loss during alloying was negligibly small. From the master alloys, ribbon samples about 1.5 mm wide and 30 μm thick were prepared using a single roller melt-spinning apparatus in an argon atmosphere. The amount of melted alloys per run was about 1 g and the rotation speed of the roller of 20 cm diameter was controlled to be about 50 s^{-1} .

The identification of the as-quenched structure was made by transmission electron microscopy and X-ray diffraction. The TEM sample was prepared by thinning ribbons electrolytically in a 1:9 volumetric ratio of perchloric and ethanol solution immersed in ice water. The X-ray diffraction experiment was carried out using $\text{Cu-K}\alpha$ radiation at room temperature. The thermal properties were examined in an argon atmosphere with a differential thermal analyzer (DTA) at a heating rate of 3.3 K/s. The electrical resistivity was measured by a conventional four-probe method in a wide temperature range from 4.2 to 250 K. The temperature was measured using a calibrated germanium thermometer at temperatures below about 90 K and a calibrated diode thermometer in the higher

temperature range with accuracy better than ± 0.01 K and ± 0.1 K below and above 90 K, respectively.

III. Results and Discussion

A transmission electron micrograph of typical melt-quenched structure of Al-14.3 at%Mn alloy is shown in Fig. 1. The quenched alloy consists of grains with an average size of about 1 μm , which show a morphology of dendrites growing from the center. Selected area diffraction patterns from the dendrites reveal the fivefold, threefold and twofold symmetries as shown in Fig. 2(a) to (c), in good agreement with the results reported by Schechtman *et al.*⁽⁵⁾. Diffraction patterns from another area indicate the existence of crystalline Al. Therefore, it is confirmed that the melt-quenched Al-14.3 at%Mn alloy is composed of the quasicrystalline and Al phases. Figure 3 shows X-ray diffraction patterns of several kinds of melt-quenched Al-Mn alloys. The patterns are composed of the icosahedral and Al phases as mentioned above, and the intensity of crystalline Al decreases with increasing Mn content. Similar results have been reported by Kimura *et al.*⁽¹¹⁾. The peak positions of the icosahedral phase are slightly shifted to higher angle sides. Furthermore, it should be noted that the Al-22.5%Mn alloy shows no diffraction peaks of crystalline Al. In contrast to the micrograph of Al-14.3 at%Mn alloy given in Fig. 1, the transmission electron micrograph of

Fig. 1 Transmission electron micrograph of melt-quenched Al-14.3 at%Mn alloy.

Fig. 2 Selected area diffraction patterns of melt-quenched Al-14.3 at%Mn alloy revealing the fivefold (a), threefold (b) and twofold (c) symmetries.

Fig. 3 X-ray diffraction patterns of several kinds of melt-quenched Al-Mn alloys (X: at%Mn). The peaks of the quasicrystalline structure are indicated by the capital letter of Q.

the Al-22.5%Mn alloy shows no Al phase and the dendritic growth structure was not observed as shown in Fig. 4.

Figure 5 shows exothermic curves obtained

Fig. 4 Transmission electron micrograph of melt-quenched Al-22.5 at%Mn alloy.

at a heating rate of 3.3 K/s for several kinds of the melt-quenched Al-Mn alloys. In connection with the structural change, a relatively sharp exothermic peak with high intensity is shifted to the range of higher temperature with increasing Mn content. In order to make clear this point, the transformation temperature T_i against the Mn content is plotted in Fig. 6. The temperature T_i was defined as an intersection point of the two dotted lines as shown in Fig. 5, and it varies from about 690 K to 870 K with increasing Mn content. The increment of T_i below 14 and 20 at%Mn alloys is not so steep as that of the intermediate composition of Mn. It is worth noting that the liquidus temperature line in the phase diagram also goes up with increasing Mn content⁽¹²⁾.

Temperature dependence of the electrical resistivity of several kinds of the melt-quench-

Fig. 5 Exothermic curves of several kinds of melt-quenched Al-Mn alloys with the heating rate of 20 K/min.

Fig. 6 Concentration dependence of the transformation temperature determined from the exothermic curves of melt-quenched Al-Mn alloys.

Fig. 7 Temperature dependence of the electrical resistivity of several kinds of melt-quenched Al-Mn alloys, together with that of crystalline Al_6Mn and a melt-quenched Al-14.3 at%V alloy. The results are shown by the solid lines since the measurement was carried out every 1 K.

ed Al-Mn alloys is shown in Fig. 7, together with that of crystalline Al_6Mn and a melt-quenched Al-14.3 at%V alloy. The magnitude of the electrical resistivity ρ of the quenched Al-Mn alloys is extremely large, and it is almost independent of temperature in wide temperature ranges just as those of amorphous alloys⁽¹³⁾. The value of ρ at 4.2 K increases with increasing Mn content, as shown in Fig. 8, and its increment becomes remarkably large above 20 at%Mn. This fact means that the conductive crystalline Al decreases with increasing Mn content, as mentioned in the connection with Fig. 3, and eventually disappears above about this composition⁽¹⁰⁾⁽¹¹⁾. The high electrical resistivity of the quasicrystalline phase is explained by taking into consideration the resonance state of the Fermi electrons and the nonperiodic potential⁽¹⁰⁾. That is, in the Al-based Al-Mn alloys, a resonance state of the

Fig. 8 Electrical resistivity at 4.2 K as a function of the Mn content for melt-quenched Al-Mn alloys.

Fermi electrons with the d-state of Mn occurs, because the center of the virtual bound state is very close to the Fermi level, resulting in a high electrical resistivity⁽¹⁴⁾. Furthermore, there is no long range translational symmetry but the nonperiodic potential due to the quasicrystalline structure. According to the resonance state model, it is expected that Al-V alloys composed of the quasicrystalline phase also have an extremely high electrical resistivity similar to that of Al-Mn quasicrystals. In fact, the value of a melt-quenched Al-14.3 at%Mn alloy is about $2.74 \mu\Omega \cdot m$, being comparable to that of Al-14.3 and 17.5 at%Mn alloys as seen from Fig. 7. By annealing at 773 K for 3.6 ks (1 h), the Al-14.3 at%Mn alloy is transformed to the Al_6Mn crystalline alloy, and the temperature dependence and the magnitude of electrical resistivity is drastically changed, as shown in the same figure. In order to make clear the temperature dependence of ρ , the data on the crystalline Al_6Mn alloy in Fig. 7 are plotted by another scale in Fig. 9. A linear temperature dependence is observed in a wide temperature range above 70 K, and it is a typical behavior associated with the phonon scattering, namely the scattering probability depends on the mean square amplitude of the lattice vibrations and it is proportional to the temperature at high temperatures⁽¹⁵⁾. The result

Fig. 9 Temperature dependence of the electrical resistivity of crystallized Al_6Mn alloy by annealing at 773 K for 3.6 ks (1 h).

for the crystalline Al_6Mn alloy is very different from the data for the crystalline alloys containing higher Mn content⁽¹⁰⁾. That is, the values of crystalline alloys of higher Mn content are much higher than those of the crystalline Al_6Mn alloy, and the temperature curve is convex upwards.

IV. Summary

Structure-sensitive properties of the melt-quenched Al-Mn alloys have been investigated by means of electron microscopy, X-ray diffraction, thermal analysis and electrical resistivity measurements, and the relationship between the physical properties and the quasicrystalline phase has been discussed. The main results are summarized as follows.

(1) By melt-quenching, a large grain size about $1 \mu m$ in diameter was obtained in the Al-14.3 at%Mn alloy, and its diffraction patterns showed the fivefold, threefold and twofold symmetries of the quasicrystalline structure.

(2) The melt-quenched samples consist of the quasicrystalline and Al phases. The diffraction peaks of Al become weaker with increasing Mn content and no peaks are observed at 22.5 at%Mn.

(3) The peak positions of the quasicrystalline phase are slightly shifted to the higher angle side depending on the Mn content.

(4) The peak intensity of the exothermic curves becomes weaker with the increase of the Mn content.

(5) The transformation temperature determined from the exothermic curves increases as

the Mn content increases.

(6) The electrical resistivity ρ is extremely large, and it is almost temperature independent in wide temperature ranges. This large value is closely correlated with the quasicrystalline structure and with the resonance state.

(7) The value of ρ increases with increasing Mn content. Especially the drastic increase occurs above about 20 at%Mn at which the high conductive crystalline Al phase disappears.

(8) The Al-14.3 at%Mn alloy is transformed to the Al₆Mn crystalline single phase by annealing, and its electrical resistivity is not so large compared with that of the quenched counterpart.

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