Production of Mg-Pd-Al Based Icosahedral Quasicrystals

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As-quenched alloys of quaternary systems of $\text{Mg}_{45}(\text{Pd}_{1-x}\text{Ag}_x)_{14}\text{Al}_{41}$ and $\text{Mg}_{45}(\text{Pd}_{1-x}\text{Cu}_x)_{14}\text{Al}_{41}$ form an icosahedral phase (I-phase) in all compositions. On heating, as-quenched $\text{Mg}_{45}(\text{Pd}_{1-x}\text{Ag}_x)_{14}\text{Al}_{41}$ I-phase alloys with ($x=0.3$ and 0.5) are decomposed into two I-phases of Pd-rich and Ag-rich alloys and finally transformed to a Frank-Kasper crystalline phase for $x=0.5$. $\text{Mg}_{45}(\text{Pd}_{1-x}\text{Cu}_x)_{14}\text{Al}_{41}$ I-phase is stable up to the melting point for $0 \leq x \leq 0.5$. Growth forms of thermodynamically stable Mg-Pd-Al I-phase particles were observed to be of rhombic triacontahedron or of some intermediate shape between rhombic triacontahedron and pentagonal dodecahedron.

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I. Introduction

It is known that there are two types of Icosahedral quasicrystals. They are called the Mackay icosahedron type (MI-type) and the rhombic triacontahedron type (RT-type) according to the form of atomic clusters existing in quasicrystals⁽¹⁾⁽²⁾. For MI-type, a number of thermodynamically stable I-phases have been found out by Tsai *et al.*⁽³⁾⁻⁽⁵⁾; they are all aluminum based alloys containing transition metal element (s). For RT-type, Al-Li-Cu⁽⁶⁾ and Mg-Ga-Zn⁽⁷⁾ were earlier discovered as the stable I-phase. All the I-phase alloys of RT-type, including the above two, were simple-metal systems, consisting only of non-transition metal elements. In a previous paper, we have shown for the first time that an alloy system, Mg-Pd-Al, containing a transition metal Pd, forms a stable I-phase of the RT-type in a certain compositional range⁽⁸⁾.

In the present paper, we have investigated the structure of pseudo-binary alloys of Mg-Pd-Al and Mg-Ag-Al, and those of Mg-Pd-Al and Mg-Cu-Al; it has been reported that the icosahedral phase can be produced by melt-quenching in Mg-(Ag or Cu)-Al alloys of certain compositions⁽⁹⁾⁻⁽¹¹⁾.

Growth morphology of icosahedral quasicrystals has been reported to have an icosahedral symmetry reflecting the symmetry of the atomic structure⁽⁵⁾⁽⁷⁾⁽¹²⁾⁽¹³⁾. In this paper we have also studied growth morphology of Mg-Pd-Al I-phase particles produced by the solidification process.

II. Experimental Procedures

By use of pure metals (better than 99.9% purity except Mg (99.8%)), mother alloys of quaternary systems of Mg-(Pd, Ag)-Al and Mg-(Pd, Cu)-Al were produced by arc-melting in an argon atmosphere. The composition selected were $\text{Mg}_{45}(\text{Pd}_{1-x}\text{Ag}_x)_{14}\text{Al}_{41}$ and Mg_{45}

$(\text{Pd}_{1-x}\text{Cu}_x)_{14}\text{Al}_{41}$ both with $x=0.3$, 0.5 and 0.7 . It is reported that for $x=1$ these alloys form I-phase in as-quenched state⁽⁹⁾⁽¹¹⁾, and for $x=0$ the alloy forms a stable I-phase⁽⁸⁾. Mg content in the initial composition before the arc melting was 52%; about 7% of Mg was lost by vaporization during the alloying process. The mother alloys were melt-quenched in an argon atmosphere on a rotating copper-roller, the tangential speed of which was 43 m/s. DTA (differential thermal analysis) or DSC (differential scanning calorimetry) measurements were performed with a heating rate 20 K/min. The structures of melt-quenched and annealed samples were examined by powder X-ray diffractometry by use of $\text{CuK}\alpha$ radiation.

The morphology of quasicrystalline particles, grown after holding a Mg-Pd-Al alloy for a long time near the melting temperature was observed by scanning electron microscopy. The Mg content of the alloy in this experiment was made considerably higher than that in the single I-phase composition so as to supply loss of Mg from the I-phase.

III. Results

1. $\text{Mg}_{45}(\text{Pd}_{1-x}\text{Ag}_x)_{14}\text{Al}_{41}$ system

Powder X-ray diffraction measurements showed that three melt-quenched samples with $x=0.3$, $x=0.5$ and $x=0.7$ consisted dominantly of the I-phase. Thus, it was confirmed that Mg-Pd-Al and Mg-Ag-Al ternary alloys form a continuous solid solution of I-phase in the as-quenched state.

In Fig. 1, we show DSC curve for $\text{Mg}_{45}(\text{Pd}_{0.5}\text{Ag}_{0.5})_{14}\text{Al}_{41}$ and powder X-ray diffraction spectrum for as-quenched state (a), and those for the samples heated to the temperatures indicated on the DSC curve and rapidly cooled to room temperature. We see two endothermic peaks in the DSC curve, which were found to appear reversibly during cooling the sample. The origin of these peaks are

Fig. 1 DSC spectrum of as-quenched $\text{Mg}_{45}(\text{Pd}_{0.5}\text{Ag}_{0.5})_{14}\text{Al}_{41}$ alloy and powder X-ray diffraction spectra of as-quenched sample and those after heating up to different stages indicated on the DSC curve.

not known. Incidentally, similar endothermic peaks have been reported to appear in the course of annealing of the RT-type I-phases⁽¹⁴⁾.

In the spectrum of (b) in Fig. 1, we see sharpening of peaks of the I-phase. The most characteristic feature of Fig. 1 is the splitting of all the peaks of the I-phase into two, having almost the same intensity, at an intermediate temperature, as seen in Fig. 1(c). This means that the initial I-phase of the quaternary alloy is decomposed into two I-phases with different quasi-lattice constants. At higher temperature, the structure is again transformed to a mono-phase as shown in Fig. 1(d). The spectrum of (d) can be indexed by a Frank-Kasper crystalline phase, which is represented by a 1/1 approximant crystal of the icosahedral phase⁽¹⁴⁾⁽¹⁵⁾. We also obtained a cubic 2/1 approximant crystal⁽¹⁴⁾ after a prolonged annealing (24 h) at 688 K in an argon atmosphere. Figure 2 shows the diffraction spectrum indexed by the cubic 2/1 approximant crystal. This 2/1 approximant phase is probably the thermal-equilibrium phase in a low temperature region in the $\text{Mg}_{45}(\text{Pd}_{0.5}\text{Ag}_{0.5})_{14}\text{Al}_{41}$ alloy.

Structural changes by annealing of the as-quenched $\text{Mg}_{45}(\text{Pd}_{0.7}\text{Ag}_{0.3})_{14}\text{Al}_{41}$ I-phase are given in Fig. 3; (a) shows sharpened peaks of I-phase after annealing at 693 K and (b) shows again the splitting of the peaks of the I-

Fig. 2 X-ray diffraction spectrum of $\text{Mg}_{45}(\text{Pd}_{0.5}\text{Ag}_{0.5})_{14}\text{Al}_{41}$ alloy annealed at 688 K for 24 h, showing the structure of 2/1 cubic approximant crystal.

Fig. 3 Powder X-ray diffraction spectra for annealed samples (heated to 693 K (a) and 773 K (b) followed by rapid-cooling) of $\text{Mg}_{45}(\text{Pd}_{0.7}\text{Ag}_{0.3})_{14}\text{Al}_{41}$ alloy.

phase after annealing at 773 K. In this splitting, the intensity ratio between the split peaks is roughly correspond to the concentration ratio between Pd and Ag.

2. $\text{Mg}_{45}(\text{Pd}_{1-x}\text{Cu}_x)_{14}\text{Al}_{41}$

Also in this quaternary alloy system, the structures of the as-quenched alloys of all compositions ($x=0.3, 0.5$ and 0.7) were confirmed to be I-phase by powder X-ray diffraction analysis. Furthermore, in the alloy with $x=0.5$, the I-phase was stable even after annealing at 773 K, a temperature just below the melting point. Figure 4 shows the diffraction spectrum of as-quenched I-phase (a) and that after annealing at 773 K (b). This fact indicates that $\text{Mg}_{45}(\text{Pd}_{1-x}\text{Cu}_x)_{14}\text{Al}_{41}$ quaternary alloys with $0 \leq x \leq 0.5$ form the I-phase as a thermodynamically stable phase.

Figure 5 shows X-ray diffraction spectra for annealed $\text{Mg}_{45}(\text{Pd}_{0.3}\text{Cu}_{0.7})_{14}\text{Al}_{41}$ alloy; (a) after heated to 683 K and (b) to 773 K. It is found that the as-quenched I-phase undergoes transition to a 1/1 approximant crystal of the Frank-Kasper phase at a lower temperature and then at a higher temperature the Frank-Kasper phase is decompos-

Fig. 4 X-ray diffraction spectra of as-quenched (a) and annealed (b) (heated to 773 K followed by rapid-cooling) samples of $\text{Mg}_{45}(\text{Pd}_{0.5}\text{Cu}_{0.5})_{14}\text{Al}_{41}$ alloy.

ed into two similar phases with slightly different lattice constants, in the same manner as the decomposition of I-phase in Mg–Pd–Ag–Al alloys. The intensity ratio between the two separate peaks corresponds almost to the composition ratio between Pd and Cu.

3. Growth morphology

Figure 6 shows scanning electron micrographs of typical shapes of the stable I-phase of Mg–Pd–Al grown from the melt. The composition was around $\text{Mg}_{42}\text{Pd}_{14}\text{Al}_{44}$. The pentagonal dodecahedral shape of Fig. 6(a) was obtained after the following heat treatment; heated to 1023 K (above the melting point) in an argon atmosphere, cooled to 673 K (below the melting point) in

Fig. 5 X-ray diffraction spectra of annealed samples (heated to 683 K (a) and 773 K (b) followed by rapid-cooling) of $\text{Mg}_{45}(\text{Pd}_{0.3}\text{Cu}_{0.7})_{14}\text{Al}_{41}$ alloy.

30 min, held at 753 K for 3 h and then cooled to room temperature. We solidified the melt with a rather fast speed in order to suppress the formation of a Laves phase (MgZn_2 type) in the temperature range between the liquidus temperature and the solidifying temperature of the I-phase. Figure 6(b) to (e) were obtained after further heat-treatment at 753 K for 48 h. In a certain portion of the heat-treated sample, we observed a particular shape either of (b), (c), (d) or (e). This means that the growth form depends on a subtle difference of the growth condition or on a slight difference in the composition.

Fig. 6 Growth forms of Mg–Pd–Al stable I-phase. For the heat treatment, see text.

IV. Discussion

It is quite natural that the Mg-Pd-Al I-phase forms a continuous solid solution with the Mg-Ag-Al I-phase and the Mg-Cu-Al I-phase, because the quasi-lattice constants of these three phases are not much different from each other.

The most interesting observation in the present experiment is the phase separation of as-quenched I-phase alloys of the Mg-(Pd, Ag)-Al system. Considering the fact that ratio of the X-ray diffraction intensity between the two decomposed I-phases corresponds to the ratio between the Pd and Ag contents, it is natural to conclude that the separated I-phases are Pd-rich and Ag-rich ones. In fact, the quasi-lattice constant of the one phase is almost equal to that of the ternary Mg-Pd-Al I-phase⁽⁸⁾. However, that of the other phase is considerably smaller than the reported value for ternary Mg-Ag-Al I-phase⁽⁹⁾. This discrepancy may partly be ascribed to the fact that the reported value is for the as-quenched state while the present value of the Ag rich I-phase is for an annealed state in which Al and Ag atoms will be more orderly arranged in the I-phase, leading to the reduction of the quasi-lattice constant.

The phase separation of the I-phase takes place possibly in the form of modulation of the lattice by diffusion of Pd and Ag atoms in the I-phase lattice, because this phase separation occurs only as a metastable state. Transmission electron microscopy experiment is planned to clarify the process of the phase separation. The main physical origin of the phase separation must be the reduction of the total free energy by the formation of the stable I-phase of ternary Mg-Pd-Al with a low free energy. In the quaternary alloy of the Mg-(Pd, Cu)-Al

system, the separation of the I-phase was not observed. This is probably because the free energy of the quaternary Mg-(Pd, Cu)-Al I-phase is already low enough for the system to be stable up to the melting point and the phase separation will not cause the free energy reduction.

So far, the growth form of icosahedral quasicrystals has been reported to be either the pentagonal dodecahedron⁽⁵⁾⁽⁷⁾, the rhombic triacontahedron⁽¹²⁾, or icosidodecahedron (soccer ball)⁽¹³⁾. Theoretically, it has been shown that the equilibrium shape of icosahedral quasicrystal can take the form of pentagonal dodecahedron, rhombic triacontahedron or some intermediate polyhedron between them, depending on the parameters of atomic interactions⁽¹⁶⁾. The intermediate forms are 42-faced polyhedra composed of 12 pentagonal facets and 30 hexagonal facets. A series of the polyhedra between the pentagonal dodecahedron and rhombic triacontahedron are given in Fig. 7. It is found that the growth forms of Mg-Pd-Al I-phase belong to this series of polyhedrons. The present experiment indicates that intermediate 42-faced polyhedra are also equilibrium growth form of the icosahedral quasicrystal as well as rhombic triacontahedron. (Pentagonal dodecahedron shown in Fig. 6(a) appeared only during the growth stage and does not seem to be an equilibrium form for Mg-Pd-Al I-phase.) The present observation suggests that the surface free energy of the plane perpendicular to fivefold axis (forming pentagonal facets) and that to the twofold axis (forming hexagonal facets) are comparable to each other, and a slight difference in the growth condition will change the relative values of the surface energy and modify the quasicrystalline form.

Finally, we report here results of our trials to produce I-phase by other substitutions to the stable Mg-Pd-Al I-phase. By replacing Pd with other noble or platinum

Fig. 7 Various forms of polyhedra between pentagonal dodecahedron (a) and rhombic triacontahedron (f).

group elements, we produced $\text{Mg}_{43}(\text{Rh, Ni or Pt})_{14}\text{Al}_{43}$ alloys, melt-quenched them and examined their structure by powder X-ray diffractometry. However, we could detect neither the I-phase nor the Frank-Kasper phase in any of these ternary alloys. This means that Pd can be regarded as a special I-phase forming element, as in the MI-type I-phase of the Al-Pd-TM (TM: transition metal) systems.

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