Preparation of a Large Al\textsubscript{70}Pd\textsubscript{20}Mn\textsubscript{10} Single-Quasicrystal by the Czochralski Method and Its Electrical Resistivity

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A partial isothermal phase diagram in the Al–Pd–Mn system was examined with the aim of determining a liquidus composition which equilibrates with a stoichiometric icosahedral(I) phase. The I phase precipitates as a primary phase in the range of 3 to 9 at\% Mn and 18 to 25 at\% Pd. The accurate composition of the liquid which equilibrates to the stoichiometric I–Al\textsubscript{13}Pd\textsubscript{50}Mn\textsubscript{37} phase at 1143 K was determined to be Al\textsubscript{13.5}Pd\textsubscript{39}Mn\textsubscript{47}. By choosing the liquidus composition, the growth of a seed single-quasicrystal of Al\textsubscript{13}Pd\textsubscript{50}Mn\textsubscript{37} was tried by using the Czochralski method. The maximum size of the single domain ingot reached as large as 10 mm in diameter and 50 mm in length. The electrical resistivity of the single-quasicrystal has a negative temperature dependence in the range of 40 to 270 K and shows a maximum value of 65 to 107 \(\mu\Omega\)m at about 40 K. The magnitude of the resistivity is dependent on orientation and tends to increase with increase of deviation from the growth direction of five fold direction presumably due to an anisotropy of internal defects.

(Received November 18, 1991)

Keywords: stable icosahedral phase, aluminum-palladium-manganese alloy, pseudo-binary phase diagram, partial isothermal section, Czochralski method, single-quasicrystal, electrical resistivity

I. Introduction

Since the discovery of an icosahedral phase in a rapidly solidified Al\textsubscript{63}Mn\textsubscript{14} alloy\textsuperscript{(1)}, great efforts have been devoted to find a new icosahedral phase in Al-based alloys. As a result, stable icosahedral and decagonal quasicrystals have been found in the Al–Cu–TM (TM=Fe,Ru or Os)\textsuperscript{(20)} and Al–Co–TM (TM=Cu or Ni)\textsuperscript{(9-15)} systems, respectively. It has been reported\textsuperscript{(9-10)} that these stable quasicrystals have a nearly constant outer electron concentration (\(e/\alpha\)) of 1.75 and are regarded as a kind of electronic compound belonging to the Hume-Rothery type phase. On the basis of this empirical criterion, we searched other icosahedral alloys and succeeded in discovering stable icosahedral alloys in the Al–Pd–TM (TM=Mn or Re) systems\textsuperscript{(9,10)}.

There is an advantage that the icosahedral phase in the Al–Pd–TM system forms in a wide compositional range. This is different from the previous result\textsuperscript{(9-10)} that the formation of the single icosahedral phase in the Al–Cu–TM system is limited to very narrow composition range. Subsequently, we have also reported that the stable Al–Pd–Mn I-phase precipitates as a primary phase directly from liquid phase without peritectic reaction in a limited composition range. This implies the possibility that an icosahedral single domain with a large scale is prepared at the limited alloy composition.

The production of a large I-ingot with a single domain is expected to enable clarification of physical and mechanical properties inherent to quasicrystals. This paper is intended to examine an equilibrium phase diagram in the Al–Pd–Mn system and the possibility of producing a large single-quasicrystal in the Al–Pd–Mn system and to present the size, morphology and electrical resistivity of the resulting large single quasicrystal.

II. Experimental Procedure

Al–Pd–Mn ternary alloys in the composition range of 14 to 26 at\% Pd and 3 to 15 at\% Mn were used in the present study. The alloy ingots were prepared from palladium of 99.996 mass\% purity and aluminum and manganese of 99.999 mass\% purity by arc-melting in an argon atmosphere. Subsequently, the ingots were annealed for 12 h at 1123 and 1143 K in an evacuated state, followed by water quenching, in order to obtain an equilibrium state at 1123 and 1143 K in the Al–Pd–Mn system. In addition, the pre-alloyed ingots were heated in an argon atmosphere for 1 h at 1400 K which was higher than the melting temperature and the solidification behavior was examined at a cooling rate of 0.033 K/s using a differential thermal analyzer (DTA). An Al\textsubscript{2}O\textsubscript{3} cell was used in the DTA measurement in order to avoid the reaction between the molten metal and the cell. The determination of alloy composition was made by energy dispersive X-ray (EDX) microanalysis. Identification of solidified phases was made by X-ray diffractometry and optical microscopy (OM). The samples for the optical microscopic observation were etched chemically in a mixed solution of fluoric acid and nitric acid.

Figure 1 shows an illustration of the Czochralski method which was used to produce a single-quasicrystal through the incongruent solidification reaction. It should be noted that the composition (C\textsubscript{0}) of the seed quasicrystal is different from the composition of the molten alloy (C\textsubscript{L}). Evaluation of a single-quasicrystalinity and determination of the growth direction for the ingot

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prepared by the Czochralski method were made by backscattering X-ray Laue diffractometry. The four probe technique was used to measure the temperature dependence of electrical resistivity ($\rho$) in the range of 5 to 270 K.

III. Results and Discussion

Figure 2 shows the pseudo-binary phase diagram of $\text{Al}_{80-x}\text{Pd}_{20}\text{Mn}_x$ ($X = 3$ to 15 at%) alloys. At a constant temperature of 1123 K, the I phase with the composition of $C_s$ (point a; $\text{Al}_8\text{Pd}_{20}\text{Mn}_8$) grows directly from the liquidus phase with the composition $C_L$ (point b) without peritectic reaction. However, the I phase in the Mn concentration range of 8.0 to 10.3 at% solidifies through a peritectic reaction between cubic-$\beta$ phase and liquid in the case of conventional solidification. Figure 3 shows the partial isothermal phase diagram of the Al–Pd–Mn system at 1123 K. One can determine from this figure that the accurate composition of the liquid which equilibrates to the $\text{Al}_8\text{Pd}_{20}\text{Mn}_8$ I phase is a $\text{Al}_{55}\text{Pd}_{20}\text{Mn}_{25}$.

The Bridgman method is not always suitable for producing the stoichiometric single-quasicrystal, because the control of composition during the incongruent solidification reaction is difficult for this method. Furthermore, the whole liquid changes to a single solidus phase and the resulting ingot has a poly-quasicrystalline structure with widely distributed compositions. In addition, it is very difficult to avoid the reaction between the melt and BN-crucible, leading to the generation of gases such as $\text{B}_2\text{O}_3$ and $N_2$. The generation of the gases results in the residual existence of pinhole near the surface of the ingot. Similary, the traveling solvent floating zone method\textsuperscript{(10)-(13)} is not also appropriate because the controls of the incongruent reaction and temperature in the floating zone are very difficult, leading to the change of composition along the longitudinal direction of the resulting ingot. It is therefore concluded that the Czochralski method is the only preparation process which enables to produce the stoichiometric Al–Pd–Mn quasicrystal consisting of a single domain through the incongruent reaction.

Figure 4 shows the partial isothermal phase diagram of the Al–Pd–Mn system at 1143 K. The composition range of the single I phase at 1143 K is considerably narrower than that at 1123 K shown in Fig. 3, and hence a severe control of the liquidus composition in the crucible is required. Although the $\text{Al}_{55}\text{Pd}_{20}\text{Mn}_{25}$ composition is located just near the stoichiometric composition, the achievement of an equilibrium state between the solidus $\text{Al}_{80}\text{Pd}_{20}\text{Mn}_{10}$ and the liquidus $\text{Al}_{35.5}\text{Pd}_{19.5}\text{Mn}_{6.8}$ is necessary for the production of a large $\text{Al}_{80}\text{Pd}_{20}\text{Mn}_{10}$ single-quasicrystal. However, as shown in the result of chemical analysis in Fig. 5, the alloy composition in the liquidus phase was confirmed to vary continuously along the longitudinal direction in the crucible. The compositional variation between the bottom- and the top-side in the crucible was in the range of 6.5 to 5.5 at% Mn, 20.5 to 19.5 at% Pd and 73 to 75 at% Al. Thus, one must be
reminded of the slight variation in alloy composition near the liquid surface which is in equilibrium with the growing quasicrystal.

Figure 6 shows the surface morphology of a seed quasicrystal of Al$_{10}$Pd$_{30}$Mn$_{10}$ prepared by the pseudo-Czochralski process described in Ref. (14), along with the X-ray Laue pattern taken from the longitudinal direction. In the Czochralski method, the seed quasicrystal was set at the position where the longitudinal direction of the seed rod was parallel to the 5-fold direction. Figure 7 shows an Al$_{10}$Pd$_{30}$Mn$_{10}$ single-quasicrystal grown along the 5-fold direction by the Czochralski method, along with the back-scattering X-ray Laue diffraction pattern taken from the growing direction of the single-quasicrystal. Distinct separation of individual reflection spots even in the X-ray Laue pattern was obtained from ten different areas in the same ingot, indicating the formation of a single-quasicrystalline structure.

It has previously been reported$^{(15)}$ that the electrical resistivity of the icosahedral quasicrystal is very high and increases with an increase of the quality of quasicrystal. Figure 8 shows the temperature dependence of electrical resistivity in the range of 5 to 270 K for the Al$_{10}$Pd$_{30}$Mn$_{10}$ single-quasicrystal along the five-, three- and two-fold symmetrical directions. The resistivity shows a negative temperature dependence in the temperature range of 40 to 270 K, followed by a maximum around 40 K and then a positive temperature dependence in the range of 4.2 to 40 K. The slope in the positive temperature dependence below 40 K is larger than that$^{(15)}$ for other 1-quasicrystals which do not contain magnetic elements. The feature of the temperature dependence is almost independent of the orientation. However, one can see significant difference in the magnitude of the resistivity ranging from 45 to 75 $\mu$\Omega m at room temperature among the five-, three- and two-fold directions. That is, the resistivity is the smallest for the five-fold symmetry which is the preferential growth direction and tends to increase with an increase in the angle between the growth direction and the direction selected for the measurement. Accordingly, the difference in the magnitude of electrical resistivity seems to reflect an anisotropy in internal defects. That is, it is

Fig. 4 Partial isothermal section of the Al-Pd-Mn system at 1143 K. L: liquid, I: icosahedral phase.

Fig. 5 Change of the chemical compositions in the icosahedral Al-Pd-Mn ingot along the longitudinal direction in the crucible.

Fig. 6 (a) and (b) Al$_{10}$Pd$_{30}$Mn$_{10}$ seed quasicrystals prepared by the arc-melting$^{(16)}$. (c) X-ray Laue pattern revealing the five-fold symmetry taken from the longitudinal direction of the seed quasicrystal.
presumed that the contribution of internal defects to the increase in electrical resistivity is the lowest for the longitudinal growth direction (the five-fold direction) and increase with deviation from the growth direction. At any event, the Al–Pd–Mn single-quasicrystal is concluded to have a large electrical resistivity.

Fig. 7  (a) Outer appearance of an Al$_{20}$Pd$_{30}$Mn$_{10}$ single-quasicrystal grown from the seed quasicrystal shown in Fig. 6 by the Czochralski method. (b) X-ray Laue pattern revealing the five-fold symmetry taken from the growth direction.

Fig. 8  The temperature dependence of electrical resistivity measured along the five-, three- and two-fold directions of Al$_{20}$Pd$_{30}$Mn$_{10}$ single quasicrystal.

IV. Summary

The partial isothermal phase diagram of the Al–Pd–Mn system at 1123 K and 1143 K was examined with the aim of determining the liquidus composition which equilibrates to the Al$_{20}$Pd$_{30}$Mn$_{10}$ quasicrystalline phase. On the basis of the information on the optimum alloy composition, the preparation of a large single-quasicrystal was tried by using the Czochralski method. The results obtained are summarized as follows:

1. The stoichiometric Al$_{20}$Pd$_{30}$Mn$_{10}$ quasicrystal was found to be in equilibrium with the liquidus composition of Al$_{73.5}$Pd$_{10.7}$Mn$_{15.8}$. The Al$_{20}$Pd$_{30}$Mn$_{10}$ seed quasicrystal was grown to a large single-quasicrystal from the Al$_{73.5}$Pd$_{10.7}$Mn$_{15.8}$ melt at a constant temperature of 1143 K, and the maximum size was as large as 10 mm in diameter and 50 mm in length.

2. The electrical resistivity increases with increasing temperature from 4.2 K, shows a maximum at around 40 K and then decreases in the temperature range of 40 to 270 K. The temperature dependence is almost independent of orientation. The maximum electrical resistivity at room temperature is 75 $\mu\Omega$m for the five-fold direction, 53 $\mu\Omega$m for the three-fold direction and 45 $\mu\Omega$m for the two-fold direction and there is a tendency for the resistivity to increase with increase of deviation from the growth direction.
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