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Stable Icosahedral Al–Pd–Mn and Al–Pd–Re Alloys

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A thermodynamically stable quasicrystalline phase with an icosahedral structure was found to be formed at atomic compositions of $Al_{70}Pd_{20}Mn_{10}$ and $Al_{70}Pd_{20}Re_{10}$ in conventionally solidified and fully annealed states as well as in a rapidly solidified state. The substitution of Mn by Re leads to an increase in the intensity of the X-ray reflection peaks resulting from the fundamental lattice, while the intensity of the superlattice reflection remains unchanged. This result suggests that Re and Mn atoms occupy predominantly the fundamental lattice site and the superlattice site is occupied by Pd. These icosahedral alloys with an ordered structure remain stable up to the onset temperature of fusion and the icosahedral Al–Pd–Mn alloy has solidification morphology of an icosidodecahedron with a size of 0.3 mm. The formation and stability of these icosahedral alloys were examined in terms of electronic parameter and atomic size and the criterion of the high stability was clarified to be analogous to that for the Hume-Rothery type compounds.

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Keywords: *stable icosahedral phase, aluminum-palladium-manganese, aluminum-palladium-rhenium, fundamental lattice, superlattice, icosidodecahedron, Hume-Rothery rule*

I. Introduction

Since the discovery of an icosahedral phase in a rapidly solidified $Al_{86}Mn_{14}$ alloy$^{(1)}$, great efforts have been devoted to find the alloy composition where the icosahedral phase is formed in metastable and stable states, in addition to the clarification of fundamental properties of the new phase. As a result, stable icosahedral and decagonal quasicrystals have been found in Al–Cu–M (M=Li, Fe, Ru or Os)$^{(2)-(4)}$ and Al–Co–M (M=Cu or Ni)$^{(5)(6)}$ alloy systems, respectively. These stable quasicrystals have given a good opportunity to clarify the structure, growth morphology, stability and fundamental properties of the quasicrystalline alloys$^{(9)(10)(11)}$. It has been reported$^{(7)(8)(12)}$ that the stable Al–Cu–(Fe, Ru or Os) and Al–Co–(Cu or Ni) quasicrystals have the same valence electron concentration (e/a) of approximately 1.75 and are regarded as an electronic compound belonging to a Hume-Rothery type phase. On the basis of the empirical rules for the formation of thermodynamically stable icosahedral alloys which were derived from the Al–Cu–M and Al–Co–M quasicrystals, a new quasicrystalline alloy was searched in some Al–TM (TM=transition metal) alloys. As a result, a mostly single ordered icosahedral phase was found in rapidly solidified Al–Pd–Mn and Al–Pd–Re alloys$^{(13)}$ ranging from 15 to 20 at% Pd and 10 to 15 at% Mn or Re. It was subsequently found that the icosahedral Al–Pd–Mn and Al–Pd–Re alloys with a limited composition of about 20 at% Pd and 10 at% Mn or Re remain stable up to the onset temperature of fusion and are formed as a thermodynamically stable phase in slowly solidified and fully annealed states. This paper intends to clarify alloy composition, structure and growth morphology of the new stable icosahedral Al–Pd–Mn and Al–Pd–Re quasicrystals.

II. Experimental Procedure

The specimens used in the present work were Al–Pd–Mn and Al–Pd–Re ternary alloys ranging from 10 to 25 at% Pd and 10 to 20 at% Mn or Re. Mixtures of electrical Al, Pd and Mn or Re metals were melted in an argon atmosphere using an arc furnace. The subsequent annealing treatment was made for 36 ks (10 h) at temperatures between 1123 and 1173 K in an evacuated state, in order to obtain a truely equilibrium structure. The quasicrystallinity of the as-solidified and annealed samples was examined by X-ray diffraction, differential scanning calorimetry (DSC), differential thermal analysis (DTA), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and optical microscopy (OM).

III. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of rapidly solidified $Al_{70}Pd_{15}Mn_{15}$ (a) and $Al_{70}Pd_{20}Mn_{10}$ (b) alloys. The former alloy has been identified to consist of a mostly single icosahedral phase in our earlier paper$^{(13)}$. Identification of the icosahedral structure in the present study was made by using Elser's indices$^{(14)}$ and all peaks of $Al_{70}Pd_{20}Mn_{10}$ can be indexed as an icosahedral phase without any traces of second phase. It is known that the substitution of a lattice site by an atom with a larger atomic number leads to an increase of relative intensity of X-ray diffraction peaks in a low angle region. Accordingly, the relative intensity of the (111000), 1/2(311111)

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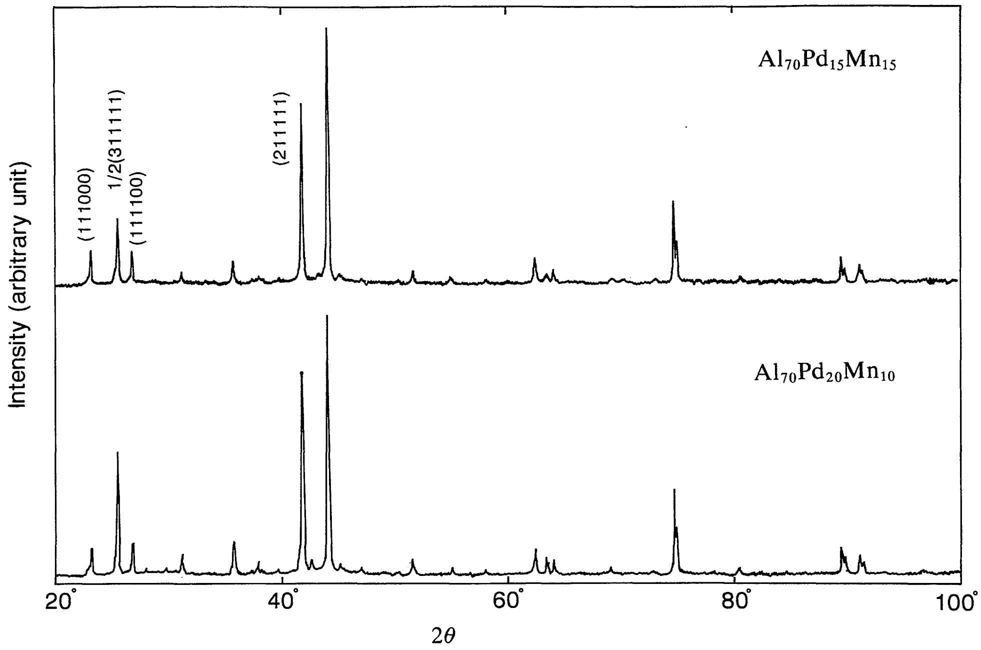

Fig. 1 X-ray powder-diffraction patterns of rapidly solidified $Al_{70}Pd_{15}Mn_{15}$ (a) and $Al_{70}Pd_{20}Mn_{10}$ (b) alloys.

and (111100) peaks is thought to be sensitive to the substitution of Al and Mn by Pd or Re in the icosahedral phase. It is to be expected that the increase in the relative intensity for the three peaks is nearly equal in the case of random substitution while the relative intensity of the 1/2(311111) reflection peak increases in the case of preferential substitution at ordered atomic sites. It is seen in Fig. 1 that the intensity of the superlattice 1/2(311111) reflection for $Al_{70}Pd_{20}Mn_{10}$ is about twice as high as that for $Al_{70}Pd_{15}Mn_{15}$, though the (111000) and (111100) peaks remain unchanged. This significant change agrees with the earier result(13) that the intensity of the superlattice 1/2(311111) peak for the Al-Pd-Mn quasicrystals successively increases with increasing Pd content, suggesting that Pd occupies predominantly the superlattice site in the Al-Pd-Mn icosahedral structure. When the icosahedral alloys are heated to 868 K, neither exothermic peak on DSC curve nor reflection peak of other phases in X-ray diffraction patterns is seen. It is therefore expected that the icosahedral phase has a high thermal stability and can be obtained even in conventionally solidified and fully annealed states.

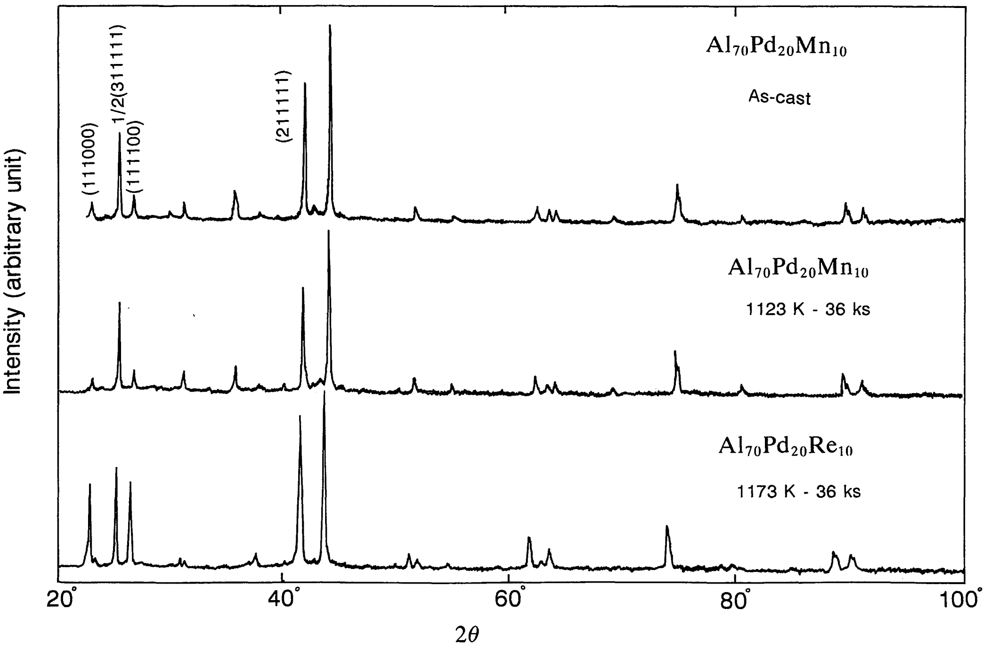

Fig. 2 X-ray powder-diffraction patterns of $Al_{70}Pd_{20}Mn_{10}$ alloy in a conventionally solidified state (a) and annealed at 1123 K for 36 ks (b) and of $Al_{70}Pd_{20}Re_{10}$ alloy annealed at 1173 K for 36 ks (c).

Figure 2 shows the X-ray diffraction patterns of an $Al_{70}Pd_{20}Mn_{10}$ alloy in a conventionally solidified state (a) and annealed at 1123 K for 36 ks (b) and an $Al_{70}Pd_{20}Re_{10}$ alloy annealed at 1173 K for 36 ks (c). The conventionally solidified and annealed structures of the Al–Pd–Mn alloy are similar to the rapidly solidified structure of $Al_{70}Pd_{20}Mn_{10}$ alloy. It is therefore concluded that the $Al_{70}Pd_{20}Mn_{10}$ alloy consists of a stable icosahedral phase. It is further seen that the relative intensity of (111000) and (111100) peaks for $Al_{70}Pd_{20}Re_{10}$ is about five times as high as that for $Al_{70}Pd_{20}Mn_{10}$, in good contrast to the result that the intensity of the 1/2(311111) superlattice peak remains unchanged. This suggests that Mn and Re predominantly occupy the fundamental site in the quasicrystalline lattice, while Pd occupies the superlattice site(13). In comparison with the stable icosahedral Al–Cu–Fe alloy, it is predicted that Pd and Mn (or Re) play a similar role as Cu and Fe, respectively, in the constitution of the icosahedral quasilattice.

Figure 3 shows the selected area electron diffraction patterns taken from the conventionally solidified $Al_{70}Pd_{20}Mn_{10}$ alloy. The diffraction patterns (a) and (b)

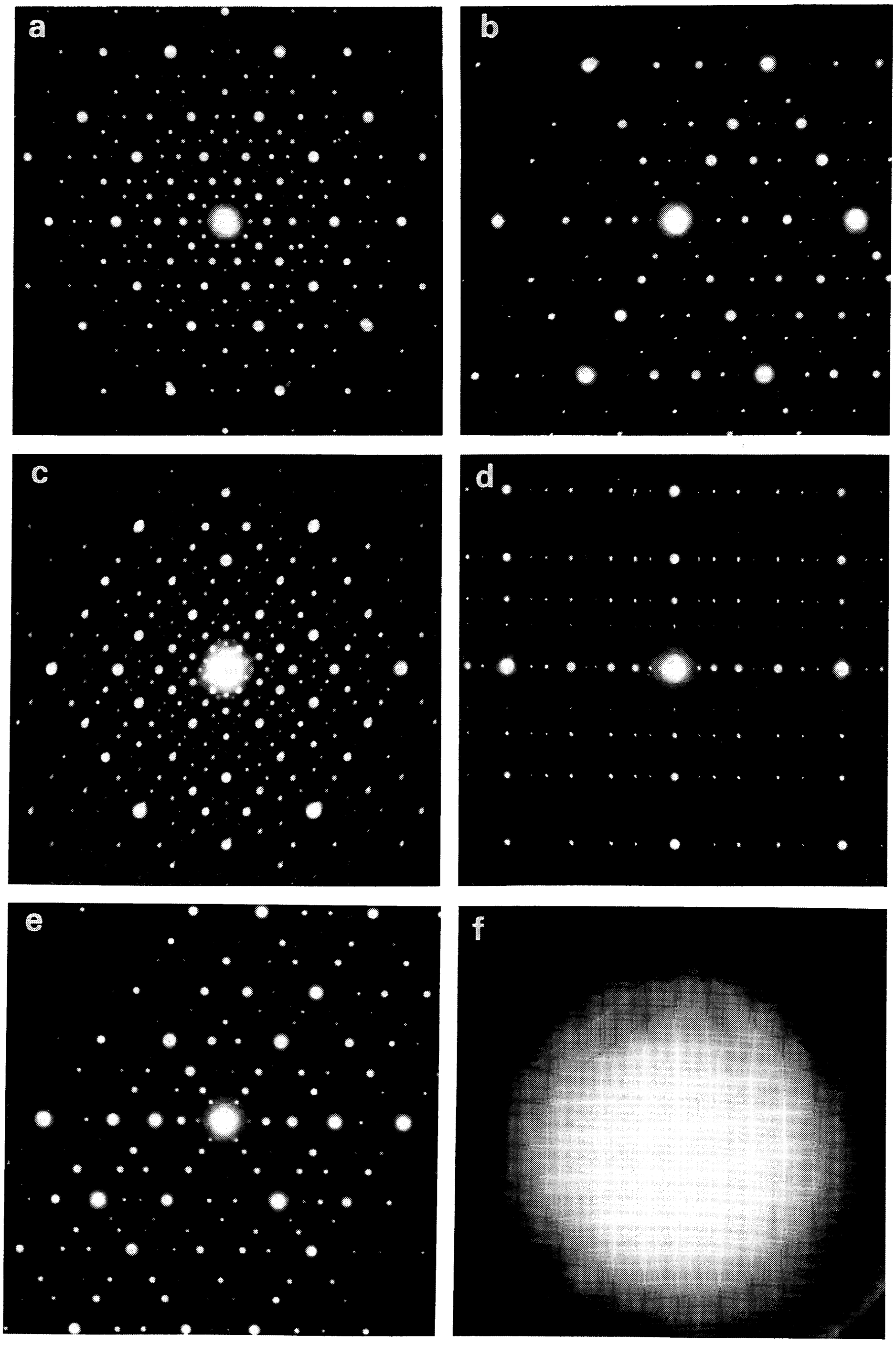

Fig. 3 Selected-area electron diffraction patterns along the directions of 5-fold (a), 3-fold (b) and 2-fold (c), (d) and (e) for an icosahedral $Al_{70}Pd_{20}Mn_{10}$ quasicrystal prepared by conventional solidification.

reveal the existence of 5- and 3-fold symmetries, respectively, and the patterns (c), (d) and (e) correspond to the 2-fold symmetry. We can notice that all diffraction spots in the 5-fold direction are located well at the icosahedral symmetry position in Fig. 3(a), in contrast to the result that an as-cast icosahedral Al–Cu–Ru alloy reveals a systematical displacement from the icosahedral symmetry positions reported by Hiraga *et al.*(19). This indicates that the phason disorder in the as-cast state is much smaller for $Al_{70}Pd_{20}Mn_{10}$ than that for $Al_{65}Cu_{20}Ru_{15}$. Figure 3(f) shows an electron diffraction pattern taken along 5-fold direction with a shorter camera length. The Kikuchi lines with regular intensity distribution reveal the 10-fold rotational symmetry and the shape drawn with bright and dark Kikuchi lines can be identified to be a pentagonal shape.

Similar electron diffraction patterns revealing the 5-, 3- and 2-fold symmetries were obtained for $Al_{70}Pd_{20}Re_{10}$ alloy annealed for 36 ks at 1173 K after conventional solidification. As exemplified in Fig. 4, the arrangement and intensity of reflection spots in the diffraction patterns are just the same as those for the $Al_{70}Pd_{20}Mn_{10}$ alloy, indicating that the quasicrystalline structure is very analogous in both alloys. Considering that Mn and Re metals have an equal outer electron concentration and different periodicity and atomic size, the formation of stable icosahedral Al–Pd–Mn and Al–Pd–Re alloys seems to be dominanted by an electronic structure.

Figure 5 shows the DTA curves of conventionally solidified $Al_{70}Pd_{20}Mn_{10}$ (a) and $Al_{70}Pd_{20}Re_{10}$ (b) icosahedral alloys. The measurement was made in the temperature range below 1500 K at a heating rate of 0.17 K/s. Only an endothermic peak due to fusion is observed at 1150 K for $Al_{70}Pd_{20}Mn_{10}$ and 1320 K for $Al_{70}Pd_{20}Re_{10}$ and there is no exothermic peak in the solid state, indicating the icosahedral structure remains stable up to fusion.

An optical micrograph shown in Fig. 6 reveals the cross sectional structure of a conventionally solidified $Al_{70}Pd_{20}Mn_{10}$ alloy. No distinct contrast of the second phase is seen, indicating that a mostly single icosahedral phase is formed in the vicinity of $Al_{70}Pd_{20}Mn_{10}$.

Figure 7(a) shows a scanning electron micrograph of the icosahedral $Al_{70}Pd_{20}Mn_{10}$ alloy prepared by conventional solidification. A part of the icosahedral Al-Pd-Mn ingot appears to have an icosidodecahedral facet with a size of 0.3 mm from the comparison with the illustration shown in Fig. 7(b). This morphology is different from a rhombic triacontahedron and a pentagonal dodecahedron which have been observed for stable icosahedral Al-Li-Cu(2) and Al-Cu-Fe(3) alloys, respectively. A number of theoretical models(17)(18) on the

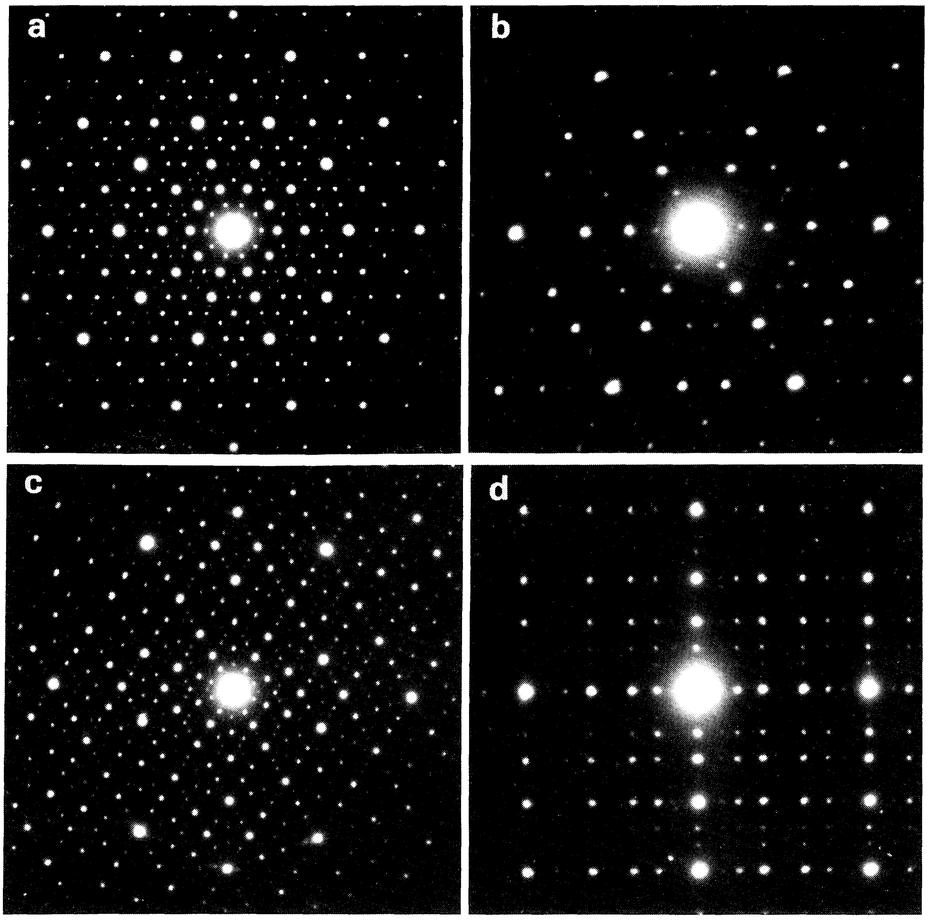

Fig. 4 Selected-area electron diffraction patterns along the directions of 5-fold (a), 3-fold (b) and 2-fold (c) and (d) for an icosahedral $Al_{70}Pd_{20}Re_{10}$ alloy annealed at 1173 K for 36 ks after conventional solidification.

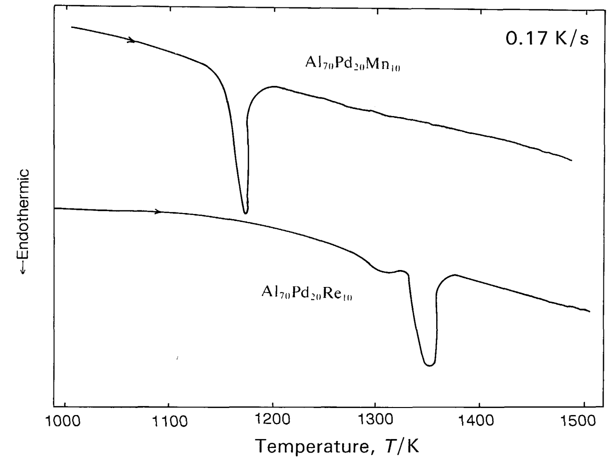

Fig. 5 Differential thermal analysis curves of conventionally solidified $Al_{70}Pd_{20}Mn_{10}$ (a) and $Al_{70}Pd_{20}Re_{10}$ (b) alloys, after conventional solidification.

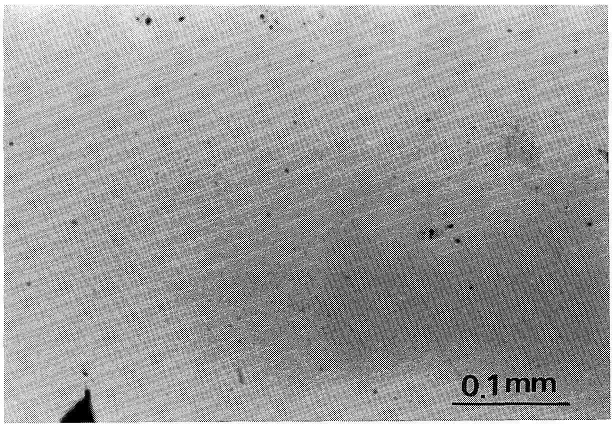

Fig. 6 Optical micrographs of an icosahedral $Al_{70}Pd_{20}Mn_{10}$ alloy prepared by conventional solidification.

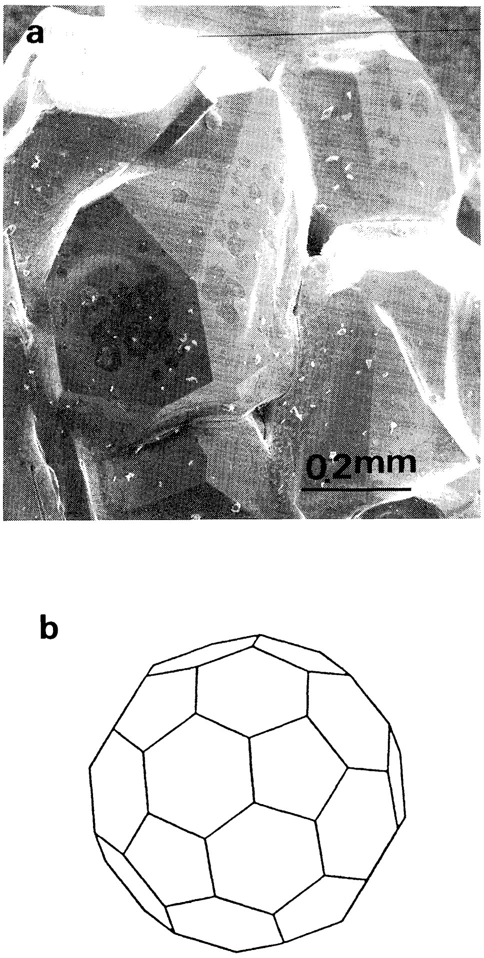

Fig. 7 Scanning electron micrograph revealing the growth morphology of an icosahedral $Al_{70}Pd_{20}Mn_{10}$ alloy prepared by conventional solidification (a) and an illustration of icosidodecahedron (b).

growth morphology of the icosahedral phase have been proposed in an attempt to explain the growth morphology which was experimentally observed. It has been presumed that the equilibrium shape is determined by minimizing the interfacial free energy as a function of orientation and the anisotropy of the interfacial free energy leads to a unique growth morphology. The formation of the pentagonal dodecahedron in the icosahedral Al-Cu-Fe alloy is presumably because the growth rate along the 3-fold axis is much faster than that along the 5-fold direction. The appearance of the icosidodecahedral facetting in the icosahedral Al-Pd-Mn alloy is explained by the assumption that there is hardly any difference in the growth rate between 3- and 5-fold directions.

There has been an attempt to interpret the formation and stability of the icosahedral phase in various kinds of alloys by the concept of Hume-Rothery rule(15) which was originally proposed to explain the dependence of structure on the electron concentration in noble metal-based alloys. It has been proposed(16) that the stability of an alloy is maximum when the free electron like Fermi sphere of the valence electrons just touches the Brillouin-zone boundary for a given structure. Recently, stable quasicrystals, including icosahedral and decagonal phases have been reported(8) to exist in narrow composition ranges where the criteria $e/a=1.75$ and $K_P/2k_F=1.0$ are satisfied simultaneously. It is notable that the criteria are just the same as those for the Hume Rothery-Jones phase. Here, K_P is a scattering vector at the most intense diffraction peak, corresponding to a diameter of the Brillouin Zone, and k_F is the Fermi radius deduced from atomic density and e/a in the frame of free electron model. Figure 8 shows the relationship between $K_P/2k_F$ and e/a or λ for the stable icosahedral Al-Pd-Mn and Al-Pd-Re alloys, together with the other stable Al-Cu and Al-Ni base quasicrystals. Here, λ is the atomic size factor and the definition has been given in previous papers(8). The e/a and $K_P/2k_F$ of the stable phase are approximately 1.74 and 1.0, respectively for both $Al_{70}Pd_{20}Mn_{10}$ and $Al_{70}Pd_{20}Re_{10}$. Consequently, it is concluded that the previously proposed criteria for the formation of the stable icosahedral and decagonal quasicrystals are also satisfied for the stable Al-Pd-Mn and Al-Pd-Re icosahedral alloys found in the present study. However, as plotted in Fig. 8, the λ value is 0.056 for $Al_{70}Pd_{20}Mn_{10}$ and 0.036 for $Al_{70}Pd_{20}Re_{10}$, being much

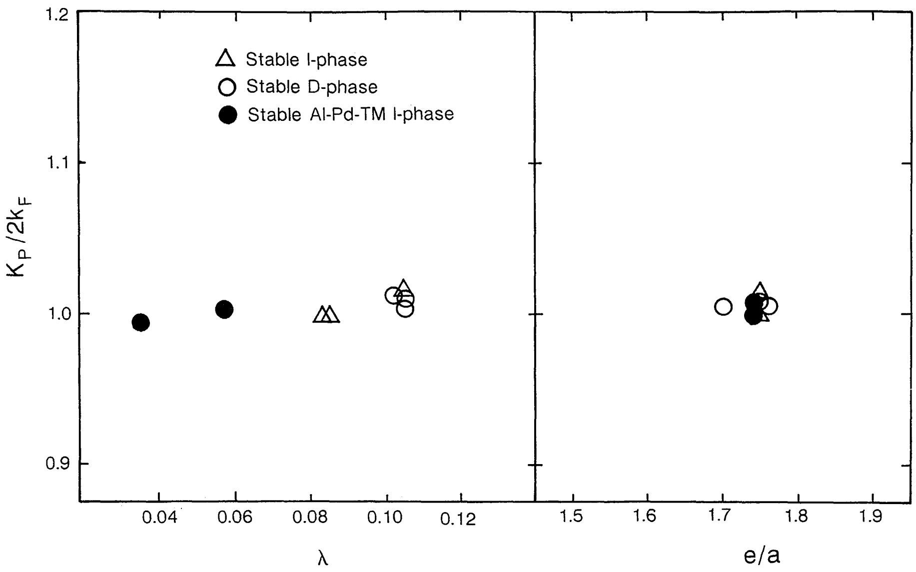

Fig. 8 Relationship between the $K_P/2k_F$ value and average outer electron per atom ratio (e/a) or the atomic size factor (λ) for stable icosahedral $Al_{70}Pd_{20}Mn_{10}$ and $Al_{70}Pd_{20}Re_{10}$ alloys. The data of stable icosahedral Al-Cu-(Fe, Ru or Os) and stable decagonal Al-Co-(Cu or Ni) alloys are also plotted for reference.

smaller than those (0.07 to 0.1) of a number of icosahedral alloys reported to date. This large difference in the values allows us to interpret that the atomic size is not a significant factor for the formation of the stable icosahedral structure and the electronic structure plays a dominant role in the construction of the stable icosahedral phase.

IV. Conclusion

New thermodynamically stable icosahedral alloys were found at atomic compositions of $Al_{70}Pd_{20}Mn_{10}$ and $Al_{70}Pd_{20}Re_{10}$. From the relative intensity of the reflection peaks corresponding to the fundamental- and super-lattices of the icosahedral phase, it is interpreted that Pd and Mn (or Re) predominantly occupy the superlattice and the fundamental lattice sites, respectively. The icosahedral Al-Pd-Mn alloy has a solidification morphology of icosidodecahedron with a size of 0.3 mm. The e/a, $K_P/2k_F$ and λ values of the stable icosahedral alloys are 1.74 ,1.0 and 0.056, respectively, for $Al_{70}Pd_{20}Mn_{10}$ and 1.74, 1.0 and 0.036, respectively, for $Al_{70}Pd_{20}Re_{10}$. The good agreement of the $K_P/2k_F$ and e/a values in both icosahedral alloys indicates that the present icosahedral alloys are regarded to be the Hume-Rothery phase. On the other hand, the significant difference of the λ values implies that the atomic size factor does not play a dominant role in the formation of the stable icosahedral structure.

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