Formation of Icosahedral Quasicrystals and 1/1 Crystal Approximants in Al-Pd-RE (RE: Rare Earth Metals) Systems

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We have investigated the formation of an icosahedral quasicrystal (i-phase) and its 1/1 crystal approximant (1/1-phase) in the (Al, Ga)-Pd-RE (Rare earth metals) systems. Consequently, the Ga-Pd-Sc 1/1-phase, the Al-Pd-RE (RE = Yb, Tm and Er) 1/1-phase and the Al-Pd-Yb i-phase have been newly found by the substitution of Al for Ga, or Sc for other RE in the constituent elements of the Al53Pd30Sc16 i-phase previously reported. For the i- and the 1/1-phases studied in this work, the number of valence electrons per atom (e/a) ratio is 2.10 and the atomic radius ratio of the rare earth element to that of the other base elements is in the range 1.15–1.24, which fulfilled the formation conditions previously reported for other Tsai-type i-phases. On the other hand, the stability of the i-phases becomes lower with increasing the atomic radii of the RE elements, which indicates that the atomic radius ratio plays important role in the formation of the Al-Pd-RE i- and 1/1-phases. [doi:10.2320/matertrans.M2011162]

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1. Introduction

Quasicrystals are condensed matters having long-range order with crystallographically forbidden rotational symmetry such as icosahedral symmetry.1,2 Since the discovery of an icosahedral phase (i-phase) in a rapidly quenched Al-Mn alloy in 1984,3,4 much effort has been devoted to searching for new alloy systems in which i-phases are formed. As a result, the i-phases have so far been found to form in more than 70 different alloy systems, including about 40 systems, in which thermodynamically stable i-phases are formed.

It is widely believed that the i-phases consist of quasi-periodic arrangement of an atomic cluster with icosahedral symmetry. In most cases, such an atomic cluster is identical to the cluster found in periodic phases based on giant unit cells, called crystal approximants, in the same alloy system. There are three types of atomic clusters known so far: Mackay-type, Bergman-type and Tsai-type.3–5) The i-phases can be classified into three groups in terms of the above cluster type.

Among them, Tsai-type i-phases have recently attracted a lot of interest for their formations, structural and physical properties. They are only known thermodynamically stable i-phases that have been found to form in binary alloy systems: Cd-(Ca,Yb)6,7) and Zn-Sc8) systems. The unique structural feature of the Tsai-type i-phases is the existence of the tetrahedron consisting of four atoms located at the icosahedral cluster center, which breaks icosahedral symmetry in the phases.5,6) Moreover, Tsai-type i-phases have been found to form in a variety of ternary or quaternary alloys: Ag-In-(Ca, Yb),9) Au-In-Ca,10) Zn-Mg-Sc,11) Zn-(Ag, Au, Pd, Pt)-Sc,12) Zn-Cu-Sc,13) Zn-(Mn, Fe, Co, Ni)-Sc,14) Cu-Ga-Mg-Sc15) and Cu-(Ga, Al)-Sc.16) Consequently, the Tsai-type i-phases constitute the largest of the three groups of i-phases.

The formation conditions of i-phases have often been discussed in terms of the number of valence electrons per atom ratio (e/a ratio). The Tsai-type i-phases mentioned above are formed in the compositions with specific e/a values, i.e., e/a = 2.0–2.15.17) Moreover, the ratio of the atomic radius of the large element to that of the other base elements is in the range 1.1–1.27 and the concentration of the large element is 15–16 at%.17) In most cases, the concentration of the large element in the i-phases is slightly higher than that in the approximate phases found in the same alloy system.

Recently, we have reported the formation of an i-phase and its 1/1-approximant phase (1/1-phase) in the ternary Al-Pd-Sc system.18) The formation area of the i-phase is limited to very small area around the composition of Al53Pd30Sc16 where the e/a value is 2.10. The i-phase satisfies well the above formation conditions established for the Tsai-type i-phases.

In the present study, we have done further experiments to demonstrate the validity of the formation conditions of the i-phase by replacing Al with Ga, or Sc with other RE (rare earth metals) in the constituent elements of the Al-Pd-Sc alloy. We note that the replacements keep the e/a = 2.10 where all the replacement elements are assumed as trivalent except for Yb which is usually assumed as divalent in the quasicrystalline formations.

2. Experimental Procedures

Ternary Al-Pd-RE (RE = Sc, Yb, Tm, Er, Ho and Dy) and Ga-Pd-Sc alloys with various compositions around (Al, Ga)53Pd30RE16 were prepared from elemental constituents with purity better than 99.9 mass% by arc-melting under an argon atmosphere. Among them, the Al-Pd-RE (RE = Yb, Tm, Ho and Dy) alloys were subsequently subjected to single roller melt-spinning in argon atmosphere to produce melt-quenched ribbon samples. Some of the samples were sealed in evacuated silica tubes and annealed at various temperatures. All of samples were crushed and powdered, and X-ray diffraction measurements were done using a rotating anode...
X-ray generator (CuKα-radiation, 40 kV, 200 mA) with a graphite monochromator. Electron diffraction measurements were performed at an acceleration voltage of 200 kV. Differential scanning calorimetry (DSC) measurements were carried out in the temperature range from room temperature to 1473 K under an argon atmosphere with a heating rate of 10 K/min.

3. Results and Discussion

3.1 (Al, Ga)-Pd-Sc alloys

Figures 1(a)–(c) show the X-ray diffraction spectra for the as-solidified alloys of Al_{53.4}Pd_{30.0}Sc_{16.4} (a) and Al_{53}Pd_{30}Sc_{15} (b) and Ga_{55}Pd_{30}Sc_{15} (c), respectively. All the diffraction peaks in the spectrum of Fig. 1(a) are indexed as an P-type i-phase with the quasilattice constant \( a_1 \) of 0.507 nm. As discussed previously, the i-phase can be classified into the Tsai-type. These results are attributable to the introduction of a phason strain. The i-phase remains unchanged by the annealing at 873 K for 100 h whereas the i-phase transformed to crystalline phase(s) by the annealing at temperatures higher than 973 K. The diffraction intensities and peak widths of the alloy annealed at 873 K were essentially the same as those of the as-solidified alloy.

Figures 1(b) and (c) show the diffraction spectra for the single 1/1-phase. The Ga-Pd-Sc 1/1-phase was newly found by the substitution of Al for Ga in the Al-Pd-Sc 1/1-phase. Although the peak intensities of the Ga_{55}Pd_{30}Sc_{15} alloy in Fig. 1(c) are slightly different from those of the Al-Pd-Sc 1/1-phase, the peak positions indicate that the phase is the 1/1-approximant. The Ga-Pd-Sc 1/1-phase has a body centered cubic structure with the lattice constant of 1.392 nm, which is slightly smaller than that of 1.395 nm of the Al-Pd-Sc 1/1-phase because the atomic radius of the constituent Ga is slightly smaller than that of Al. The single phase region of the 1/1-phase in the Ga-Pd-Sc system extends along the 15 at% Sc line in analogy with that in Al-Pd-Sc system, i.e., Ga_{55.5}Pd_{30}Sc_{15} \((x = 0-2)\), as shown in Fig. 2. For the Ga-Pd-Sc system, the i-phase has not been found in the alloy compositions we studied.

Figures 3(a)–(c) show the DSC spectra during heating for the as-solidified alloys of i-Al_{53.4}Pd_{30.0}Sc_{16.4} (a), 1/1- \( \text{AlPd}_{35.6}Sc_{15} \) (b) and 1/1- \( \text{GaPd}_{30}Sc_{15} \) (c), respectively. For the single i-phase(a), the exothermic peak was observed at 1128 K, indicating that non-equilibrium phase transforms to more stable phase(s) at the temperature. The i-phase forms a bulk sample by arc-melting and it is stable against the annealing at 873 K for 100 h. However, the result of the DSC measurements confirmed that the i-phase is thermodynamically metastable. For the 1/1-phases(b)–(c), only endothermic peaks corresponding to melting were observed, indicating the 1/1-phases are thermodynamically stable. Several annealing studies showed that both the Al-Pd-Sc and Ga-Pd-Sc 1/1-phases are stable up to high temperatures near the melting point.

Formation conditions of the i-phases have often been discussed in terms of Hume-Rothery mechanism. The Tsai-type i-phases, the stable i-phases found so far are formed in the compositions with \( \epsilon/a = 2.0-2.15 \). As shown in Fig. 2, both i- and 1/1-phases are formed in the
compositions along $e/a = 2.10$ line where the valences of Al (or Ga), Pd and Sc are assumed as +3, +0 and +3, respectively. The formation area of the i-phase is limited to the very narrow composition area around the Al$_{32}$Pd$_{30}$Sc$_{16}$, whereas the formation area of the 1/1-phases is extended along 15 at%Sc line. As discussed previously,16) 16 at%Sc and $e/a = 2.10$ are crucially important in the formation of the Tsai-type i-phases. We note that $e/a = 2.10$ is also important in the formation of the 1/1-phase, although the condition for the 1/1-phase is not much strict in comparison with that for the i-phase. On the other hand, the Sc content clearly distinguishes between the i- and the 1/1-phases. However, the Ga-Pd-Sc i-phase has not been found to form even at the composition of Ga$_{34}$Pd$_{30}$Sc$_{16}$ which satisfies the above conditions.

### 3.2 Al-Pd-RE (RE = Yb, Tm, Er, Ho and Dy) alloys

For the other Al-Pd-RE alloys, neither i- nor approximant phases could be obtained by arc-melting. Figures 4(a)–(e) show the X-ray diffraction spectra for the melt-quenched alloys of Al$_{32}$Pd$_{30}$RE$_{16}$ (RE = Yb, Tm, Er, Ho and Dy), respectively. For the RE = Yb, Tm and Er, we found the 1/1-phase with contaminant phase(s) in the alloys. Here, in the spectrum for the RE = Yb, we notice a small shoulder in the (532) peak indicated as an arrow. In general, the (221001) peak shows the strongest intensity in the diffraction spectrum of an i-phase, whose position is slightly lower angle to that of the (532) peak in the spectrum of a corresponding 1/1-phase. The shoulder observed in Fig. 4(e) can be attributed to the (221001) peak of the i-phase, which signals a formation of the i-phase in the alloy. The (211111) and (311111) peaks of the i-phase overlap with the (530) and (640) peaks of the 1/1-phase, respectively. Figures 5(a)–(c) show the selected area electron diffraction patterns in the Al$_{32}$Pd$_{30}$Yb$_{16}$ melt-quenched alloy. The patterns in Figs. 5(a)–(c) correspond to the 2-fold, 3-fold, and 5-fold patterns, respectively, which are typical of P-type i-phases. The diffraction spot positions in Fig. 5 slightly deviate from the ideal positions due to a phason strain, which is a similar feature to the Al-Pd-Sc i-phase. Figures 4(e) and 5(a)–(c) confirm that the melt-quenched Al$_{32}$Pd$_{30}$Yb$_{16}$ alloy mainly consists of the i- and the 1/1-phases. The quasilattice constant for the i-phase and the lattice constant for the 1/1-phase are evaluated to be 0.516 nm and 1.423 nm, respectively. In the case of the Al-Pd-Sc system, the single i-phase was formed in the specific composition of the Al$_{31}$Pd$_{32}$Sc$_{16}$. Similarly, it is expected that single phase region of the Al-Pd-Yb i-phase is limited to a very small area around the composition of the Al$_{32}$Pd$_{30}$Sc$_{16}$. To determine the single phase region of the Al-Pd-Yb i- and 1/1-phases, tuning of the alloy compositions with 0.1 at% order precision was required. However, the constituent Yb in the alloy has relatively lower boiling point, 1467 K, so that precise tuning of the composition is difficult by the combination of arc-melting and melt-spinning. Although no single i-phase has been obtained in the Al-Pd-Yb alloy so far, the annealing test at 773 K indicates that the i-phase is metastable. On the other hand, the 1/1-phase in the Al-Pd-RE (RE = Yb, Tm and Er) alloys are stable against the annealing at 773 K for 100 h. For the RE = Dy and Ho, we could find neither i- nor 1/1-phases.

Here, the formation conditions of the i-phases are again discussed for the Al-Pd-RE alloys. Assuming that the valences of Al, Pd and all the rare earth metals are +3, +0 and +3, respectively, the $e/a$ value of Al$_{34}$Pd$_{30}$RE$_{16}$ is calculated to be 2.10, which is within the $e/a$ range for the
Tsai-type i-phases. This condition is applicable to the formation of the i- or the 1/1-phases in the Al$_{54}$Pd$_{30}$RE$_{16}$ (RE = Yb, Tm and Er) alloys. On the other hand, neither i- nor approximant phases have been found in the Al$_{54}$Pd$_{30}$RE$_{16}$ (RE = Ho and Dy) alloys, indicating that $e/a = 2.10$ is not sufficient condition for their formations.

Another factor that has been claimed to be important in the formation of the Tsai-type i-phases is the atomic radius ratio $t = r_C/r_{A,B}$, where $r_C$ is the atomic radius of the 15–16 at% element and $r_{A,B}$ is the weighted-average of atomic radius of the other two elements. The $t$ values for the stable Tsai-type i-phases found so far range $t = 1.1–1.27$. The calculated $t$ values for Al$_{54}$Pd$_{30}$RE$_{16}$ were summarized in Table 1, where the atomic radius in Ref. 20) were used in the calculation. The $t$ values for other Tsai-type i-phases containing trivalent RE were also shown in Table 1. For the Al$_{54}$Pd$_{30}$RE$_{16}$ alloys studied in this work, the $t$ values are in the range 1.16–1.26, which are within the range of the values reported for other Tsai-type i-phases. Nevertheless, for the RE = Ho and Dy ($t = 1.25$ and 1.26, respectively), neither i- nor approximant phases were found. For the RE = Tm and Er ($t = 1.24$), the i-phase was not found but rather the 1/1-phase was found in the melt-quenched alloys. For the RE = Yb ($t = 1.23$), only the meatastable i-phase was found by melt-spinning. For the RE = Sc ($t = 1.16$), the i-phase was found by arc-melting and it is stable against the annealing at 873 K for 100 h. These results indicate that the $t$ values correlate with the formation and stability of the Al-Pd-RE i-phases; the $t = 1.16$ for the Al$_{54}$Pd$_{30}$Sc$_{16}$ is appropriate condition for the formation of the i-phase and with increasing the $t$ values the stability of the i-phases becomes lower. The $t = 1.16$ is close to the values for stable Zn-based i-phases as shown in Table 1. The $t$ values for the Al$_{54}$Pd$_{30}$Ho$_{16}$ and Al$_{54}$Pd$_{30}$Dy$_{16}$ alloys appear to be too large to form the i- or 1/1-phases. The upper limit of $t$ value for the formation of the Al-Pd-RE i- and 1/1-phases is 1.25. The substitutions between the RE elements change only $t$ values; $e/a = 2.10$ does not change. Thus, our results clearly indicate that the atomic radius ratio plays important role in the formation of the Al-Pd-RE i- and 1/1-phases.

In the above discussion, we assumed that all the RE elements show trivalent in the Al-Pd-RE alloys. Here, Yb is usually assumed as divalent in the quasicrystalline formations. Using the atomic radius for divalent Yb ($r = 0.1940$ nm), the $t$ value for the Al$_{54}$Pd$_{30}$Yb$_{16}$ is calculated to be 1.37, which is beyond the range of the formation condition. This suggests that the Yb in the Al-Pd-Yb i-phase act as trivalent rather than divalent. Very recently, intermediate valence state has been reported for Yb in the Au-Al-Yb i-phase. In the Al-Pd-Yb i-phase may show such intermediate valence state.

4. Conclusions

We have investigated the formation of an icosahedral quasicrystal (i-phase) and its 1/1-crystal approximant (1/1-phase) in the (Al, Ga)-Pd-RE (Rare earth metals) systems. In Al-Pd-Sc system, the single phase sample of the i-phase has been obtained at the composition of Al$_{53}$Pd$_{30}$Sc$_{16}$:4. Although the i-phase remained unchanged by the annealing at 873 K for 100 h, the DSC measurements showed the i-phase is thermodynamically metastable. The Ga-Pd-Sc 1/1-phase has been newly found by the substitution of Al for Ga in the Al-Pd-Sc i-phase. In the Al$_{54}$Pd$_{30}$RE$_{16}$ (RE = Yb, Tm and Er) melt-quenched alloys, the 1/1-phase has been found to form. Moreover, the metastable i-phase has been found in the Al-Pd-Yb alloy. For the i- and the 1/1-phases found in this study, the number of valence electrons per atom ($e/a$) ratio is 2.10 and the atomic radius ratio of the rare earth element to that of the other base elements is in the range 1.15–1.24, which fulfilled the formation conditions reported for other Tsai-type i-phases. On the other hand, the stability of the i-phases becomes lower with increasing the atomic radius.
radii of the RE elements. For the Al$_{54}$Pd$_{30}$RE$_{16}$ (RE = Ho and Dy) alloys, neither i- nor approximant phases were found. Our results indicate that the atomic radius ratio plays important role in the formation of the Al-Pd-RE i- and 1/1-phases.

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REFERENCES


Table 1 Formation and stability of the Tsai-type i-phases containing trivalent RE. For each system, the number of valence electrons per atom ($e/a$) ratio and the atomic radius ratio ($t = r_C/r_{A,B}$) are shown, where the $r_C$ is the atomic radius of the 15–16 at% element and $r_{A,B}$ is the weighted-average of atomic radius of the other two elements.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$e/a$</th>
<th>$t$</th>
<th>Formation and stability of i-phases</th>
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<tbody>
<tr>
<td>Al$<em>{54}$Pd$</em>{30}$Sc$_{16}$</td>
<td>2.10</td>
<td>1.16</td>
<td>metastable, found in as-solidified alloy</td>
</tr>
<tr>
<td>Zn$<em>{33}$Mg$</em>{32}$Sc$_{15}$</td>
<td>2.15</td>
<td>1.17</td>
<td>stable</td>
</tr>
<tr>
<td>Zn$<em>{33}$(Ag, Au, Pd, Pt)$</em>{33}$Sc$_{16}$</td>
<td>2.06–2.07</td>
<td>1.17–1.18</td>
<td>(except for Zn-Mn-Sc)</td>
</tr>
<tr>
<td>Zn$<em>{33}$(Mn, Fe, Co, Ni)$</em>{33}$Sc$_{16}$</td>
<td>2.09</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>Zn$<em>{33}$Cu$</em>{12}$Sc$_{16}$</td>
<td>2.04</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{46}$Al$</em>{36}$Sc$_{16}$</td>
<td>2.08</td>
<td>1.22</td>
<td>not clear, found in as-solidified alloy</td>
</tr>
<tr>
<td>Al$<em>{54}$Pd$</em>{30}$Yb$_{16}$</td>
<td>2.10</td>
<td>1.23</td>
<td>metastable, found in melt-quenched alloy</td>
</tr>
<tr>
<td>Al$<em>{54}$Pd$</em>{30}$Tm$_{16}$</td>
<td>2.10</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>Al$<em>{54}$Pd$</em>{30}$Er$_{16}$</td>
<td>2.10</td>
<td>1.24</td>
<td>not found, only 1/1-phase was found</td>
</tr>
<tr>
<td>Al$<em>{54}$Pd$</em>{30}$Ho$_{16}$</td>
<td>2.10</td>
<td>1.25</td>
<td></td>
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<td>Al$<em>{54}$Pd$</em>{30}$Dy$_{16}$</td>
<td>2.10</td>
<td>1.26</td>
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