Original Paper

Symmetry and Periodicity in $Al_{75}(Co_{1-x}Pd_x)_{25}$ Decagonal Quasicrystal Phase

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By electron diffraction (ED) measurements, a structural variety on symmetry and *c*-axis periodicity of decagonal quasicrystal phases (DQC-phases) in rapidly solidified $Al_{75}(Co_{1-x}Pd_x)_{25}$ (x = 0-1) alloys was observed. In the range of $x \leq 0.28$, the DQC-phase has a 0.8 nm periodicity along the *c*-axis with a non-center symmetry. On the other hand, in the Pd-rich region, the DQC-phase has a 1.6 nm periodicity and a center symmetry. Similar to previous high-resolution electron microscope (HREM) studies for DQC-phases, the cluster sizes of atom columns with 0.8 nm and 1.6 nm periodicity along the *c*-axis are 2.0 nm and 0.76 nm, respectively.

Key Words: *Al-Co-Pd Ternary System*, *Decagonal Quasicrystal*, *Center/non-center Symmetry*, *Electron Diffraction*

1. Introduction

A two-dimensional quasicrystal with five and/or ten-fold rotational symmetry which is periodic along the *c*-axis was first studied in rapidly solidified Al-Mn alloys by Bendersky[1]. Until now, the DQC-phases are discovered in many systems, e.g. Al-(Ni,Cu)-Co, Al-Pd-Mn and Al-Ni-(Fe,Ru). Recently, Yurechko *et al*. investigated the phase diagram of Al-Co-Pd system with the thermodynamically stable state[2,3]. Figure 1 shows a part of the compositional diagram of the ternary phases in Al-Co-Pd. In the ternary Al-Co-Pd system, Tsai *et al*. found the DQC-phase in rapidly solidified alloys with a thermodynamically metastable state[4] and Yubuta *et al*. reported an approximant crystalline phase, the W-phase[5]. The local atomic arrangement of the DQC-phase is considered to be close to that of these crystalline phases. Important crystalline phases for understanding the crystal structures of the DQC-phases exist in binary compositions of the Al-Co-Pd. In the binary Al-Co system, monoclinic (*m*)- and orthorhombic (*o*)-$Al_{13}Co_4$[6,7] phases, and ε-Al_3Co phase[8] (Z phase in [2,3]), which was referred to as the primitive τ^2-$Al_{13}Co_4$ phase, exist as the related crystalline phases to the 0.8(0.4) nm periodicity DQC-phase. Compositions of *m*- and *o*-$Al_{13}Co_4$ ($Al_{76.47}Co_{23.53}$) phases are very close to $Al_{75}Co_{25}$. From the HREM observation, it is pointed out that the ε-Al_3Co phase is the link between the Al-Co DQC-phase and the $Al_{13}Co_4$ ones. Those crystalline phases have pentagonal atomic clusters with four layers along the *c*-axis. Likewise, in the binary Al-Pd system, orthorhombic Al_3Pd phase (ε phase in [2,3]) exist as the related crystalline phase to the 1.6 nm periodicity DQC-phase. Matsuo and Hiraga reported that the crystal structure of Al_3Pd alloy consists of decagonal atomic columns with eight layers along the *c*-axis, which are periodically arranged on two-dimensional planes[9].

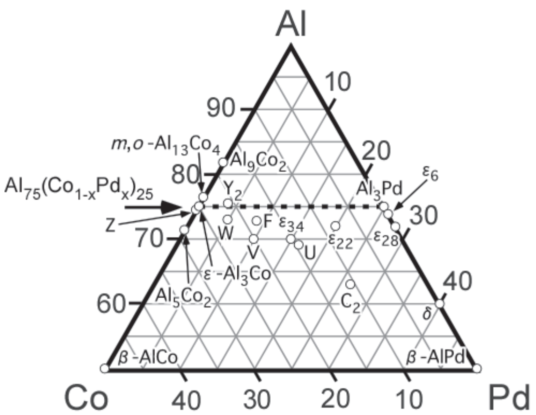

Fig.1 A part of compositional diagram of the binary and ternary phases in Al-Co-Pd. A dotted line is that of $Al_{75}(Co_{1-x}Pd_x)_{25}$ alloy.

The crystal structure of the DQC-phase is very sensitive to make clear the effect of the chemical compositions. Tsai *et al*. and Tanaka *et al*. investigated a composition dependence of the periodicity along the *c*-axis and the symmetry in Al-Ni-Co[10] and Al-Ni-Fe[11] systems. In this paper, to make clear the chemical effect to the symmetry and *c*-axis periodicity of the DQC-phase in the rapidly solidified ternary $Al_{75}(Co_{1-x}Pd_x)_{25}$ alloys, we have employed the ED measurements.

2. Experiment

Polycrystalline samples of $Al_{75}(Co_{1-x}Pd_x)_{25}$ (x = 0, 0.2, 0.28, 0.3, 0.32, 0.36, 0.48, 0.72, 1) alloys were synthesized by an arc melting method using 99.9 % pure Al, Co and Pd as raw materials. Because it was not found that DQC-phases exist in the stable Al-Co-Pd alloys, a rapidly solidification procedure was employed in order to obtain DQC-phases. Parts of the product were rapidly solidified using a melt-spinning apparatus with a single Cu roller of 30 cm diameter. The rotation speed was 2500-3000 rpm. Thin specimens for transmission electron microscopy were prepared by dispersing crushed materials on holey C films. ED patterns and HREM images were obtained using a 400 kV electron microscope (JEM-4000EX) with a resolution of 0.17 nm.

3. Results and Discussions

Figure 2 shows ED patterns from $Al_{75}(Co_{1-x}Pd_x)_{25}$ alloys of x = 0 (a), 0.28 (b), 0.3 (c), 0.48 (d) and 1 (e), taken with the incident beams along *c*- (in the left columns), *p*- (in the middle column) and *q*- (in the right columns) directions. Although all ED patterns exhibit typical features of the DQC-phase, there is an apparent difference between (a)-(b) and (c)-(e), i.e., former and latter alloys have 0.8 nm and 1.6 nm periodicities along the *c*-axis, respectively. Intensity distributions in Fig.2(a)-(b) are very similar in a Co-rich Al-Ni-Co DQC-phase, which has the non-center 5-fold symmetry[12]. Characteristic features in Fig.2(c)-(e) correspond to that of the Al-Pd DQC-phase[13], which has 1.6 nm periodicity with the center symmetry. As a summary of Fig.2, a Co/Pd content dependence of the periodicity along the *c*-axis and the symmetry in

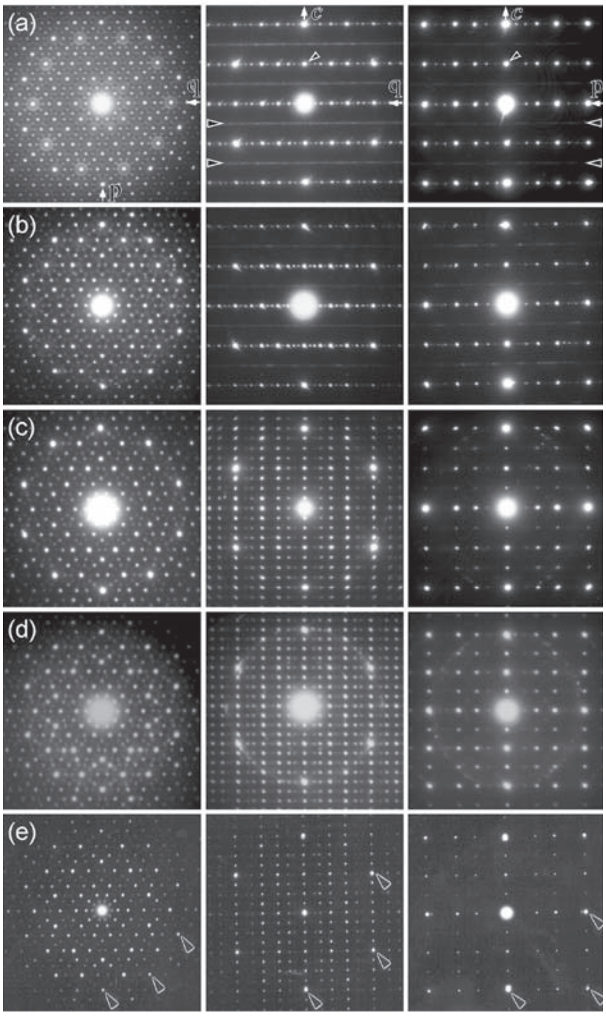

Fig.2 Electron diffraction patterns of the $Al_{75}(Co_{1-x}Pd_x)_{25}$ alloy, x = 0 (a), 0.28 (b), 0.3 (c), 0.48 (d) and 1 (e), taken with the incident beams along *c*- (in the left columns), *p*- (in the middle column) and *q*- (in the right columns) directions.

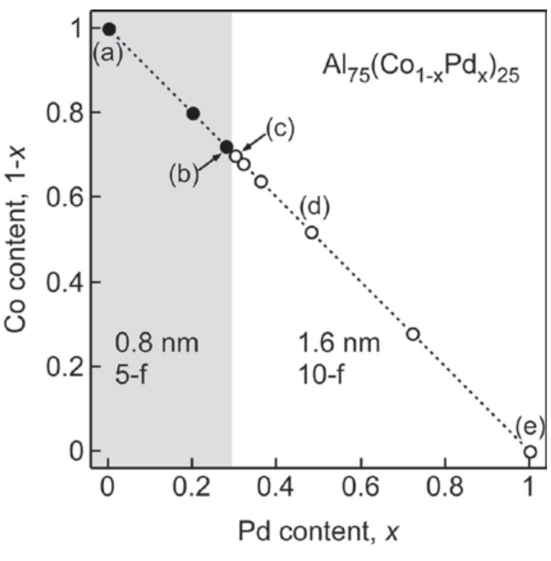

Fig.3 A Co/Pd content dependence of the periodicity along the *c*-axis and the symmetry in $Al_{75}(Co_{1-x}Pd_x)_{25}$ alloys. Close and open circles represent 0.8 nm periodicity with non-center symmetry and 1.6 nm periodicity with center symmetry phases, respectively.

$Al_{75}(Co_{1-x}Pd_x)_{25}$ alloys was illustrated in Fig.3. Close and open circles represent 0.8 nm periodicity with the non-center symmetry, and 1.6 nm periodicity with the center symmetry phases, respectively. It was found that a phase boundary exists between x = 0.28 and 0.30.

Figure 4 shows HREM images of the $Al_{75}(Co_{1-x}Pd_x)_{25}$ alloy, x =

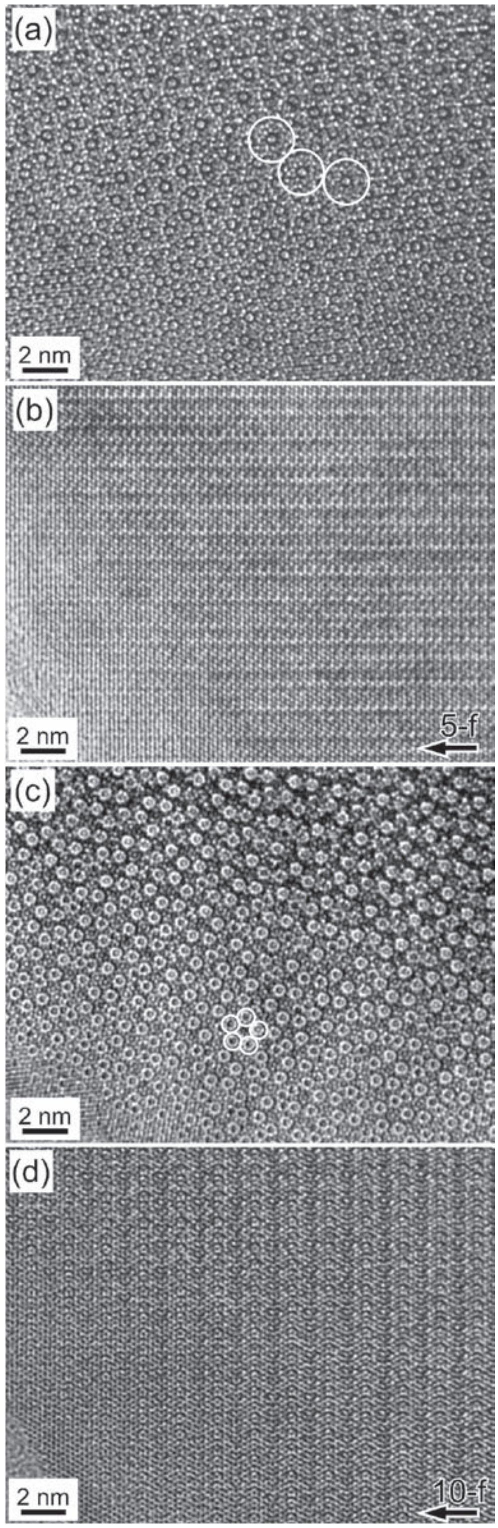

Fig.4 HREM images of the $Al_{75}(Co_{1-x}Pd_x)_{25}$ alloys, x = 0 (a,b) and 0.32 (c,d), taken with the incident beams along *c*- (a,c) and *p*- (b,d) directions. Large and small white circles indicate 2.0 nm and 0.76 nm diameter atom columns.

0 (a,b) and 0.32 (c,d), taken with the incident beams along *c*- (a,c) and *p*- (b,d) directions. It can be recognized that columnar atomic clusters having wheel-like contrasts exist in the $Al_{75}Co_{25}$ alloy [Fig.4(a)]. On the other hand, $Al_{75}(Co_{0.68}Pd_{0.32})_{25}$ alloy in Fig.4(c) consists of small columns. The diameter of the two type of atomic columns in $Al_{75}Co_{25}$ and $Al_{75}(Co_{0.68}Pd_{0.32})_{25}$ alloys are 2.0 nm (large white circles) and 0.76 nm (small white circles), respectively. The former and latter atomic columns resemble those of the DQC-phases in Al-(Ni, Pd)-Co and Al-Pd(-Fe) systems, respectively.

The size relationship can be expressed using τ (=$(1+\sqrt{5})/2$; the golden ratio) as 2.0 nm = 0.76 nm $\times$ τ^2. Figure 5 shows framework of the projection of the decagonal columnar atom cluster[15]. The basic framework is formed with two types of rhombic tiles, called fat and skinny rhombuses, with an edge of 0.25 nm. The atom column is divided into a decagon and 10 pentagons (labeled D) with an edge length of 0.47 nm. In the framework, decagons of three sizes A, B, C, inflated with τ scaling, are shown. The three decagons and the D pentagon are fundamental atomic clusters forming the structures of the DQC-phase and crystalline approximants. The DQC-phases with 0.8 nm and 1.6 nm periodicity along the *c*-axis consist of decagons A with a diameter of 2.0 nm and C that of 0.76 nm, respectively.

Let us focus on the compositional range of relationship between DQC- and related crystalline phases. Yurechko *et al*. found that a number of periodic phases are formed in Al-Co-Pd in the compositional range corresponding to the DQC-phase in Al-Ni-Co from a comparative study of the Al-Co-Pd and Al-Ni-Co alloy systems[14]. Because the ε-Al_3Co phase consists of 2.0 nm diameter atomic columns[8], which are very similar to the wheel-like contrasts in Fig.4(a), the ε-Al_3Co phase is strongly related to the Al-Co DQC-phase. From the ED observation in the present study, it is natural to consider that the DQC-phase observed in $0 \leq x \leq 0.28$ of our samples corresponds as a metastable phase at high temperature to those stable crystalline phases. On the other hand, in the Pd-rich area with the metastable state, the region of the DQC-phase with 1.6 nm periodicity along the *c*-axis related to the Al_3Pd phase (ε phase) tends to be extended to the Co-rich area.

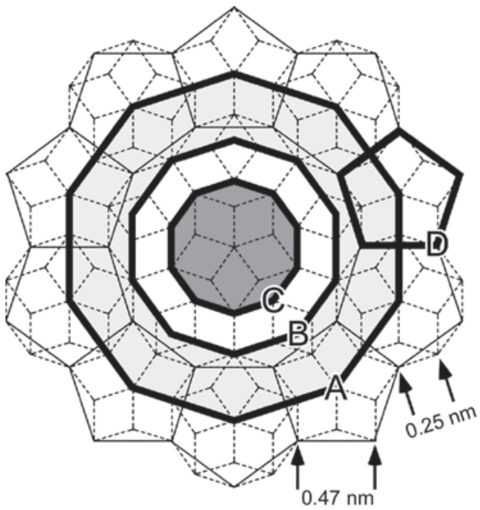

Fig.5 Framework of the projection of the decagonal columnar atom cluster.

4. Conclusion

We have studied the chemical effect on symmetry and *c*-axis periodicity of DQC-phases in rapidly solidified $Al_{75}(Co_{1-x}Pd_x)_{25}$ (x = 0-1) alloys by electron diffraction measurements. It was revealed that the alloys with $0 \leq x \leq 0.28$ has a 0.8 nm periodicity along the *c*-axis with the non-center symmetry and those with $0.3 \leq x \leq 1$ has a 1.6 nm periodicity with the center symmetry. High-resolution images show that the cluster sizes for DQC-phases with 0.8 nm and 1.6 nm periodicity along the *c*-axis are 2.0 nm and 0.76 nm, respectively.

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References

1) L. Bendersky, *Phys. Rev. Lett.*, **1985**, *55*, 1461.
2) M. Yurechko, B. Grushko, *Mater. Sci. Eng. A*, **2000**, *294–296*, 139.
3) M. Yurechko, B. Grushko, T. Velikanova, K. Urban, *J. Alloys Compd.*, **2002**, *337*, 172.
4) A. P. Tsai, Y. Yokoyama, A. Inoue, T. Masumoto, *Jpn. J. Appl. Phys.*, **1990**, *29*, L1161.
5) K. Yubuta, W. Sun, K. Hiraga, *Philos. Mag. A*, **1997**, *75*, 273.
6) R. C. Hudd, W. H. Taylor, *Acta Cryst*., **1962**, *15*, 441.
7) J. Grin, U. Burkhardt, M. Ellner, K. Peters, *J. Alloys Compd*., **1994**, *206*, 243.
8) X. Z. Li, K. Hiraga, *J. Alloys Compd*., **1998**, *269*, L13.
9) Y. Matsuo, K. Hiraga, *Philos. Mag. Lett.*, **1994**, *70*, 155.
10) M. Tanaka, K. Tsuda, M. Terauchi, A. Fujiwara, A. P. Tsai, A. Inoue, T. Masumoto, *J. Non-Cryst. Solids*, **1993**, *153&154*, 98.
11) A. P. Tsai, A. Inoue, T. Masumoto, *Philos. Mag. Lett.*, **1995**, *71*, 161.
12) S. Ritsch, C. Beeli, H.-U. Nissen, *Philos. Mag. Lett.*, **1996**, *74*, 203.
13) K. Hiraga, E. Abe, Y. Matsuo, *Philos. Mag. Lett.*, **1994**, *70*, 163.
14) M. Yurechko, B. Grushko, T. Velikanova, K. Urban, *J. Alloys Compd.*, **2003**, *367*, 20.
15) K. Hiraga, *High-Resolution Electron Microscopy of Quasicrystals*, *Vol.101, Advances in Imaging and Electron Physics*, Academic Press, **1998**, pp.37-98.