Novel Morphology of Voids in Single-Quasicrystalline Icosahedral $Al_{70.5}Pd_{21.0}Mn_{8.5}$

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This paper deals with the morphology and surface chemistry of faceted voids existing in single-quasicrystalline icosahedral $Al_{70.5}Pd_{21.0}Mn_{8.5}$. By observation with a scanning electron microscope of surfaces obtained by cleavage of the quasicrystal, the habit planes of the dodecahedral voids were identified. The chemical surface composition of the void surface was determined by Auger electron spectroscopy after cleavage in ultra-high vacuum.

I. Introduction

Natural minerals [1] and also quasicrystals consisting of metallic elements may exhibit characteristic morphologies. For example, a dodecahedral or triacontahedral outer shape has been observed for icosahedral quasicrystals of Al-Li-Cu [2], Al-Mn [3], Al-Cu-Fe, [4] and Mg-Ga-Zn [5] grown under suitable conditions. Besides the outer morphology of these quasicrystals, faceted voids have sometimes been observed inside icosahedral Al-Pd-Mn quasicrystals [6]. In this paper we present the results of a detailed investigation of the morphology and surface chemistry of such voids in single-quasicrystalline icosahedral $Al_{70.5}Pd_{21.0}Mn_{8.5}$.

II. Experimental

A rod of single-quasicrystalline Al-Pd-Mn of about 70 mm in length and 7 mm in diameter was grown by the Czochralski technique [7, 8] with the long axis parallel to a fivefold axis. Chemical analysis by inductively coupled plasma optical emission spectroscopy yielded a composition of 70.5 at% Al, 21.0 at% Pd and 8.5 at% Mn. From this rod cuboid samples of $2 \times 2 \times 10$ mm^3 were cut by spark erosion with the long axis parallel to the fivefold direction of the quasicrystal lattice.

The sample was transferred into the ultra high vacuum chamber (pressure $< 3 \cdot 10^{-8}$ Pa) of a PHI 5600

Auger electron spectroscopy (AES) system equipped with a hemispherical analyzer. There the sample was cleaved parallel to the fivefold plane perpendicular to the long axis of the sample. A primary electron energy of 10 keV was used for the AES analysis. The electron beam was focused to a spot 5 µm in diameter. After analysis, both surfaces of the cleaved sample were investigated at 15 keV in the secondary-electron imaging mode in a HITACHI S-4100L scanning electron microscope equipped with a field emission gun.

III. Results

Figure 1 shows two corresponding surfaces of the cleaved sample. Four voids can clearly be seen. Their diameter ranges from about 10 to 20 µm. By comparing the two pictures it can be recognized that the pattern consisting of voids and a cleavage-induced hill and valley structure exhibits an overall mirror symmetry. However, the mirror symmetry does not hold for the inner part of the void images.

In order to investigate the morphology of the void facets more closely, the two halves of a selected void were studied in detail as shown in Figure 2. The outer pentagons of the images of the two void halves are in mirror symmetry orientation. Since the edges of the dark central pentagon are parallel in both halves, they are rotated by 72° with respect to the outer pentagon in Fig. 2(a) while they are parallel in Figure 2(b). In order to reproduce the original shape of the void prior to cleavage, the void half of Fig. 2(b) has to be rotated by 180° around a vertical axis and placed on top of the
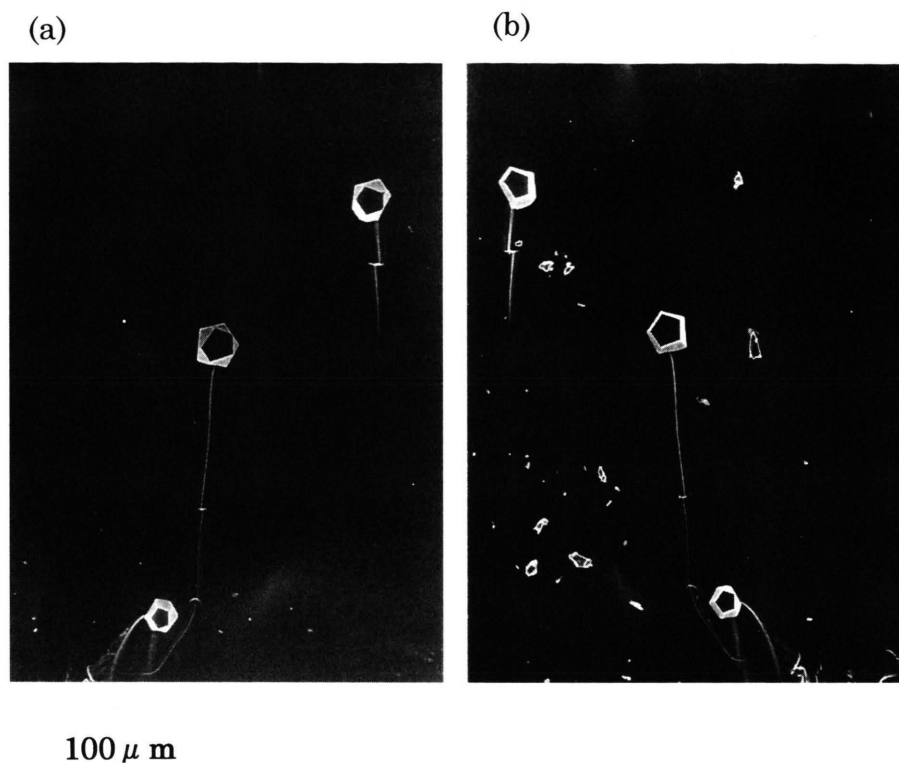
(a)   (b)

100 μ m

Fig. 1. Scanning electron microscope image of the two corresponding parts of a single-quasicrystal of icosahedral $Al_{70.5}Pd_{21.0}Mn_{8.5}$ cleaved perpendicular to the fivefold axis. The cleavage pattern exhibits an overall mirror symmetry, but the images of the voids do not. The original shape of the voids in the two halves of the sample is obtained by folding (b) on to (a) around a vertical axis.
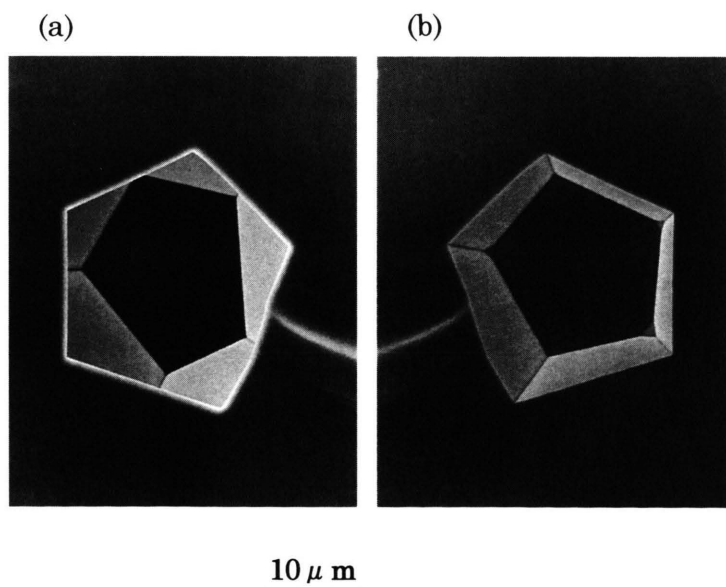
(a)   (b)

Fig. 2. Images of the two halves of a selected void. The crack has traversed the void slightly inclined to the pentagonal plane. Note the bright wedge contrast in (a).
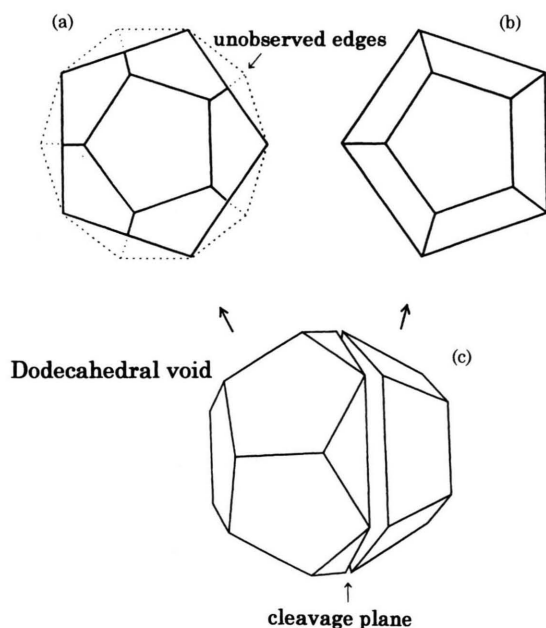
10 μ m

Fig. 3. Schematic drawing of a dodecahedral void; (a) left half, (b) right half (seen from the cleavage surface) after cleavage of the dodecahedral void shown in (c). The dotted lines in (a) indicate the edges obscured from sight.

other half in Figure 2(a). In this way a dodecahedron is obtained with the plane normals of the pentagonal void facets parallel to the fivefold directions of the quasicrystal lattice. The edges of the dodecahedron are parallel to the twofold lattice directions.

The result of the cleavage process, if the crack passes the void slightly off-center, is shown schematically in Figure 3. If the cleavage crack passes through the edges of the dodecahedron as shown, the shape of the left half of the void is biconvex while that of the right half is convex. The dotted lines in Fig. 3(a) indicate the edges obscured from sight in the scanning electron microscope. This means that the outer pentagon of Fig. 3(a) and Fig. 2(a) consists of wedges. Since, at wedges, the secondary electron emission is enhanced [9] a bright contrast is observed around the outer pentagon in Figure 2(a). Our analysis shows that the voids exhibit substantial deviations from the ideal dodecahedral shape. In addition the edges are often truncated by the formation of additional triangular facets parallel to the threefold planes.

The effect of a high-temperature treatment after quasicrystal growth (prior to cleavage) is demonstrated in Figure 4. It shows two voids in one half of a sample which was kept at 800 °C for one day.

The voids exhibit a more complicated shape. We find that the facets parallel to the threefold planes are more extended and additional facets parallel to the twofold planes between two adjacent threefold planes can be seen in the lower part of the void image of Figure 4(b).

Figure 5 shows the AES spectrum for an area far away from voids (a) and inside a void (c), together with the respective first-derivative spectra (b) and (d). Disregarding peaks which are due to a small amount of adsorbed residual oxygen, compositional differences can clearly be seen between the inner surface of the voids and the bulk. Using the peak heights measured for Al *KLL*, Pd *MNN* and Mn *LMM* in the bulk as a reference, we find, on the basis of six point measurements, for the composition of the inner surface of the void 67 at% Al, 30 at% Pd and 3 at% Mn. This means that, with respect to the bulk composition, the manganese content of the alloy is considerably reduced while the palladium concentration is enhanced.

IV. Discussion

The structure and the local composition of quasicrystal surfaces have been the subject of a number of recent investigations. The results of low-energy electron diffraction studies on icosahedral Al-Pd-Mn were interpreted in terms of a perfect quasicrystal lattice extending right into the surface [10,11]. Similar conclusions were drawn on the basis of a scanning tunneling microscope (STM) study on the same material [12]. In both studies the atomically clean surface required for the investigations was produced by ion bombardment followed by thermal annealing. On the other hand, in another STM investigation on icosahedral Al-Pd-Mn the clean sample surface was, as in the present work, produced by cleavage in the ultra high vacuum [13]. The images obtained in this way provided direct evidence for the cluster substructure of icosahedral quasicrystals, thus corroborating the model derived earlier on the basis of X-ray and neutron scattering results [14].

Although the ion-sputtering and annealing route is a standard technique in surface physics its application to studies in metallic alloys is problematic. Due to an element-sensitive sputtering yield and non-stoichiometric Langmuir desorption during the annealing treatment, the stoichiometry of the sample surfaces follows quite complicated evolutionary paths. Indeed, depending on the details of the annealing procedure, substantial deviations from the original
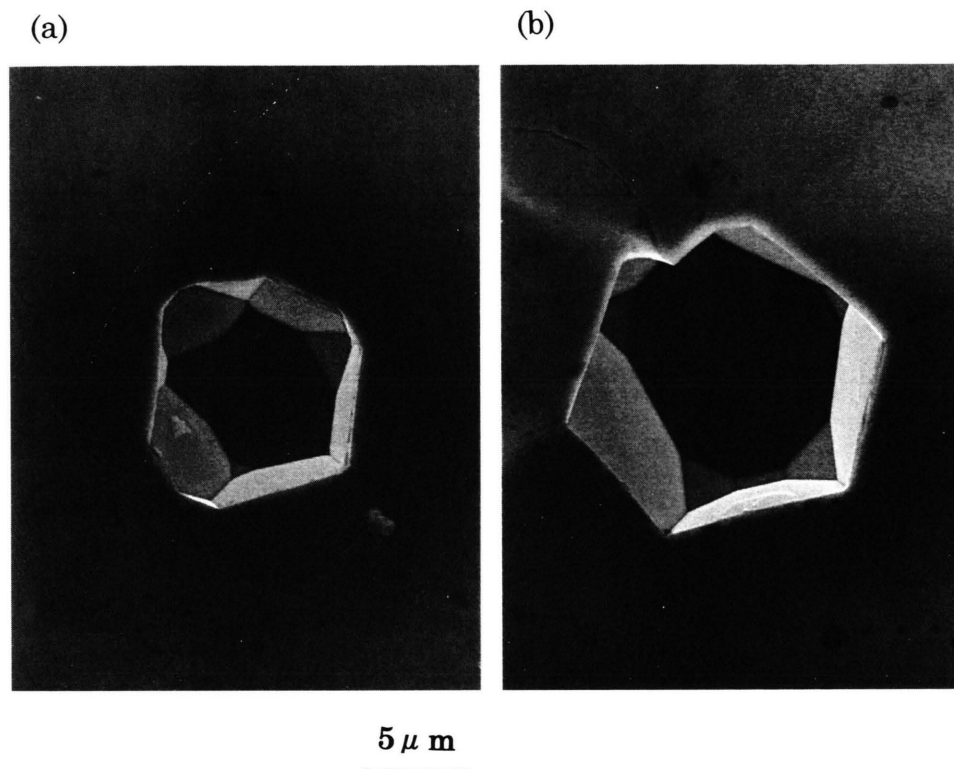
(a)　　　　　　　　　　　　　　(b)

$5\,\mu\,\mathbf{m}$

Fig. 4. Images of two voids in a single-quasicrystal which was annealed at 800 °C for one day and subsequently cleaved perpendicular to the fivefold axis.

sample stoichiometry have been reported [11]. Therefore, it is very difficult to judge whether a surface thus obtained corresponds to an equilibrium situation. In contrast, it can be presumed that the voids investigated in the present work exhibit surfaces which, with respect to structure and composition, should be very close to equilibrium. The quasicrystal is grown at a rate of a few millimeters per hour only, and the product is cooled to ambient temperature very slowly, i. e. within about seven hours. In addition, the void surfaces are internal surfaces of the quasicrystal and have, prior to cleavage, never been exposed to air or vacuum. We therefore consider our observation of a substantial deviation of the void surface composition from bulk stoichiometry as a remarkable result. In fact, according to the detailed phase-diagram study of [6], the surface composition measured lies far outside the single-phase region of icosahedral Al-Pd-Mn.

Quasicrystals have the character of intermetallics owing their stability not only to a particular structure but also to chemical order. It is now generally accepted that deviations from the ideal stoichiometry in

the order of less than one percent destabilize the quasicrystal structure. This should make the quasicrystal surface particularly sensitive to changes in composition. We therefore suggest that the structure of the void surfaces and, more generally, the structure of a quasicrystal surface close to equilibrium is different from that in the bulk. This conclusion is supported by the following argument. As already mentioned, quasicrystals owe their particular structure and stability to short-range order based on clusters. The basic cluster has a diameter of about 1 nanometer and is of the Mackay type [15]. It has icosahedral symmetry and consists of 51 atoms arranged in three shells. It exhibits not only well defined stoichiometry but also distinct chemical order in its individual shells. At a surface, the long-range atomic interactions are disturbed and in addition, as shown in the present paper, the stoichiometry is not maintained. It is therefore unlikely that the cluster-based structure can extend right into the surface and, as a consequence, the surface structure of a quasicrystal cannot be expected to be the same as that of the quasilattice in the bulk.
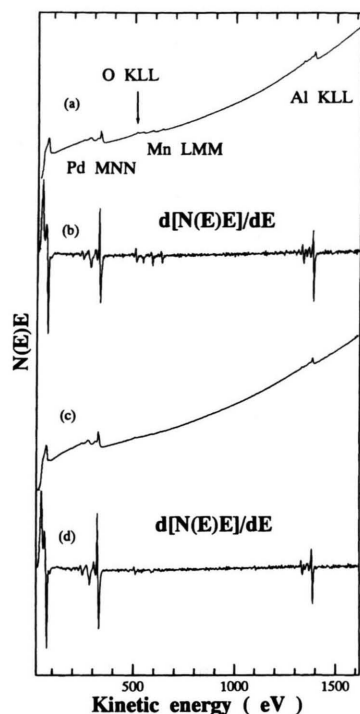
Fig. 5. Auger electron spectra from an area far away from voids (a) and inside a void (c), together with the respective first-derivative spectra (b) and (d).

Analogously to the nucleation and growth of precipitates in supersaturated alloys [16], the growth of the voids can be expected to be strongly affected by the surface energy. The surface energies of alloys in equilibrium are known to vary with surface orientation and stoichiometry according to the Gibbs adsorption relation. Thus, the effect of temperature on void morphology observed in Fig. 4 can be interpreted as evidence for the approach of an equilibrium shape of the voids where the area of the individual types of facets is related to the relative surface energy. Since both, the equilibrium surface composition and the related surface energy, may vary with temperature we cannot exclude an additional slight change in composition during the long-time heat treatment at 800 °C. Obviously this leaves the general energy relation of the surfaces unchanged. We can conclude from our study that, under close-to-equilibrium conditions, the fivefold plane has minimum surface energy followed by the threefold and twofold planes.

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