Unique Shapes of Micro-Pits Formed in an Al-Pd-Mn Icosahedral Quasicrystal by Anodic Etching

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The shapes of micro-pits formed in an Al-Pd-Mn icosahedral quasicrystal have been examined by alternating sequence of electrochemical etching and scanning electron microscopy (SEM) observations. Anodic etching was executed on fivefold and twofold surfaces of the single-quasicrystal. Prolonged anodic etching in a solution of $\text{CH}_3\text{OH} + \text{HNO}_3$ (volume ratio 3 : 1) followed by SEM observations has revealed that two different types of micro-pits, *i.e.* pre-existing micro-voids and electrochemical etch-pits, develop into the same regular shape. The micro-pits develop into a pentagonal pyramid on the fivefold surface, and a flat-bottomed rhombic pyramid on the twofold surface. It is shown that these two polyhedral etch-figures correspond to two different sections of a regular rhombic triacontahedron.

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1. Introduction

The growth shapes of small icosahedral quasicrystal grains are often found to have a morphology with icosahedral symmetry, such as a regular pentagonal dodecahedron and a rhombic triacontahedron, while decagonal quasicrystal grains show a decaprismatic morphology with tenfold symmetry.¹⁻⁴⁾ Besides, micro-voids that are formed in the bulk of Al-Pd-Mn icosahedral single-quasicrystals during growth, which are regarded as 'negative quasicrystals', have been also found to be faceted, and indeed they occur in a variety of shapes approximating Archimedian polyhedra possessing icosahedral symmetry.^{5,6)} Meanwhile, the equilibrium faceted shapes of quasicrystals have been theoretically predicted.^{7,8)}

While the elaborate shapes of the growing quasicrystals as well as the incorporated micro-voids as described above have been greatly appreciated, the morphology of dissolution patterns occurring on quasicrystals is not much known.⁹⁻¹¹⁾ It is highly probable that the dissolution process observed in quasicrystals is the reverse phenomena of their growth process in analogy to crystalline materials. In view of this assumption, the dissolution patterns resulting on their surfaces may also show a specific morphology, reflecting their structural symmetry. Recently we reported an effective experimental method for obtaining crystallographic dissolution patterns, *i.e.* etch-pits on the surface of a single-quasicrystal of an Al-Pd-Mn icosahedral phase.¹¹⁾ It was shown that anodic etching treatment in a solution of $\text{CH}_3\text{OH} + \text{HNO}_3$ creates etch-pits of a pentagonal pyramid on the definite surface normal to a fivefold axis of the sample. In addition, it was indicated by optical microscopy observations that a number of micro-voids pre-existing in the form of various icosahedral shapes underwent successive variations of morphology in the course of etching,

approaching to a regular pentagonal pyramid. The morphological change of the micro-voids, however, was not fully ascertained owing to poor resolution of optical microscopy.

In the present study, the anodic etching treatment was made on fivefold and twofold surfaces of a single-quasicrystal of an Al-Pd-Mn icosahedral phase. We made mainly scanning electron microscopy observations of micro-pits in specific areas on the surfaces after different etching periods in order to examine the morphological change of micro-voids as well as the creation of etch-pits.

2. Experimental Procedure

A master alloy ingot having the nominal composition $\text{Al}_{72}\text{Pd}_{19.5}\text{Mn}_{8.5}$ was prepared from the pure metals Al (99.999%), Pd (99.9%) and Mn (99.9%) in an Ar atmosphere using an arc furnace. A single quasicrystal was grown in a floating-zone furnace with infrared heating using two halogen lamps at a growth rate of 1 mm/h in a highly purified Ar atmosphere. Two specimens having definite flat faces normal to either a fivefold axis or a twofold axis were cut from the resultant single quasicrystal. These two specimen faces will hereafter be referred to as the 'fivefold surface' and the 'twofold surface', respectively. The face orientations were confirmed by back-scattered X-ray Laue diffraction. Prior to subsequent etching treatment, the specimen faces were finished by polishing with alumina abrasives finer to a 0.1 μm size.

Etching conditions selected in the present experiment were basically the same as those in the previous attempt,¹¹⁾ *i.e.* using a solution of $\text{CH}_3\text{OH} + 61\% \text{HNO}_3$ (volume ratio 3 : 1) and a Pt-wire cathode, performed at an anodic voltage of 3.5 V and room temperature for various etching periods. The corresponding electrical current density was then measured to be approx. $7 \times 10^7 \text{ A/m}^2$. The experimental set-up employed is shown in Fig. 1. The specimen was held by Pt-made tweezers as an anode in the solution, while a Pt-wire of $\phi 0.5 \text{ mm}$ as a cathode was set approx. 5 mm apart in front of the specimen

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Fig. 1 Experimental set-up for anodic etching employed in the study.

face of interest. Hereby, the specimen face for the etching-test had a contact with d.c. power supply via the Pt-tweezers. Immediately after etching, the specimen was washed with methanol first and subsequently with distilled water for several minutes each, and finally the wet specimen face was dried in a N_2 gas blast.

Scanning electron microscopes (SEM; JEOL JSM-5800 and JXA-733) and an optical microscope were used to inspect etched-surfaces of the specimens. The SEM instruments were both operated at an accelerating voltage of 20 kV. At the beginning, a microscopic region on each specimen face containing a couple of well-recognized micro-voids was selected as a target for detailed SEM observations. The anodic etching followed by the SEM observations were successively made at every 10 or 15 min interval over the longest period of 75 min.

Dissolution rates of the fivefold surface and the twofold surface of the specimens during etching were evaluated by using a surface texture measuring instrument (Surfcom 1400A, designed by TOKYO SEIMITSU, CO.). Before the etching, a small region on the specimen face of interest was masked by a fragment of acid-proof tape, while the other region was

kept intact. During etching, the etchant attacked exclusively the intact area, making a finite difference in height between the masked-region and the other. The surface texture measuring instrument was utilized to measure these heights difference resulting after a definite etching period. The analyses made for two individual cases, *i.e.* on the fivefold surface and the twofold surface, indicated that the dissolution rate of the twofold surface was approx. $0.34 \mu\text{m}/\text{min}$, and indeed the rate was 20% higher than that of the fivefold surface.

It should be emphasized here that two different classes of faceted 'micro-pits' differing in their origins are revealed on the etched faces: One type originates from pre-existing 'micro-voids', and the other type consists of 'etch-pits' probably formed at some intrinsic defects.¹¹⁾ The terms, *micro-pit*, *micro-void* and *etch-pit* will be used in the following text.

3. Results and Discussion

Figure 2(a) is a SEM micrograph showing a certain microscopic area on the fivefold surface after continuous 60 min etching. The etching has resulted in the occurrence of a number of faceted micro-pits of different sizes. In fact, these micro-pits are classified into two different types: one type for pre-existing micro-voids and the other for etch-pits which probably originate from intrinsic defects. Although the shapes of these micro-pits appear less faceted, they are mostly found to exhibit a pentagonal pyramid shape having fivefold symmetry as is shown by Fig. 2(b). The result evidently shows that the micro-pits take the form of a regular pyramid shape after a substantially long etching time, *e.g.* 60 min. Morphological variation of these micro-pits deduced from optical microscopy observations is completely documented elsewhere¹¹⁾ in light of characteristic growth forms of Mg-Pd-Al icosahedral quasicrystal grains reported by Koshikawa *et al.*¹²⁾

In addition, we made combined analyses of SEM observations and etching treatment, aimed at demonstrating the time dependence of dissolution shapes of micro-pits. Figures 3(a)–(c) present a SEM micrograph montage showing two specific micro-voids inspected at different etching

Fig. 2 SEM micrographs of (a) micro-pits typically found on the fivefold surface after 60 min etching, and (b) the enlarged image of etch-pit enclosed by square in (a).

Fig. 3 SEM micrograph montages of micro-voids found in a specific area of the fivefold surface, taken at different etching times and corresponding schematic illustrations.

times, in addition to corresponding schematic illustrations. Before etching, the micro-voids specified by **A** and **B** each had in common pentagonal basal facets at the bottoms. Indeed, micro-void **A** is seen to be associated with an Archimedean {3,4,5}-polyhedron, while micro-void **B** is associated with an Archimedean {5,6}-polyhedron⁵⁾ as shown in the top figure. With an increasing time, both micro-voids **A** and **B** are found to lessen their pentagonal basal facets and instead to make some of surrounding facets more dominant. It is, thus, confidently expected that these micro-voids will make further changes of shape by prolonged etching, approaching to a regular shape of pentagonal pyramid as shown in Fig. 2(b).

Besides, the etching experiment was made on the twofold surface of another specimen. Figure 4 is an optical micrograph of a specific area in the surface taken after 20 min etching, and this clearly shows the dense creation of etch-pits as well as a few micro-pits originating from pre-existing micro-voids (recognized in a larger size). The etch-pits are each found to have an equivalent shape and size of approx. 10 μm, showing an aspect of diamond shape with twofold symmetry. The density of the etch-pits created in this area is estimated to be approx. $10^{10}/\text{m}^2$. It should be noted here that the population of occurring etch-pits was found to be rather variable from one area to the other within the surface. The definite reason of the non-uniform nucleation of etch-pit is uncertain and is currently under investigation.

Furthermore, the successive etching test was made on a definite area of the twofold surface. Figures 5(a)–(f) show SEM micrograph montages showing the specific area containing micro-pits formed at different etching times. Before etching, a micro-void of indefinite shape was present in the view (see Fig. 5(a)). Remarkably, the successive etchings have caused morphological changes of the micro-void and additionally created several etch-pits in the surrounding. Ob-

Fig. 4 Optical micrographs showing the dense creation of etch-pits having a diamond shape resulting on the twofold surface after 20 min etching.

viously, the micro-pits consisting of both micro-voids and etch-pits have developed an equivalent form constituted by a basal diamond face together with four other surrounding lateral faces. The overall feature of this shape apparently has twofold rotational symmetry. Among the micro-pits recognized in Fig. 5(e), those of relatively larger sizes have been found to originate from micro-voids pre-existing in the specimen and the others, for instance those marked by the arrows, are etch-pits. These results indicate that the flat-bottomed rhombic pyramid shape, which is constituted by a basal diamond face together with four surrounding lateral faces, is preferable in the dissolution of the twofold surface.

In the previous study focused on the fivefold surface,¹¹⁾ the tilt angle of the sides of pentagonal pyramid pits with respect to the surface was estimated to be approx. 30° each by means of a light figure technique. It was therefore claimed from a geometric point of view that those pyramidal facets correspond to a set of five rhombi sharing one apex found in a regular rhombic triacontahedron. Indeed, the present results support this contention. Figure 6 shows a schematic illustration of a rhombic triacontahedron in addition to their projected figures along a fivefold as well as a twofold axis. A rhombic triacontahedron is constructed by a set of equivalent 30 diamonds and each facet is oriented normal to a twofold axis. It is found that each of the projected figures has a characteristic form in the interior (defined in shade) which is comparable to the dissolved shape experimentally obtained from the corresponding etched-face: the form of a pentagonal pyramid in the fivefold projection and that of a basal diamond face with four surrounding lateral faces in the twofold projection. It is therefore concluded that an overall image of the dissolved shapes of micro-pits, which appear different depending on the

Fig. 5 SEM micrograph montages of micro-pits found in a specific area of the twofold surface, taken at successive 15 min etching intervals. Note that micro-pits specified by the arrows are etch-pits, while the others originate from micro-voids.

etched-faces, is in effect represented by a regular rhombic triacontahedron. In this way, the dissolution shape occurring in the Al-Pd-Mn icosahedral quasicrystal can be uniquely defined in contrast to variable forms resulting from the 'positive' or 'negative quasicrystal' growth. Classical kinematical theory of etch-pit formation explains that a set of lattice planes of higher etch rate will dominate the resultant facet planes of etch-pit.¹³⁾ Taking account of the fact that the dissolution rate of the twofold surface is considerably higher than that of the fivefold surface (see text in section 2), it can be concluded that the lattice planes normal to the twofold axes in the Al-Pd-Mn

icosahedral quasicrystal dissolve faster than any other planes under the present etching conditions.

It has been commonly found that the micro-pits make a definite increase in number till a certain etching time, *e.g.* 30 min. This seems due to the fact that the formation of etch-pits is more enhanced with progressive dissolution of a deformed thin layer present at the topmost surface: because the mechanical polishing made before etching necessarily introduces a deformed thin layer at the topmost surface, this may hinder the etch-pit formation at an initial stage. The densities of etch-pits obtained from the first 20 min etching were found

Fig. 6 Schematic illustrations of a rhombic triacontahedron and its projections along a fivefold and a twofold axis. Gray areas defined in the projections represent micro-pit figures obtained experimentally from the corresponding specimen faces by prolonged etching.

to be in the order of 10^8 m^{-2} for the fivefold surface, while the order of 10^{10} m^{-2} for the twofold surface under the same etching conditions. This also exemplifies that the dissolution behavior of the specimen is significantly different depending on the orientations of etched-face. Effectively, the higher dissolution rate of the twofold surface is responsible for the higher rate of occurring etch-pits. According to Wollgarten *et al.*,¹⁴⁾ a probable level of the dislocation density occurring in the quasicrystal is approx. 10^{10} m^{-2} , which is comparable with the etch-pit density estimated on the twofold surface of the present specimen. It can, therefore, be expected that the etch-pits especially obtained from the twofold surface originate from dislocations present in the quasicrystal. However, a dislocation-originated pit typically found in crystalline materials form a pointed apex at the bottom and this is not the case for the present result. This question remains to be solved by further investigations.

4. Conclusions

The anodic etching using a solution of $\text{CH}_3\text{OH} + \text{HNO}_3$ (3 : 1 in volume ratio) followed by SEM observations has

revealed unique dissolution patterns occurring on the fivefold and the twofold surfaces of an Al-Pd-Mn icosahedral phase. We have demonstrated that, as the dissolution progresses, two different classes of micro-pits, which consist of pre-existing micro-voids and etch-pits, both develop into the regular shapes, finally ending in a pentagonal pyramid on the fivefold surface and a flat-bottomed rhombic pyramid on the twofold surface. It has been clearly demonstrated that the facet planes constituting these polyhedral shapes correspond to different sets of five rhombi existing in a regular rhombic triacontahedron. This is due to the fact that the twofold lattice planes of Al-Pd-Mn icosahedral quasicrystals dissolve faster than the other planes. In addition, the etch-pits forming on the surface of a twofold plane could be related to dislocations existing in the specimen.

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