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# Effects of Microstructure of Aluminum Substrate on Ordered Nanopore Arrays in Anodic Alumina

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The effects of microstructure of aluminum substrate on regular nanopore arrangement in anodic alumina layer were investigated. The dissimilar microstructure and texture on aluminum sheets were prepared by various cold rollings and heat treatments, and anodic alumina nanoporous layers were fabricated by two step anodizing method at 40 V in oxalic acid solution. For the aluminum sheets with similar surface texture and annealing condition except purity, the regularity of the nanopore arrangement on the anodic alumina layer increased with purity of aluminum substrate. The difference of surface texture on Al sheets is not critical parameter for formation of ordered nanopore array compared with purity and heat treatment of substrate aluminum. The investigation suggested that the purity and reasonable annealing temperature of aluminum substrate are very important process to obtain the highly-ordered nanopore array on anodic alumina layer.


## 1. Introduction

A porous alumina layer obtained by anodic oxidation of aluminum in acidic electrolytes has unique hexagonal nanopore array and have received considerable attention due to their wide applications for renewable energy harvesting and storages[1–3], biomaterials[4], surface enhanced Raman spectroscopy (SERS)[5,6], engineered contact angle surface[7,8] and biosensors[9]. For fabrication of nanoporous alumina layers, surface of aluminum sheet should be oxidized from aluminum to alumina structure during anodizing process. Thus, anodizing process of aluminum sheet affects significantly porous anodic alumina morphology. To obtain the long range ordered nanopore array on anodic alumina layer, many investigations on anodizing conditions, such as anodic potential[10,11], electrolyte[12,13], anodizing temperature[11,14–16], have been reported. Moreover, for economic purposes, various attempts[17,18] have been also made to fabricate the highly-ordered nanopore array using low purity aluminum alloys.

In general, for controlling the shape or dimension, aluminum sheets as a starting material for anodization need to be rolled and annealed, which lead to significant changes in the surface textures and microstructures of the aluminum sheet. These changes of the microstructure and texture affect the mechanical properties[19] and corrosion resistance[20,21] of the aluminum sheet. It can also affect the nanoporous morphology on anodic alumina layer. Therefore, in order to achieve highly-ordered nanopore arrangement and wide applications for the nanoporous alumina layers, the precise formation behaviors of ordered nanopore arrays on anodic alumina layer with respect to microstructure and surface textures of aluminum substrate need to be investigated.

In this study, the effects of microstructure and surface texture of aluminum sheet on regular nanopore arrangement of anodic alumina layer were investigated. Moreover, the change in microstructure of aluminum sheet due to purity and annealing temperature can be attributed to the effect of porous anodic alumina morphology after anodizing of aluminum substrate. Thus, the effect of purity and annealing temperature of aluminum sheet on nanopore regularity of anodic alumina layer was also investigated. To observe the nanopore arrangement, the anodic alumina layer was prepared by two-step anodization process[22,23] in oxalic acid at 40 V. For investigation on microstructure and surface texture of aluminum sheet in regard with regular nanopore arrangement in anodic alumina film, aluminum sheets with various textures were prepared by cold rolling and heat treatments.

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## 2. Experimental

An initial thickness of aluminum sheets of pure and commercial AA1050 was 5 mm, respectively. In order to investigate the effect of surface texture on nanopore arrays of self-organized porous alumina, pure (Tokai Metal Co, Japan 99.99%) and commercial AA1050 alloy (99.5% purity) sheets were used in this study. The aluminum sheets were cold rolled to 90% reduction and annealed at different temperature, and then texture measurement was performed. The incomplete pole figures of (111), (200) and (220) for aluminum sheets were measured by using Co*K*α radiation in 5° steps with sample rotation of 360° and tilting sample at 5° up to a 70° tilt angle. The orientation distribution functions (ODFs) and inverse pole figures for the sheet-normal direction were evaluated by using a harmonic method[24]. The ODFs were presented as plots of constant $\varphi_2$ sections with isointensity contours in Euler space defined by the Euler angles $\varphi_1$, Φ, and $\varphi_2$. For preparing nanoporous alumina layers, two-step anodizing process was performed.

The aluminum sheets were degreased in acetone and ethanol, and then electropolished in a 1:4 mixture of 60% $HClO_4$ and $C_2H_5OH$ at 20 V. The electropolishing was performed at 5 °C for 5 min. After electropolishing, first anodization was performed at applied anodic potential in 0.3 mol/l $H_2C_2O_4$ solution for 10 h. After the first anodization, the anodic layer was removed in a mixture solution of 6% $H_3PO_4$ and 3.8% $H_2CrO_4$ solution, second anodizing was carried out in 0.3 mol/l $H_2C_2O_4$ solution for 1 h. Both of the 1st and 2nd anodizations have been done at 40 V. The process for preparing nanoporous alumina layer is illustrated in Fig. 1. The microstructure of aluminum substrate and pore arrays in anodic alumina layer were observed by transmission electron microscopy (TEM, H-9000NA, Hitachi) and field emission scanning electron microscopy (FE-SEM, XL30 ESEM-FEG, Philips). The estimations of nanopore regularity on anodic alumina layer were performed from SEM images, and average domain size with same pore orientation was directly evaluated from three FE-SEM images (20,000 × magnification) per sample.

## 3. Results and Discussion

### 3.1. Microstructure and surface texture

The various surface textures of aluminum sheets can be obtained by cold rolling up to 90% thickness reduction and annealing with different temperature. The purity, rolling condition, resultant microstructure and texture of aluminum sheets are extensively summarized in Table 1. Textures of Table 1 were obtained from the pole figures measurement and ODFs, which are exhibited in Figs. 2 and 3. These aluminum sheets exhibited different textures. Sample-1 showed major {001}<100> and minor γ-fiber [{111}<112> and {111}<110>, ND//<111>] textures; sample-2 showed major {001}<100> and minor γ-fiber [{111}<112> and {111}<110>, ND//<111>] textures; sample-3 showed {123}<634>, {112}<111> and {110}<112>] textures; sample-4 showed {112}<113> and {112}<123> textures; and sample-5 showed {123}<634> and {112}<111> textures in Figs. 2 and 3. These mixed texture samples were used for fabrication of anodic layer with nanopore arrays.

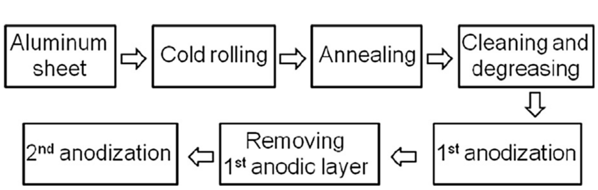


**Fig. 1.** Process for preparing nanoporous anodic alumina layer.

### 3.2. Effects of purity of aluminum substrates on nanopore regularity

To observe the effect of purity of aluminum substrate on nanopore regularity in anodic layer, AA1050 and high purity (99.99%) aluminum sheets were utilized. The aluminum sheets were cold rolled to 90% reduction with and without lubricant methods, and then annealed at 200 °C for 1 h. The aluminum samples exhibited a similar texture structure, as shown in Table 1. The anodic alumina layers with nanoporous structures were prepared by using a two-step anodization process in oxalic acid electrolyte, and changes of surface morphology on anodic layer during two-step anodization process are shown in Fig. 4.

Fig. 4(a, b) exhibits pore arrangements of alumina layer formed on AA1050 and pure aluminum (99.99%) substrate after first anodization at 40 V in oxalic acid for 10 h, which show an irregular porous structure. But for the examination of the bottom side after removing the 1st anodic layer, pore arrays show more ordered array than upper view of 1st anodic alumina layer due to volume expansion of alumina at metal/oxide interface during 1st anodization, as shown in Fig. 4(c, d). These hexagonally ordered arrays at bottom of the 1st anodic layer act as self-assembled mask for the 2nd anodization process. Therefore, it has been suggested that the well-ordered hexagonal pore arrays formed after the 2nd anodizing can be obtained on the well-ordered bottom array at metal/oxide interface formed during first anodization[25]. Thus, better arrangement of the nanoporous array after the 2nd anodizing can be also obtained from longer first anodizing time[10].

Fig. 4(c, d) shows that the more hexagonally ordered arrays at bottom of the 1st anodic layer were observed on pure aluminum substrate than on AA1050 aluminum. It was reported by Li et al.[26] that the strain energy due to the volume expansion at the metal/oxide interface can cause the resulting porous alumina layer, and therefore ordered pore structure can be obtained under controlled anodization conditions. In the case of AA1050 aluminum sheet containing more impurities, the transition of aluminum into alumina can be discontinuous during anodization, which can cause the unstable volume expansion at the metal/oxide interface. It leads to a random pore arrangement. Because the pore array in the 2nd anodic alumina was affected by the bottom arrays at metal/oxide interface, it can be expected that the higher ordered pore array is observed on pure aluminum surface with the well-ordered bottom array. The nanoporous anodic alumina was prepared by the 2nd anodization for 1 h after the 1st anodization for 10 h at 40 V. As shown in Fig. 4(e, f), for pure Al substrate, the nanopore arrays of the 2nd anodic alumina layer are more regular than those for AA1050 substrate, which is in good agreement with that mentioned above.

To observe the precise nanopore regularity of the 2nd anodic alumina layer according to purity and texture, nanopore arrangement compared with texture was investigated. These texture results of aluminum sheets are shown as inverse pole figure (IPF) plots for normal direction of the sheet. Fig. 5 shows inverse pole figures of AA1050 and pure aluminum substrates, which were 90% cold rolled and annealed at 200 °C for 1 h, and resultant nanopore arrangements on alumina layer after two-step anodization. The inverse pole figures in Fig. 5(a, b) confirm that <001> direction of grains mainly aligned, and <111> direction of grains is partially mixed in AA1050 and pure aluminum sheets. These aluminum sheets exhibit similar texture structure. However, the difference in nanopore regularity on anodic alumina layer was detected, as shown in Fig. 5(d, e). From Fig. 5(d, e), ordered nanopore domain size can be evaluated, which indicates the average diameter of domain area with same pore orientation array. The average ordered pore domain size is 0.7 μm for AA1050 and 1.3 μm for pure aluminum sheet, as shown in Fig. 6. For AA1050 and pure