SURFACE and INTERFACE ANALYSIS

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Metallographic effects of pure aluminum on properties of nanoporous anodic alumina (NPAA)

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The microstructure of aluminum substrates was investigated during the quality control of grain sizes determination and crystal orientation analysis before and after preheat (recrystallization) treatment at 500 °C, in relation to the microstructure and heat stability of nanoporous anodic alumina (NPAA) membranes formed on various preheated aluminum substrates and subsequently detached. Depending on the preheating conditions, the average grain size of the aluminum substrate increased from 3 μm to 1280 μm. Also, the preferential crystal orientation of aluminum was (311) and/or (100) or (311)/(422) or (220) under different heating conditions. Recrystallization at a higher heating rate and particularly a higher cooling rate yielded lower grain growth of the aluminum substrate, so that quenching rather than annealing resulted in smaller grains and domains as well as a larger number of grain boundaries on the top surface of related α-NPAA membranes. This induced less ordered growth in the nanopore structure and lower stability against cracking and deflection during crystallizing α-NPAA thin film membranes. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: porous anodic alumina; membrane; anodization; recrystallization; quenching; annealing; grain

Introduction

Nanoporous anodic alumina (NPAA) with a self-organized pore arrangement and a uniform pore size and pore interval[1] is a promising material for using in various research fields, such as nanomaterial fabrication, and the manufacture of photonic crystals, catalysts, electronic, magnetic, and optical devices, and filter membranes. In particular, ceramic-type (alpha) NPAA membranes with high thermal and chemical resistance are suitable for application in microsensor devices[2] or to polluted water filtration for operation at high temperatures. The nanopore regularity of the NPAA film depends on the microstructure (crystal orientations) of the aluminum substrate, which is affected by pretreatment methods such as polishing and heating.[3] In addition, the stability to thermal shocking, deflection, and cracking during the transformation of as-anodized amorphous NPAA to the α-phase is a technological requirement that is also affected by the texture of the aluminum substrate.[3] Except for a few studies,[3–8] there is a lack of detailed information regarding these subjects. In the present study, we investigated the effect of preheating (recrystallization) conditions such as heating and cooling rates, and the holding time at the annealing temperature by annealing (low heating rate along with low cooling rate) or quenching (low or high heating rate along with high cooling rate) on the microstructure of the aluminum substrate. We also investigated the nanopore regularity and thermal stability of α-polycrystalline NPAA membrane films during heat treatment at high temperatures (> 1000 °C).

Experimental

An aluminum sheet (purity of 99.99%, thickness of 0.5 mm) was cut into circular pieces (A = 9.8 cm^2) with a similar size to a commercial Anopore membrane (Anodisc 25).[9] Eight specimens, as listed in Table 1, were prepared as follows: (i) The pieces were electropolished in a 4:1 mixture of ethanol and 60% perchloric acid solution. (ii) Seven of the polished pieces were heated at 500 °C for 1 or 2 h, and the eighth was kept without heating to study the effect of preheating on the surface microstructure of the aluminum substrate and the α-NPAA membrane. Afterward, a two-step anodization of all the aluminum pieces was performed at 40 V in 0.3 mol dm^{-3} oxalic acid solution at 30 °C. The first anodization was conducted for 1 h. After the removal of the first anodized NPAA film by dipping in a solution of 6% H_3PO_4 and 2% CrO_3 at 70 °C for 20 min, the second anodization was performed with this prestructured aluminum for 3 h to obtain a film thickness of 50 μm. All the detached as-anodized NPAA films were annealed at 1250 °C for 4 h to transform them to the polycrystalline α-phase. The average grain and domain sizes of all the resulting α-NPAA films are listed in Table 2. Details of the membrane preparation will be described elsewhere.[10] The aluminum substrates as well as the α-NPAA membrane films were labeled as described in the captions of Tables 1 and 2 according to the preheating conditions of the aluminum substrate. The surface morphology, nanopore arrangement, and thermal stability of all the α-NPAA membrane films formed on different preheated aluminum sheets during the entire preparation procedure were characterized by optical microscopy (OM), field-emission scanning electron microscopy (FESEM), and X-ray diffraction (XRD) analysis.

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Table 1. Preheating (recrystallization) conditions and average grain sizes of different aluminum sheets

Al substrate (99.99%)*	Preheating conditions at 500 °C before anodization			Av. grain size (μm)
	Heating rate (°C/min)	Holding time (h)	Cooling rate (°C/min)	
Al–As-polished	-	-	-	3
Al-HQ	50	1	Q	845
Al-LQ	5	1	Q	874
Al-HL	50	1	2.5	911
Al-IQ	highest[a]	1	Q	808
Al-IQ-2h	highest[a]	2	Q	1005
Al-LL1	5	1	2.5	1280
Al-LL3[b]	5	1	2.5	1200

H: high rate (50 °C/min), L: low rate (5°C/min), Q: quenched in water

[a] Sudden exposure to 500 °C

[b] Wrapping of sample with aluminum foil

Table 2. Average grain and domain sizes of different α-NPAA membranes prepared at 1250 °C

α-NPAA	Average grain size (μm)		Average domain size (nm)	
	Top surface	Bottom surface	Top surface	Bottom surface
As-polished	65	76	660	700
HQ	45	89	560	740
LQ	57	69	670	710
HL	68	78	720	750
IQ	50	67	600	690
IQ-2h	56	74	650	700
LL1	66	72	690	720
LL3	61	71	710	730

Results and discussion

Preheating effect on aluminum microstructure (e.g. grain size and grain shape)

Figure 1 shows the surface microstructures of pure aluminum (99.99%) before and after heat treatment. The average grain size of the unheated sample (Fig. 1a) was 3 μm, while that of the preheat-treated samples at 500 °C increased to 808–1280 μm (Table 1). With decreasing heating and/or cooling rate or with increasing holding time the grain size further increases. For example the largest grain size of 1280 μm was obtained in the Al-LL1 sample, while it was 845 μm in the Al-HQ sample. This shows that the heating conditions and total exposure time to a high temperature affect the recrystallization process and thus determine the grain size.

Preheating effect on aluminum crystalline structure (crystal orientation)

Figure 2 shows the XRD patterns of the aluminum sheets before and after heat treatment at 500 °C under different conditions. The XRD pattern of the As-polished aluminum sample (Fig. 2a) fitted to that of crystalline aluminum (card 4–787) with a face-centered cubic (fcc) phase, which has the (111), (200), (220), (311), (400), (331), (420), and (422) crystalline planes. In each aluminum sheet pretreated by electropolishing and heating under various heating conditions, the fcc phase was observed, but it was found that their preferential crystal orientation is different. The recrystallization conditions such as the heating and cooling rates as well as the holding time affected the crystal orientations of the aluminum substrates. It was found that the Al-HQ sample heated at 500 °C for 1 h using high heating and cooling rates had preferential (200) and (311) reflections (Fig. 2b). With sudden exposure of the Al-IQ sample (Fig. 2c) at 500 °C for 1 h, the preferential crystal plane became (220). However, the appearance of the (200) and (400) crystal planes in the Al-IQ-2h sample shown in Fig. 2d indicated that upon increasing the holding time at 500 °C to 2 h, recrystallization occurred with different orientations. In our earlier work,[3] we found that the annealing of an unpolished aluminum substrate changes the preferential crystal orientation to (100). In contrast, in this presented study, for the Al-LL1 and Al-LL3 substrates that were subjected to electropolishing prior to annealing, the preferential plane is (311) instead of (100) as shown in Figs. 2e and f. These results showed that electropolishing may affect the orientation of aluminum crystals during preheating. Although the effect of electropolishing on the surface texture of aluminum substrate and on the self-ordering of pores in anodic alumina have already been investigated,[3,11–13] no detailed work has been conducted on the effect of preheating at various recrystallization conditions

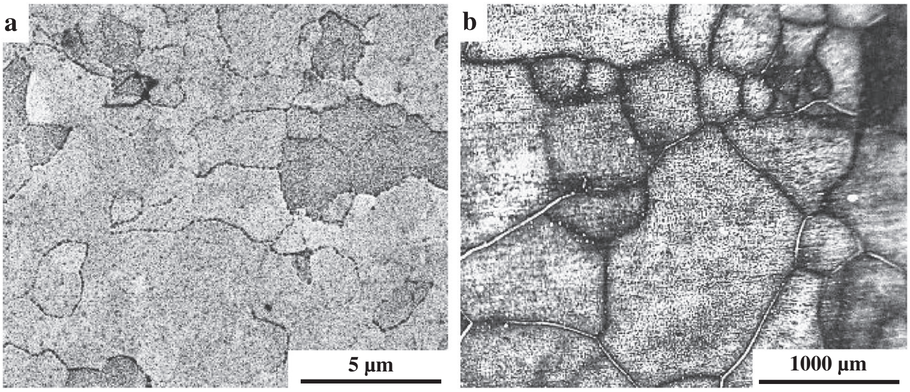

Figure 1. Microstructure surface images: (a) SEM image of Al–As-polished and (b) optical microscopy image of Al-HQ.

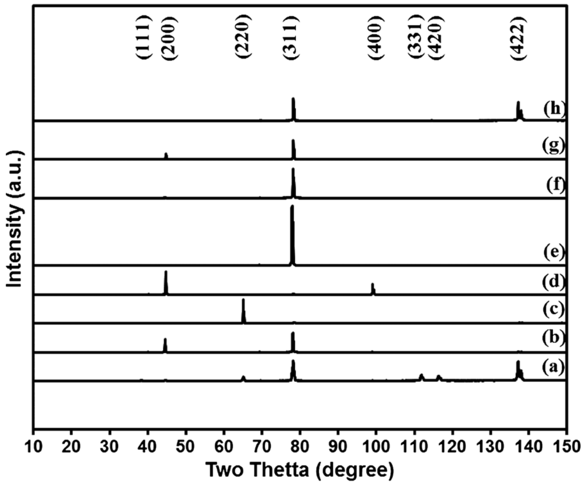

Figure 2. X-ray diffraction patterns of Al substrates before and after preheating at 500 °C for 1 or 2 h under different heating conditions: (a) Al–As-polished, (b) Al-HQ, (c) Al-IQ (d) Al-IQ-2h, (e) Al-LL1, (f) Al-LL3, (g) Al-LQ, and (h) Al-HL.

on the crystal orientation of electropolished aluminum and accordingly on its effect on both pore regularity and the stability of the amorphous NPAA formed on the aluminum substrate and particularly of the α-NPAA membrane films. Caicedo-Martinez C.E. *et al.*[11] studied the influence of the grain orientation on the surface texture obtained after the electropolishing and chemical polishing treatments of the aluminum and aluminum alloy, which discrete peaks for (100), (110), and (111) grain orientations on the texture is reveled. Since these results are interesting, further study is in progress to explore the electropolishing effect in more detail. Also, the low heating rate along with the high cooling rate (quenched) of the Al-LQ sample (Fig. 2g) resulted in the preferential orientations of (200) and (311), which are similar to those observed in the Al-HQ sample. This indicates that the crystal orientation is not affected by the heating rate if quenching is applied during the cooling step. When the heating rate is high and the cooling rate is low, the crystal orientations of (311) and (422) were observed in the Al-HL sample (Fig. 2h).

From our new results, we claim that the preferential crystal orientation of aluminum substrates heated at 500 °C for 1 or 2 h is strongly dependent on the heating conditions: [annealing, (311); sudden exposure and quenching, (220); high or low heating rate and quenching, (200, 311)]. However, in previous works[3,5] conducted on the annealing treatment of a highly pure and unpolished aluminum substrate at 500 °C, the preferential orientation of (100) has been reported. Also, we found that the electropolishing of aluminum followed by heating gives different orientation from that of a sample electropolished after heating. It exhibited that the order of the sequence (electropolishing–heating) might affect the final grain orientation of aluminum crystals. Electropolishing of the recrystallized aluminum could remove surface oxide layer and erase some of blisters (B) and γ-alumina (GA) deposits formed during preheating the aluminum substrate, which might shave the crystals oriented along (311) orientation and dominate the crystals oriented along (100) on the surface texture of aluminum.

Preheating effects on microstructure properties (e.g. grain size and grain shape) and thermal stability of as-anodized amorphous and polycrystalline α-NPAA films As-anodized amorphous NPAA films

As shown in Fig. 3, the grain features and grain sizes of preheat-treated aluminum substrates were transferred as a pattern to the detached as-anodized amorphous NPAA-IQ, NPAA-LL1, and NPAA-LL3 films prepared on the unheated, quenched, and annealed aluminum substrates, respectively. However, in the NPAA-As-polished film (Fig. 3a) formed on unheated aluminum, only lines formed during the rolling of the aluminum substrate were observed, and no grain structure was observed since the average grain sizes of the unheated aluminum substrate were too small, as shown in Fig. 1a. Also, the observed black spots, which are most prevalent in the NPAA-LL1 film, are voids due to blisters (B) and γ-alumina (GA) deposits formed when heating the aluminum substrate, which are hereafter labeled as BGA deposits in the aluminum substrate and BGA voids in the NPAA membrane film. It was found that these deposits are mostly located at grain boundaries of the aluminum substrate and consequently in the as-anodized NPAA films. From the OM images, it was found that both size and ratio of the BGA voids become larger during the second anodization and remain in the NPAA film even after film is detached as follows: [on the top > in the middle > on the bottoms surfaces]. This shows that, during preheating, the BGA deposits not only formed on the aluminum surface but also in the aluminum bulk. Figure 3b reveals that when suddenly exposing aluminum to a high temperature of 500 °C along with a high cooling rate (quenching), the Al-IQ sample produced the lowest ratio of BGA deposits. In contrast, the low heating and cooling rates (annealing) of the Al-LL1 sample shown in Fig. 3c resulted in the highest ratio of these BGA deposits both at the grain boundaries and in the grain interior. However, the generation of these deposits, especially GA deposits, could be suppressed effectively by wrapping the aluminum substrate with foil (Fig. 3d). It is suggested that wrapping with foil protects the aluminum substrate from oxygen, consequently suppressing the formation of γ-alumina particles.

Polycrystalline α-NPAA films

The crystallization of anodic films was studied on the nanoscale by Arurault's research group.[14] For the crystallization behavior, it has also been reported[15–18] that heat treatment at high temperatures of 800–1400 °C results in a change in the pore structure of the NPAA membrane, largely due to the increase in density during the phase transformation from the amorphous phase to the polycrystalline α-phase. In fact, during heat treatment at high temperatures, simultaneously with mass reduction, because of dehydration, dehydroxylation, and the loss of electrolyte anions, a substantial decrease in the total volume of the NPAA membrane is resulted. Therefore, a decrease in pore density and cracking in some areas on the top and on the bottom surfaces of the α-NPAA perpendicular to the pore channels is expected.[15] Note that, generally, no microscopic crack formation occurs through the film if a carefully programmed heating procedure is used.[10]

Domain is an array of hexagonal pores which is nucleated at the defects and grain boundaries of the aluminum substrate. Annealing treatment can reduce the defects and relieve the stresses in the aluminum substrate which result in less nucleation

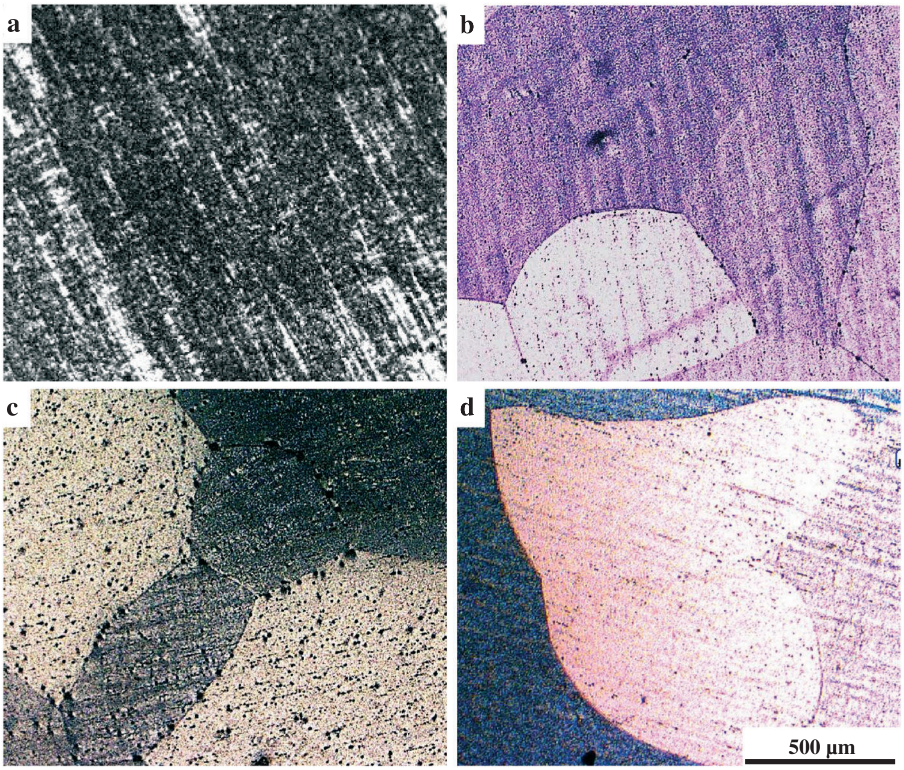

Figure 3. Optical microscopy images of detached as-anodized NPAA film formed on differently treated Al substrates: (a) NPAA-As-polished, (b) NPAA-IQ, (c) NPAA-LL1, and (d) NPAA-LL3.

sites and the formation of larger domains in the amorphous anodic film.[19] The effect of the annealing and quenching treatments on the domain size and the pore regularity of the polycrystalline α-NPAA films have remained elusive.

Figure 4 shows OM images of the bottom surface microstructure of all the α-NPAA membrane films listed in Table 2. The grain boundary of α-alumina is shown as a dark line, and BGA voids are shown as dark spots, which exist along with original aluminum grain boundary and reflect the surface structures. It was found that the domain sizes as well as the grain sizes of the top surface of the α-NPAA films are smaller than those of the bottom surface. As shown in Table 2, the average domain sizes of the self-organized pore arrangement of the NPAA films range from 560 to 720 nm on the top surface and from 690 to 750 nm on the bottom surface. Also, the average grain sizes of all the α-NPAA membranes were measured to range from 45 to 68 μm on the top surface and from 67 to 89 μm on the bottom surface. Thus, it can be concluded that the average grain sizes of the α-NPAA are related to not only the crystal orientation, but also the heating and cooling rates during the recrystallization of the aluminum substrate. With decreasing the heating and/or cooling rate, the grain size on the top surface tended to increase in the following order: α-NPAA-HQ (45 μm) < α-NPAA-IQ (50 μm) < α-NPAA-IQ-2h (56 μm) < α-NPAA-LQ (57 μm) < α-NPAA-LL3 (61 μm) < α-NPAA-LL1 (66 μm) < α-NPAA-HL (68 μm). Although the grain sizes are similar to the membrane thickness, the differences between the grain sizes on the top and on the bottom surfaces of the α-NPAA-HQ, α-NPAA-IQ, and α-NPAA-IQ-2h membranes, which are prepared on quenched aluminum substrates, were more significant. For example, the average grain size on the top surface of the α-PAA-HQ membrane was 45 μm, whereas it was 89 μm on the bottom surface. This means that the crystal growth was faster on the bottom surface than on the top surface; thus, the regularity of the pore arrangement in heated crystallized α-alumina, i.e. the domain size should affect the crystal growth rate. It is suggested that a high heating rate and especially a high cooling rate through quenching in water result in smaller aluminum grain with a larger grain boundary, which increase the thermal stress of the aluminum substrate. Then, during anodization, this stress may affect pore nucleation and pore regularity, consequently affecting the crystallization of NPAA to the α-phase. Therefore, a higher thermal stress causes a lower crystallization rate with larger differences between the top and bottom grain sizes and the domain sizes of the α-NPAA membrane, which may cause more deflections and cracks in the membrane. In spite of these differences in the α-NPAA-As-polished membrane not being evident, the low thermal stability and nonhomogenous pore regularity may be associated with high mechanical stress, residual defects, and the high dislocation density, which remain in a cold-worked Al–As-polished substrate. Furthermore, it is clear that microscopic cracks due to sintering during annealing at a high temperature of 1250 °C were formed predominantly at grain boundaries on the bottom surface of the α-NPAA membrane; however, they were formed not only at grain boundaries but also inside the grains on the top surface, so that crack ratios were higher on the top surfaces than on the bottom surface. On the other hand, it was found that the BGA voids (blister and/or γ-alumina) were mostly spread out on the top surface of the α-NPAA membrane. The ratio of these voids increased when both the heating and cooling rates were reduced, so that the formation of GA deposits in aluminum and GA voids in the NPAA film could be suppressed predominantly using very high heating and cooling rates (Figs. 4e and 4f) and by wrapping the aluminum

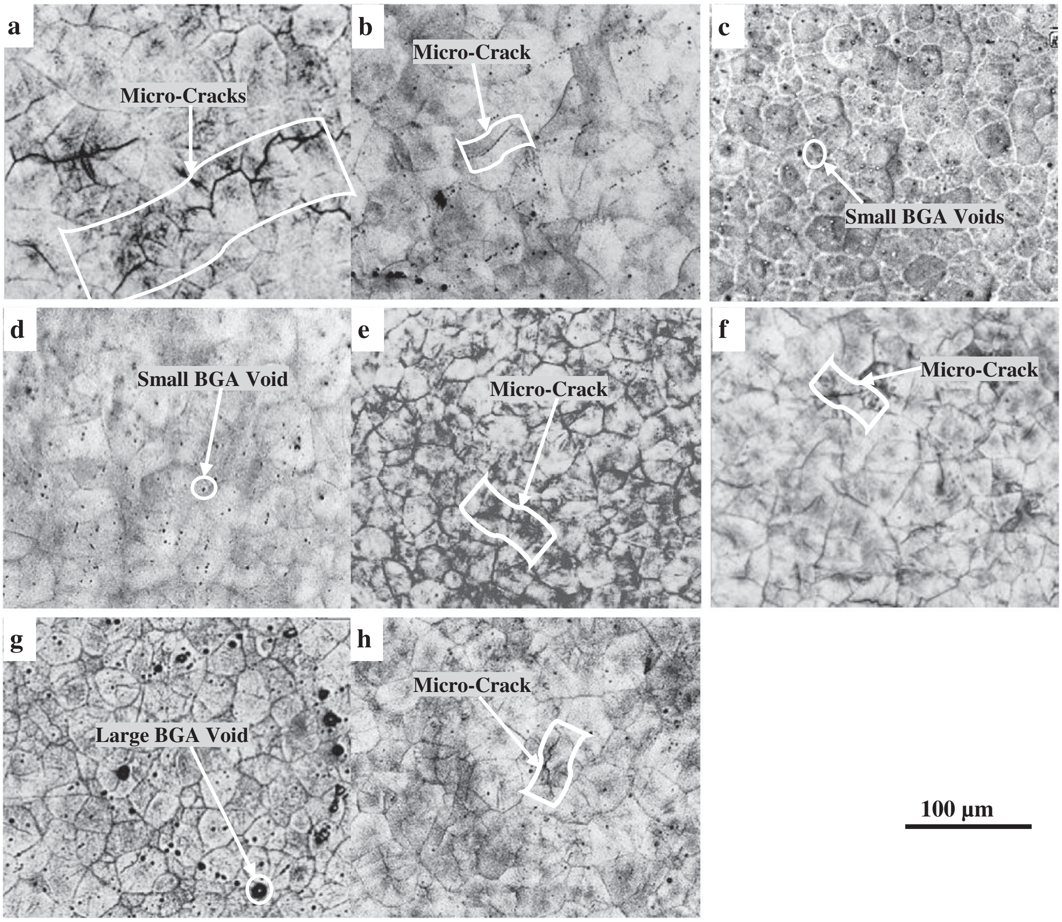

Figure 4. Optical microscopy images of bottom surface microstructures of (a) α-NPAA-As-polished, (b) α-NPAA HQ, (c) α-NPAA-LQ, (d) α-NPAA-HL, (e) α-NPAA-IQ, (f) α-NPAA-IQ-2h, (g) α-NPAA-LL1, and (h) α-NPAA-LL3.

substrate with foil (Fig. 4h) during heat treatment, which reduce the growth time and oxygen supply, respectively. From these results, it is expected that the top surface of NPAA films has less ordered pores than the bottom surface. This is in agreement with our FESEM observations (section 3.4). Also, the BGA voids may rise to the top surface of the anodized film. Although they were also observed in the middle and on the bottom surface, their ratio was lower. Moreover, the thermal stability of the α-NPAA membrane was improved and the formation of microscopic cracks was reduced when the aluminum substrate with higher stress relief is used for anodization, as shown in Table 2.

Effect of preheating conditions of aluminum substrate on pore regularity of α-NPAA

It was found that preheating the aluminum substrate improves its thermal stability against crack formation through the α-NPAA membrane, especially on the top surface. Polishing and particularly preheating increase the crystal fraction with a recrystallization texture: [cube, 100; Goss, 110; R, 124, 211], and accordingly decrease the crystal fraction with a rolling texture. Therefore, the degree of nanopore regularity is enhanced by polishing along with preheat treatment of the aluminum substrate prior to two-step anodization. The effects of (100), (111), and (110) single crystals of aluminum on the pore regularity of amorphous NPAA have already been investigated by Beck and Bretzler,[7] who showed that the (100) orientation results in a higher regularity than the (110) orientation in accordance with the results reported in our previous work.[3] The effects of different preferential orientations of cube or R or Goss in various polycrystalline aluminum substrates on the pore regularity and thermal stability of the α-NPAA membrane were investigated by FESEM observation (Figs. 5 and 6) using the top surface morphology of various prepared α-NPAA films (Table 2).

Figures 5a and b show that two types of pore arrangement on the top surface of the α-NPAA-As-polished membrane are formed: a low regularity arrangement with a higher density of cracks (Fig. 5a) and a thermally stabile arrangement without crack formation, with a high regularity degree area (Fig. 5b). According to Jessensky *et al.*,[20] various defects existing in the bulk and metal surface significantly affect the nanopore regularity and the mechanical and chemical properties of the anodic film. Our results confirmed that although electropolishing pretreatment could reduce the concentration of the macroscopic defects such as roughness and cavity on the metal (aluminum) surface and reduce the number of randomly oriented crystals in a shear texture,[3] but the microscopic defects such as grain boundaries, dislocations and point defects in the metal (aluminum) lattice have to be reduced[4,21] by recrystallization pretreatment to achieve the nanopore regularity improvement. This indicates that our performed treatments including the electropolishing and recrystallization the aluminum substrate, two-step anodizing

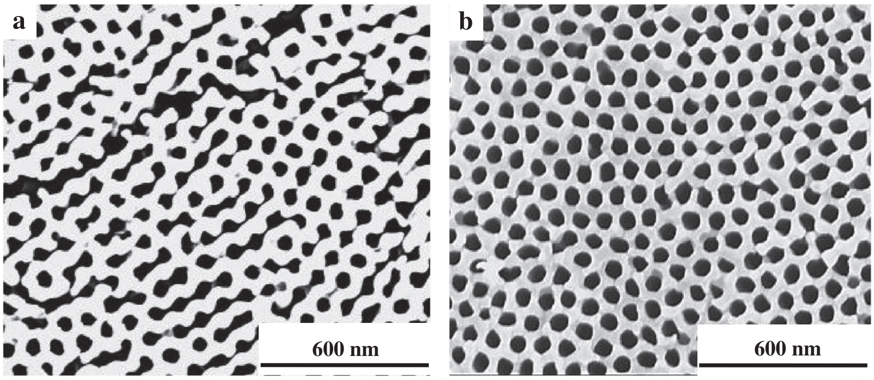

Figure 5. FESEM images of top surface of α-NPAA-As-polished: (a) low-regularity and (b) high-regularity areas.

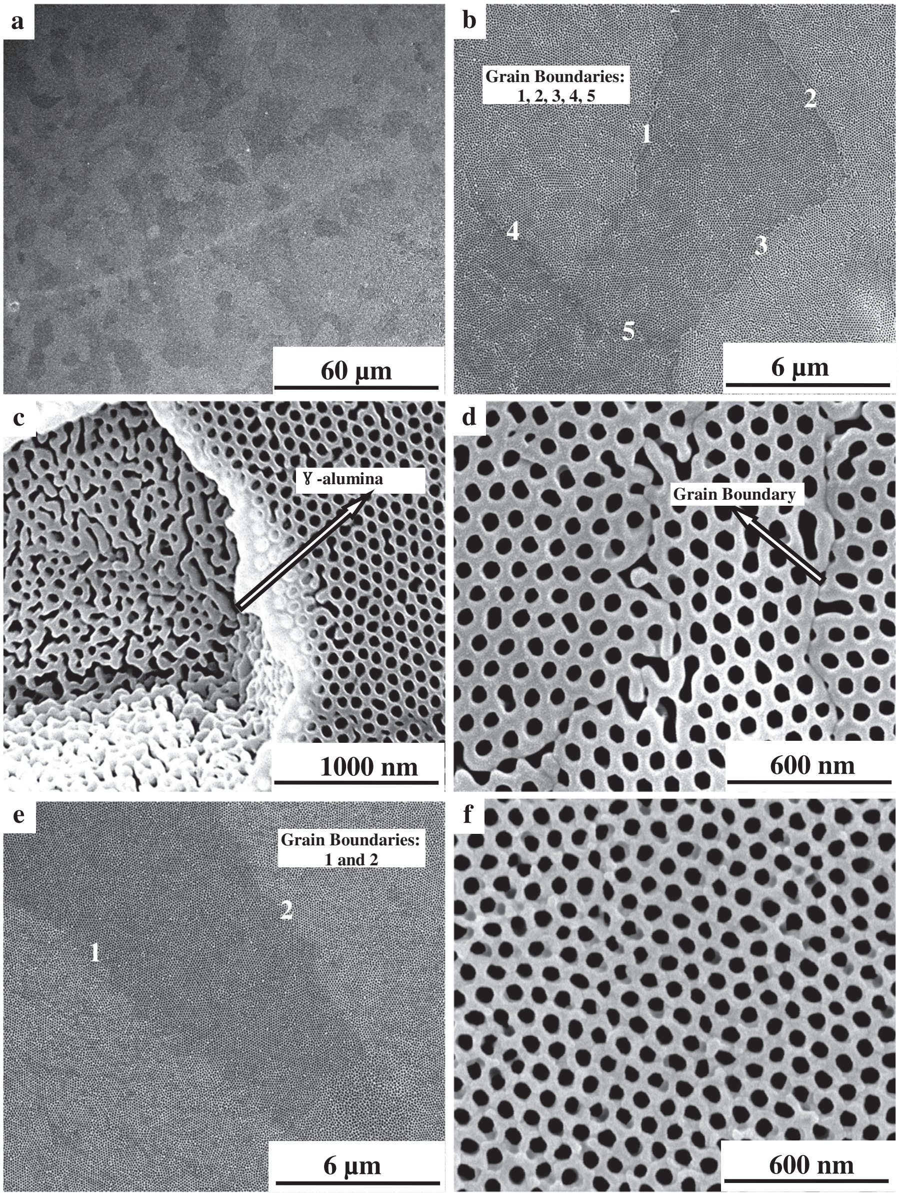

Figure 6. FESEM images of top surface: (a, b) low-magnification images of grain structure, (c) - alumina void, and (d) high-magnification image of pore structure at grain boundary of α-NPAA-HQ and (e, f) low- and high-magnification images of α-NPAA-HL.

procedure, and carefully programed crystallization procedure are required to achieve a highly ordered hexagonal structure with thermal stability in both the amorphous and α-NPAA layer.

Figure 6 shows FESEM images of the α-NPAA membranes formed on the preheated Al-HQ (a–d) and Al-HL (e, f) substrates taken at different magnifications. It was earlier mentioned (section 3.1) that the texture of the preheat-treated Al-HQ substrate changed to a mixed recrystallization textures of cube (200) and R (311). It was found that γ-alumina formation during the recrystallization of the aluminum substrate can not be avoided even at high heating and cooling rates; therefore, γ-alumina voids can be seen on the α-NPAA–HQ film (Fig. 6c). Although the pore regularity in these voids is not high, we found no relation between the dispersion of γ-alumina voids and the stability of the membrane. In addition, we confirmed that nanopore arrays of the α-NPAA-HQ membrane (Fig. 6d) formed on the quenched aluminum sheet were more collapsed at grain boundaries during the heat treatment of the as-anodized NPAA membrane at a high temperature (1250 °C), so that disorder pores were more frequently visible in this membrane than in the α-NPAA membrane formed on the annealed aluminum sheet. Also, the high-heating-rate method along with the low-cooling-rate method, which led to the recrystallization (R) texture with preferential (311) and (422) orientations in the Al-HL substrate (Fig. 2i), resulted in high pore regularity, as well as high thermal stability in the relevant α-NPAA-HL membrane film (Figs. 6e and f). These properties are also attributed to the recrystallization texture, stress relief, and grain growth due to the low cooling rate. It was suggested that the thermal stress increased with increasing heating rate and particularity the cooling rate of the aluminum substrate from the solution heat treatment temperature (500 °C) to room temperature, wich affects anodization and thus the pore arrangement of the anodic film.

Conclusions

In summary, the preheating recrystallization conditions including holding time, and heating and cooling rates have strong effects on the grain growth and preferential crystal orientation of aluminum substrates. With increasing overall heating time, the grain size increases. Therefore, smaller grains in the aluminum substrate are obtained at a high heating rate and particularly at a high cooling rate through quenching, which also causes thermal stress. Upon quenching, the preferential orientations are (200) and (311) at either high or low heating rate; however, the (220) orientation along with the lowest ratio of undesirable γ-alumina particles and blisters (BGA) deposits are dominates when a high heating rate is applied. In contrast, annealing results in a preferential (311) and/or (422) orientations. It was determined that both the crystal orientation and thermal and/or mechanical stress of the aluminum substrate affect the average sizes of grains (45–68 μm on the top surface and 67–89 μm on the bottom surface) and domains (560–720 nm on the top surface and 690–750 nm on the bottom surface) of the α-NPAA membrane, subsequently affecting the pore regularity and thermal stability. The pore regularity and thermal stability of the NPAA film are improved if a slow heating rate and particularly a slow cooling rate are used during the recrystallization of the aluminum substrate. In contrast, a large number of BGA deposits, concentrated at grain boundaries in the annealed aluminum substrate, are formed, which form BGA voids in the NPAA membrane. However, they do not strongly affect the cracking of the NPAA membrane. The quenching method, based on a high thermal stress, yields an α-NPAA membrane with small grains and small domain as well as a large number of grain boundaries, especially on the top surface. These properties induce disorders caused by mismatch in the NPAA membrane at the grain boundaries as well as imperfections arising from the BGA voids.

Acknowledgements

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