Available online at www.sciencedirect.com
SCIENCE DIRECT®

Electrochimica Acta 51 (2005) 827–833

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Self-ordering of anodic porous alumina formed in organic acid electrolytes

Sachiko Ono*, Makiko Saito, Hidetaka Asoh

Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, 1-24-2 Nishi-shinjuku, Shinjuku-ku, Tokyo 163-8677, Japan

Received 19 November 2004; received in revised form 6 May 2005; accepted 16 May 2005
Available online 8 August 2005

Abstract

New self-ordering porous alumina films were fabricated in organic acid electrolytes. Highly ordered cell arrangements of porous alumina films were realized in malonic acid at 120 V and tartaric acid at 195 V having 300 nm and 500 nm pore intervals, respectively. Self-organization was achieved at the maximum voltage required to induce high-current-density anodization while preventing burning, i.e., an extremely high-current flow concentrated at local points. The cells of the film grown at a high field must be pressed against each other, so that the self-ordering proceeds with the porous layer growth. When the self-ordering of cell arrangement proceeds, the cells became smaller. To improve the regularity of the cell configuration, a low electrolyte temperature and a relatively high electrolyte concentration were effective for maintaining a high-current-density to prevent burning. Surface flatness was an essential factor for self-ordering, however, the surface oxide film produced by electropolishing an aluminum substrate prevented quick pore growth in the organic acids having a low dissociation constant. It is confirmed that electropolishing followed by alkaline treatment was most appropriate as the pre-treatment in preparing flat surfaces.

Keywords: Anodic porous alumina; Self-ordering; High-current-density; Organic acid; Pre-treatment

1. Introduction

Because of its self-ordered and nanosized-pore arrangements in addition to the ease in the control of its pore interval by changing anodization voltage, anodic porous alumina is a promising candidate starting material for the nanofabrication of various devices [1–5]. Except for the pre-texturing methods for an aluminum substrate, such as an imprinting process [6,7] and other nanoindentation processes using scanning probe microscopy [8,9] or focused ion beam lithography [10], highly ordered self-organizing porous alumina is suggested to be obtained only in three types of electrolyte at specified self-ordering voltages: sulfuric acid at 25 V, oxalic acid at 40 V and phosphoric acid at 195 V, giving 63 nm, 100 nm and 500 nm pore intervals, respectively [11–13]. To expand the application field of anodic porous alumina, the fabrication of ordered porous alumina with arbitrary pore intervals is highly required.

Recently, we have found that the homogeneity of cell size and cell configuration increases with increasing formation voltage accompanied by an exponential increase in current density [14]. The self-ordering of the pore arrangement of anodic porous alumina can be achieved at the maximum voltage required to induce high-current-density anodization while preventing “burning”, i.e., an extremely high-current flow concentrated at local points leading to local film thickening or electric breakdown at the entire surface accompanying vigorous gas evolution [14,15]. Such a maximum voltage was identical with the previously established self-ordering voltage. In addition, barrier layer thickness as well as cell size of the center of the burnt film is significantly thinner than that of the standard film. Thus, it is suggested that the condition inducing film growth

---

* Corresponding author. Tel.: +81 3 3340 2732; fax: +81 3 3340 2732.
E-mail address: sachiono@cc.kogakuin.ac.jp (S. Ono).

0013-4686/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2005.05.058

under the high-current-density, namely the high electric field strength is the key factor determining the self-ordering of porous alumina rather than the self-ordering voltage itself.

With the above background, we have studied the self-ordering conditions of anodic porous alumina grown in solutions of various organic acids, such as citric acid, malonic acid, maleic acid and tartaric acid. In these acid electrolytes, a relatively large cell is available upon application of a high anodization voltage due to their low acidity. These organic acids are all carbonic acid, which is the same to oxalic acid.

Recently, Singubara et al. [16] have reported on the formation of self-ordering porous anodic alumina in a mixture of sulfuric acid and oxalic acid solutions at a voltage between 25 V and 40 V. However, little information is available for the porous alumina formed at a voltage between 40 V and 195 V and higher than 200 V. We have also reported on the formation of self-ordered porous alumina in concentrated phosphoric acid solutions in the voltage range from 160 V to 195 V [17]. In the present paper, we describe the detailed self-ordering behavior realized in malonic acid and tartaric acid solutions at high voltages giving a pore interval from 200 nm to 500 nm.

2. Experimental

High-purity (99.99%) aluminum sheets were pre-treated by four different methods. To compare the effects of surface characteristics on the subsequent anodization behavior: (1) electropolishing in a 4:1 mixture of ethanol and 60% perchloric acid at 10 °C for 3 min; (2) alkaline degreasing in 5% sodium hydroxide at 60 °C for 20 s; (3) chemical polishing in a mixture of 70% phosphoric acid, 25% sulfuric acid and 5% nitric acid at boiling temperature for 60 s; (4) electropolishing followed by chemical treatment in an alkaline mixture of 0.7% NaOH and 1.4% $NaNO_3$ at 60 °C for 30 s. We called the fourth treatment as “alkaline treatment”. Anodization was performed at a constant voltage in malonic acid and tartaric acid solutions. The surface morphology of the aluminum substrate after various pre-treatments was evaluated by atomic force microscopy (AFM; Digital Instruments Nano Scope IIIa). Cell arrangement was evaluated by field-emission scanning electron microscopy (FESEM; HITACHI S-4200) of the oxide–substrate interface after removing the anodic film by immersion in a boiling solution of 6% phosphoric acid and 2% chromic acid for 10 min, in which the selective dissolution of the oxide ensued. This is the most simple and accurate method for the evaluation of cell homogeneity. The level of self-ordering can be assessed by an ordering index, namely the fraction of regular hexagonal cells, which neighboring to six cells individually. When self-ordering progresses, the size of the domain consist of only regular hexagonal cells increases.

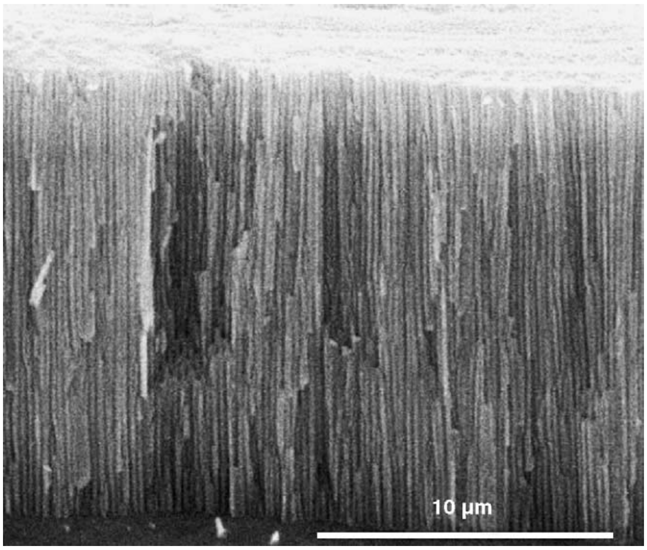

Fig. 1. SEM image of cross-section of film formed in 5 mol dm^{-3} malonic acid solution at 100 V for 1 h at 20 °C.

3. Results and discussion

3.1. Effect of pre-treatment on self-ordering of cell arrangement in malonic acid

Formation of porous anodic alumina in malonic acid solution was carried out on alkaline degreased aluminum substrates at first. As shown in Fig. 1, the cross-section of the anodic porous alumina formed in 5 mol dm^{-3} malonic acid solution at 20 °C on an alkaline degreased specimen at 100 V for 1 h has a regularly arranged cell configuration. However, when the cell arrangements of the anodic aluminas formed on an alkaline degreased substrate and a chemically treated substrate in an alkaline mixed solution after electropolishing were compared, it was found that the latter pre-treatment notably improves the homogeneity of the cell arrangement (Fig. 2). No cell domains consist of only regular hexagonal cells were found in the former case. Therefore, it is clear that surface flatness is an essential factor for self-ordering.

3.2. Effect of pre-treatment on surface morphology of substrate and pore initiation

To improve cell arrangement, the effects of pre-treatments on film structure was examined. Fig. 3 shows current–time transients during the anodization of the aluminum substrates in 5 mol dm^{-3} malonic acid solution at 100 V for 1 h at 20 °C after various pre-treatments. When an aluminum specimen was pre-treated by alkaline degreasing in 5% sodium hydroxide, a large current increase caused by initial pore nucleation immediately occurred. In contrast, such a current increase notably delayed in the case of electropolishing. Chemical polishing and electropolishing followed by alkaline treatment gave a sufficiently quick increase in current indicating quick pore initiation. When the electrolyte temperature was lower

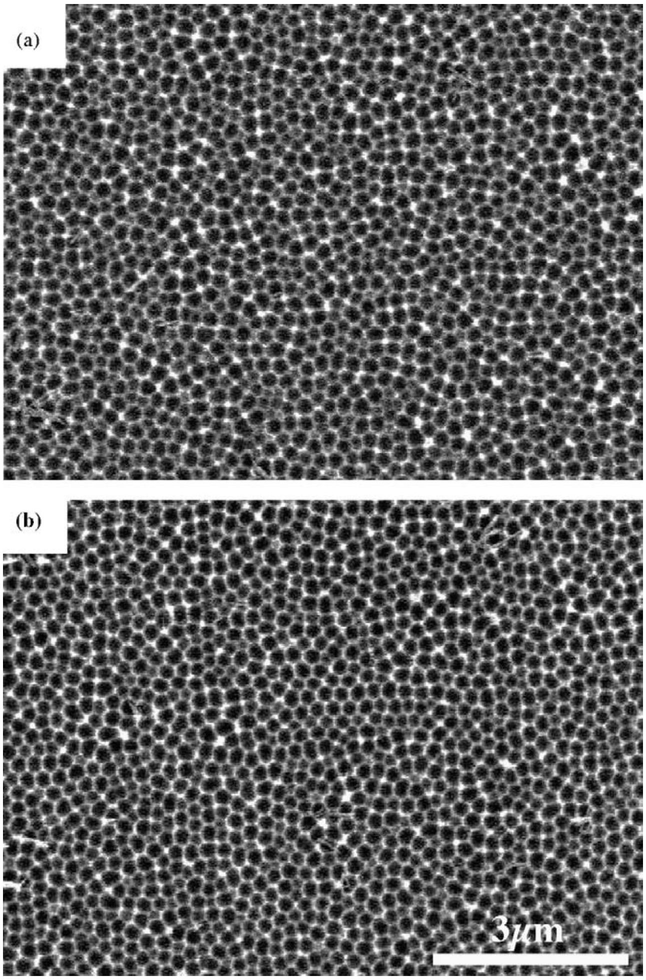

Fig. 2. SEM images of oxide–substrate interface of porous alumina formed in 5 mol dm^{-3} malonic acid at 100 V for 6 h at 20 °C. The pre-treatment was carried out in: (a) 5% NaOH solution and (b) a mixture of phosphoric acid, sulfuric acid and nitric acid solutions.

or the electrolyte concentration was lower than those in the present cases, the current increases were more retarded. Similar phenomena were also observed in tartaric acid. Thus, in some organic acid electrolytes having a low dissociation constant, electropolishing could not be adapted because the thin and probably dense oxide film formed by polishing prevented pore initiation because of the low dissolution ability of the electrolytes although the film thickness was as small as approximately 3 nm. However, a flat and smooth surface of an aluminum substrate is essentially required to realize a regular cell arrangement.

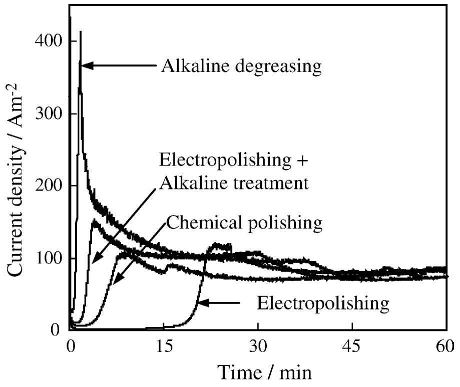

Fig. 3. Current–time transients during anodization of aluminum substrate in 5 mol dm^{-3} malonic acid solution at 100 V for 1 h at 20 °C after various pre-treatments.

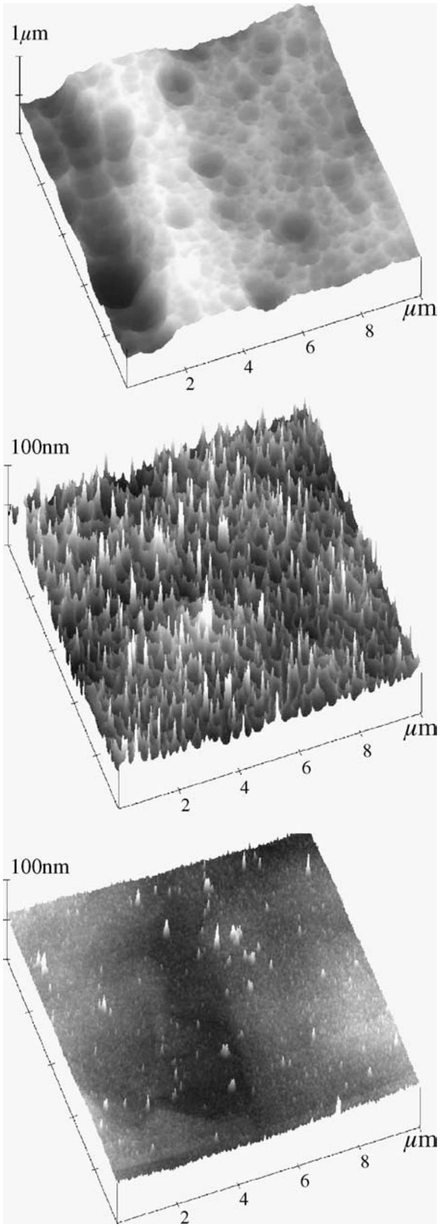

Fig. 4. AFM images of aluminum substrate after various pre-treatments: (a) alkaline degreasing; (b) chemical polishing; (c) electropolishing followed by alkaline treatment. The scale of the *z*-axis in (a) is 10 times that of the others.

The AFM of aluminum surfaces pre-treated by various methods was performed. As shown in Fig. 4a, the alkaline degreasing gave a roughness higher than 2–3 μm caused by the rolling process of aluminum sheets in addition to the presence of etched concaves approximately 0.5 μm. Although the

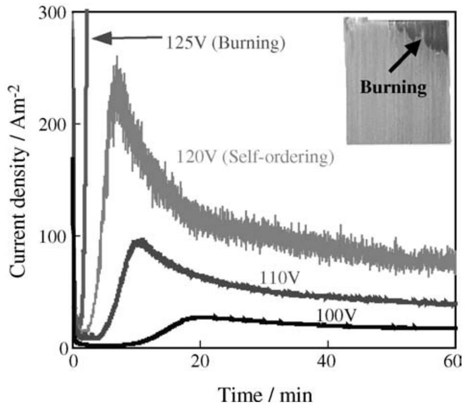

Fig. 5. Current–time curves for anodization in 5 mol dm^{-3} malonic acid at different voltages for 1 h at 5 °C. The SEM image in the panel shows a burnt specimen surface formed at 125 V.

chemical polishing attained a specular surface, the surface flatness was inferior to that of the electropolished surface as indicated in Fig. 4b. Flatness similar to that of the electropolished surface could be achieved by the electropolishing followed by the alkaline treatment, as shown in Fig. 4c. As demonstrated in Fig. 3, this treatment enables the quick current increase followed by a quick pore growth. Therefore, we utilized this pre-treatment in the preceding experiments with the aim of improving the regularity of the cell configuration.

3.3. *Confirmation of self-ordering voltage*

Concerning the effect of electrolyte temperature, we previously suggested that a low temperature under 5 °C is essential in improving homogeneity to attain high-current-density anodization while preventing burning in the case of phosphoric acid [14]. Therefore, optimum self-ordering voltage was investigated in the electrolyte of 5 mol dm^{-3} malonic acid at 5 °C by applying different voltages. Fig. 5 shows the dependence of current density on formation voltage. Current density increased with increasing formation voltage. The oxide film obtained was opaque and golden. At 125 V, current density markedly increased followed by the formation of a dark area at the edge of the specimen shown in the frame as a SEM image. The oxide film formed by burning became black because of the local thickening of the film. As we reported previously [15], a burnt porous film formed in phosphoric acid or malonic acid exhibits a highly ordered cell arrangement, which is induced by a high-current-density resulting in high electric field [14,15]. Therefore, we performed anodization at the critical voltage just below that for burning, i.e., a self-ordering voltage of 120 V in this electrolyte to maintain stable and uniform growth of anodic porous alumina.

SEM images of the cell arrangement of the aluminum specimens after removal of porous alumina formed in 5 mol dm^{-3} malonic acid solution at 5 °C are shown in Fig. 6 in relation to the effects of anodization time and burning. Domains of ordered cell arrays were clearly found in the film formed for 1 h (Fig. 6a), which was much superior to that formed at 20 °C, as shown in Fig. 2. Furthermore, the homogeneity of the cell configuration improved after prolonged anodization (Fig. 6b), as described in previous studies

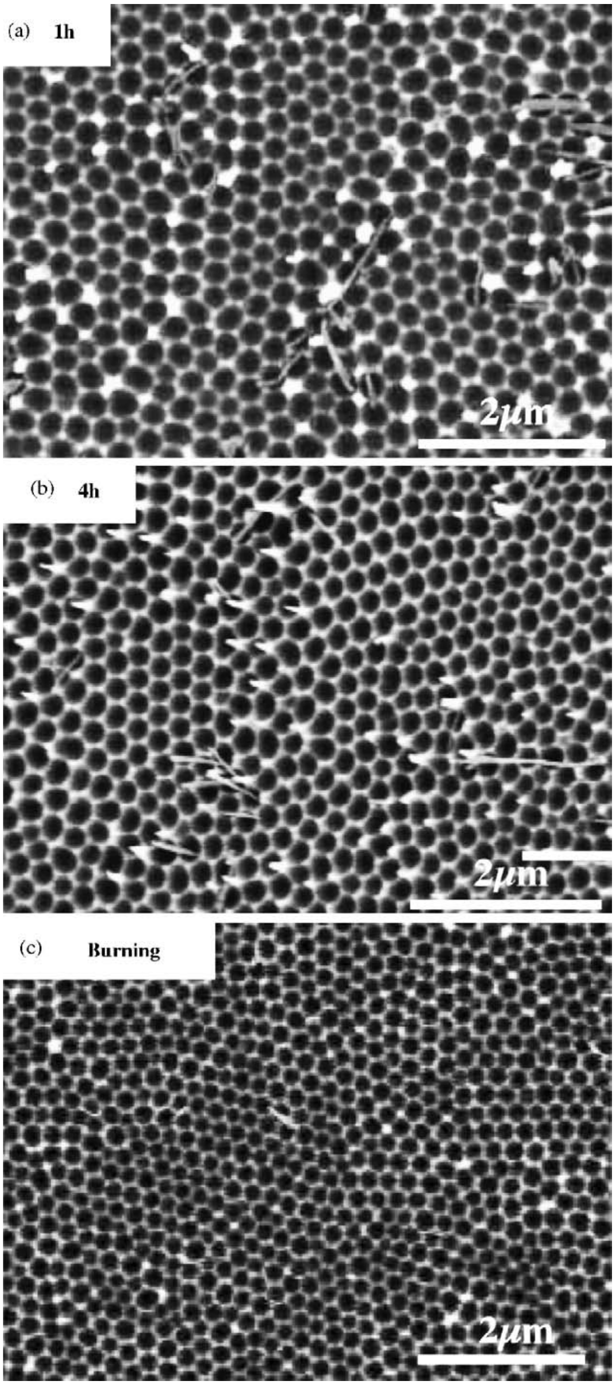

Fig. 6. SEM images of cell arrangement of aluminum specimens after removal of porous alumina formed in 5 mol dm^{-3} malonic acid solution at 5 °C, demonstrating the effects of anodization time and high-current-density; (a) 1 h; (b) 4 h; (c) a burnt spot indicated in the panel of Fig. 5. Aluminum pillars are found in (b) at the domain boundaries because this SEM image was taken from an inclined angle.

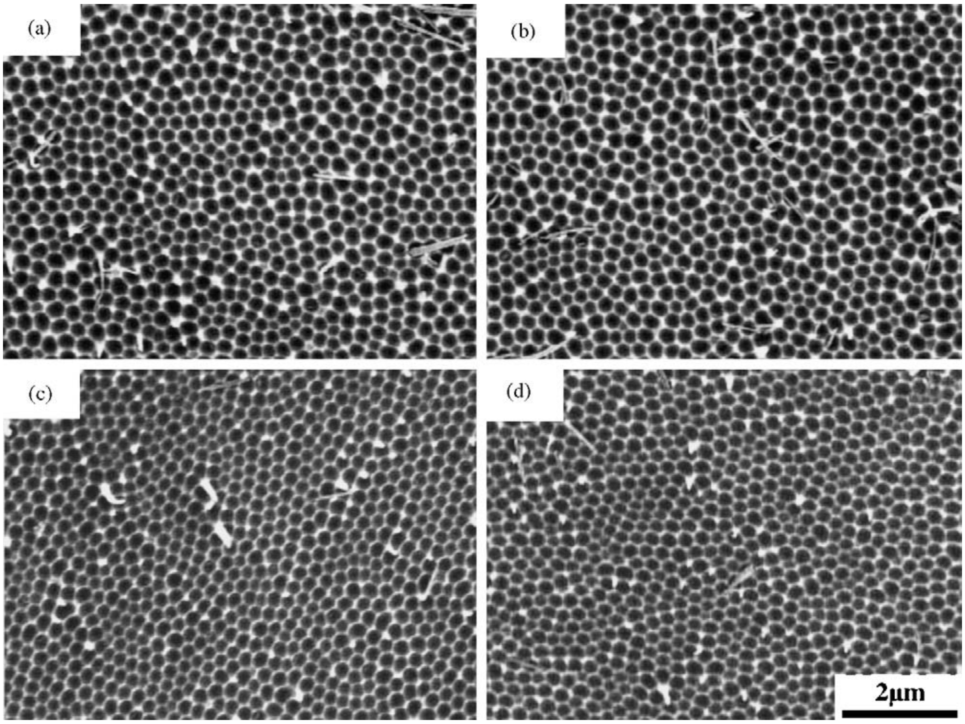

Fig. 7. SEM images of cell arrangement of aluminum specimens after removal of porous alumina formed in: (a) 2 mol dm^{-3}; (b) 3 mol dm^{-3}; (c) 4 mol dm^{-3}; (d) 5 mol dm^{-3} malonic acid solutions at 120 V for 6 h at 5 °C demonstrating the effect of electrolyte concentration.

[12,14], namely the domain size increased with increasing anodization time. Since the SEM image in Fig. 6b was taken from a declined angle fine aluminum pillars are distinguishable between cell junctions. They are necessarily formed at the fourth or fifth points of cell junctions but not at the regular triple points of adjacent hexagonal cells, namely the pillars were formed at irregular cell junctions and at the domain boundaries. Similar to the films formed in phosphoric acid, the burnt spot shown in the panel of Fig. 5 indicated highly ordered cell arrangements (Fig. 6c), which is caused by high electric field associated with high-current-density [14,15,17].

3.4. Effect of electrolyte concentration

The SEM images in Fig. 7 indicate the effect of electrolyte concentration on cell configuration. Anodic films were individualy formed in malonic acid solutions of different concentrations of 2 mol dm^{-3} to 5 mol dm^{-3} at 120 V for 6 h at 5 °C. With increasing electrolyte concentration up to 4 mol dm^{-3}, cell ordering improved as clearly shown in Fig. 7c. The ordering indices were approximately 30 for (a and b), 71 for (c) and 66 for (d). This can be explained by the higher current density consumed during anodization in the concentrated electrolyte. However, the ordering of the cell configuration became inferior when electrolyte concentration increased to 5 mol dm^{-3}. This seems to be partly caused by the high viscosity of the concentrated 5 mol dm^{-3} electrolyte used.

3.5. Self-ordering of anodic porous alumina formed in tartaric acid solution

Current–time curves obtained by anodization in 3 mol dm^{-3} tartaric acid at different voltages for 1 h at 5 °C are shown in Fig. 8. When formation voltage increased, current density increased. When the formation voltage reduced 197 V, burning occurred followed by the occurrence of an extremely high-current-density. SEM image of the burnt specimen surface formed at 197 V revealed a predominant film growth along with rolling lines, as shown in the panel of Fig. 8.

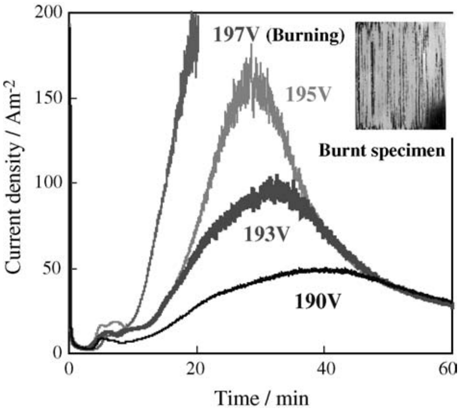

Fig. 8. Current–time curves for anodization in 3 mol dm^{-3} tartaric acid at different voltages for 1 h at 5 °C. The SEM image in the panel shows the burnt specimen surface formed at 197 V.

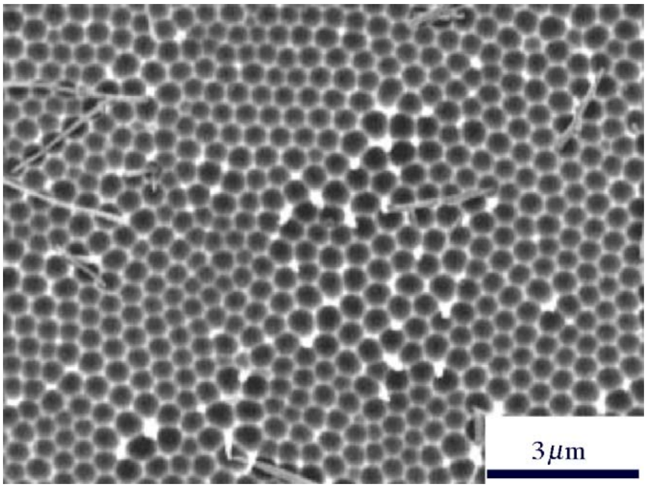

Fig. 9. SEM image of self-organized cell arrangement of aluminum specimens after removal of porous alumina formed at 195 V in 3 mol dm^{-3} tartaric acid solution at 5 °C for 35 min. Long aluminum fibers were formed at irregular cell junctions.

When the cell arrangement was verified by SEM, the high self-organization of the cell arrangement was observed in the film (Fig. 9) formed at the maximum voltage of 195 V for preventing burning, i.e., a high electric field in tartaric acid solution. This self-ordering behavior was similar to those observed in the other acid solutions, such as malonic acid and in previously reported self-organized electrolytes [14].

3.6. Mechanism and confirmed conditions of self-ordering of anodic porous alumina

Thus, new self-ordering conditions were confirmed in organic acid electrolytes using the previously suggested mechanism of anodization at a high electric field at a barrier layer [14,15,17]. The electric field strength is an impressed voltage per unit thickness of the oxide layer. According to the classical theory of ionic conduction at the high field strength for the anodic barrier film grown on various metals [18,19], the film thickness of each metal is inversely proportional to the logarithm of ionic current when the film is formed up to the same voltage. Thus, it is indicated that the log of current density $\log i$ is proportional to the electric field strength E, i.e., the formation voltage/film thickness ratio at the barrier layer. As we reported earlier, the high electric field strength E at the barrier layer of porous films is a strong controlling factor of the self-ordering [14,15,17].

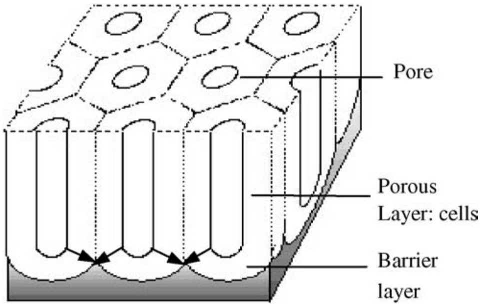

Fig. 10. Honeycomb model structure of anodic porous alumina. Arrows indicate a force generated by rapid oxide growth associated with high-current flow at the barrier layer, which induces a compressive force between cell boundaries.

Fig. 10 indicates a honeycomb model structure of anodic porous alumina. It has to be bare in mind that the porous oxide layer is only formed at the bottom of the barrier layer as a result of inward migration of oxygen ions associated with the oxide dissolution at the top of the barrier layer under the certain electric field. When a current density is high, rapid oxide growth induces a compressive force at the barrier layer between each cell boundary as shown in arrows in Fig. 10. Therefore, the bottom of cells grown at the barrier layer under a high field must be pressed against each other, so that the self-ordering proceeds with the growth of porous film.

Fig. 11 illustrates the schematic model of the self-organization of the cell arrangement under a high-current-density, i.e., a high electric field compared with the case of a

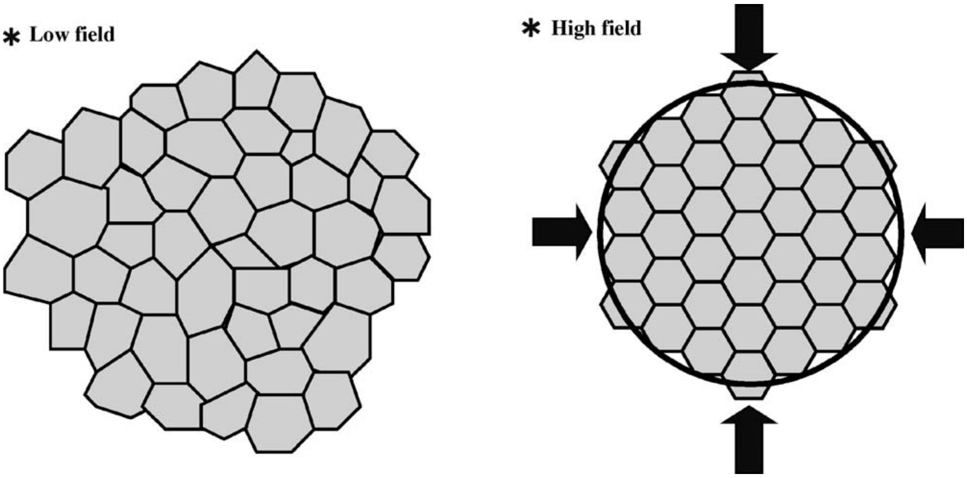

Fig. 11. Schematic representation of self-organization of cell arrangement at high-current-density, i.e., high electric field.

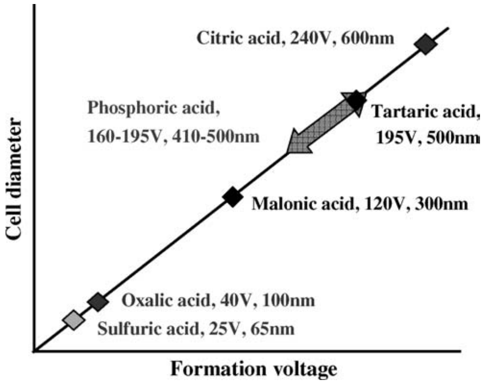

Fig. 12. Result view of self-ordering voltages and corresponding cell diameters reported until now.

low electric field. Therefore, the bottom of cells grown at the barrier layer under a high field must be pressed against each other, so that the self-ordering proceeds with the growth of porous film. When the self-ordering of cell arrangement proceeds, the cells become smaller [14,15] although the applying voltage is maintained to be the same, as it is also shown in Fig. 7. This is because of a high electric field that produces a thinner barrier layer and smaller cells.

The self-ordering voltages reported until now and the corresponding cell diameters are summarized in Fig. 12. In addition to the conventional self-ordering conditions formed in sulfuric, oxalic and phosphoric acid solutions, new self-ordering conditions realized in citric acid [15], concentrated phosphoric acid [17], malonic acid [20] and tartaric acid solutions are shown. Further, we have reported the self-ordering conditions of anodic porous alumina formed in a mixture of sulfuric acid and malonic acid solutions in the voltage range from 25 V to 195 V [21]. The details of these conditions will be published elsewhere.

4. Conclusions

New self-ordering porous aluminas having 300 nm and 500 nm pore intervals were fabricated in organic acid electrolytes, such as malonic and tartaric acid solutions. Each self-ordering voltage was observed as the maximum voltage required for maintaining a high-current-condition in the entire specimen area in the electrolytes used, while preventing an extremely high-current flow at a local spot, which leads to burning. To improve the regularity of the cell configuration, a low electrolyte temperature and a relatively high electrolyte concentration were effective for maintaining a high-current-density while preventing burning. In addition, excellent surface flatness and evenness, which were crucial to achieve the linear growth of pores, were attained by the alkaline treatment after electropolishing. Therefore, it is concluded that the self-ordering of arbitrary pore intervals can be realized by choosing an adequate electrolyte and electrolytic conditions at the appropriate formation voltage required for maintaining a high-current condition, i.e., a high electric field, as we suggested in our previous papers [14,15,17].

References

[1] S. Shingubara, O. Okino, Y. Sayama, H. Sakaue, T. Takahagi, Solid State Electron. 43 (1999) 1143.
[2] T. Iwasaki, T. Motoi, T. Den, Appl. Phys. Lett. 75 (1999) 2044.
[3] Y. Kanamori, K. Hane, H. Sai, H. Yugami, Appl. Phys. Lett. 78 (2001) 142.
[4] X. Mei, D. Kim, H.E. Ruda, Q.X. Guo, Appl. Phys. Lett. 81 (2002) 361.
[5] H. Asoh, M. Matsuo, M. Yoshihama, S. Ono, Appl. Phys. Lett. 83 (2003) 4408.
[6] H. Masuda, H. Yamada, M. Satoh, H. Asoh, M. Nakao, T. Tamamura, Appl. Phys. Lett. 71 (1997) 2770.
[7] H. Asoh, S. Ono, T. Hirose, M. Nakao, H. Masuda, Electrochim. Acta 48 (2003) 3171.
[8] H. Masuda, K. Kanezawa, K. Nishio, Chem. Lett. 31 (2002) 1218.
[9] S. Shingubara, Y. Murakami, K. Morimoto, T. Takahagi, Surf. Sci. 532–535 (2003) 317.
[10] C.Y. Liu, A. Datta, Y.L. Wang, Appl. Phys. Lett. 78 (2001) 120.
[11] H. Masuda, K. Fukuda, Science 268 (1995) 1466.
[12] H. Masuda, F. Hasegawa, S. Ono, J. Electrochem. Soc. 144 (1997) L127.
[13] H. Masuda, K. Yada, A. Osaka, Jpn. J. Appl. Phys. 37 (1998) L1340.
[14] S. Ono, M. Saito, M. Ishiguro, H. Asoh, J. Electrochem. Soc. 151 (2004) B473.
[15] S. Ono, M. Saito, H. Asoh, Electrochem. Solid State Lett. 7 (2004) B21.
[16] S. Shingubara, K. Morimoto, H. Sakaue, T. Takahagi, Electrochem. Solid State Lett. 7 (2004) E15.
[17] S. Ono, N. Kato, M. Saito, H. Asoh, The Electrochemical Society Proceedings Series, Pennington, NJ, in press.
[18] A. Güntherschulze, H. Betz, Z. Phys. 92 (1934) 367.
[19] N. Cabrera, N.F. Mott, Rept. Prog. Phys. 12 (1948) 163.
[20] M. Saito, H. Muto, H. Asoh, S. Ono, 204th Meeting of Electrochemical Society, Orlando, USA, Oct 12–16, 2003 (abstract 30).
[21] S. Tamura, H. Asoh, S. Ono, 111th Meeting of Surface Finish Society of Japan, Matsushima, Japan, September 13, 2004, p. 121 (abstracts).