

Self-Ordering Behavior of Anodic Porous Alumina via Selenic Acid Anodizing



Tatsuya Kikuchi*, Osamu Nishinaga, Shungo Natsui, Ryosuke O. Suzuki

Faculty of Engineering, Hokkaido University, N13-W8, Kita-ku, Sapporo, Hokkaido, 060-8628, Japan

ARTICLE INFO

Article history:

Received 3 February 2014

Received in revised form 11 June 2014

Accepted 12 June 2014

Available online 19 June 2014

Keywords:

Aluminum

Anodizing

Anodic Porous Alumina

Selenic Acid

ABSTRACT

The self-ordering behavior of anodic porous alumina that was formed by anodizing in selenic acid electrolyte (H_2SeO_4) at various concentrations and voltages was investigated with SEM and AFM imaging. A high purity aluminum foil was anodized in 0.1–3.0 M selenic acid solutions at 273 K and at constant cell voltages in the range of 37 to 51 V. The regularity of the cell arrangement increased with increasing anodizing voltage and selenic acid concentration under conditions of steady oxide growth without burning. Anodizing at 42–46 V in 3.0 M selenic acid produced highly ordered porous alumina. By selective dissolution of the anodic porous alumina, highly ordered convex nanostructures of aluminum with diameters of 20 nm and heights of 40 nm were exposed at the apexes of each hexagonal dimple array. Highly ordered anodic porous alumina with a cell size of 102 nm from top to bottom can be fabricated by a two-step selenic acid anodizing process, that includes the first anodizing step, the selective oxide dissolution, and the second anodizing step.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Barrier anodic oxide films and porous anodic oxide films on aluminum have been widely investigated by many researchers in the fields of surface finishing [1–3], electrolytic capacitor application [4–6], and micro- and nano-structure fabrication [7–9]. Recently, highly ordered anodic porous alumina with a cell size on the scale of 10–100 nm has been studied for potential use in various ordered-nanostructure applications [10–21]. Anodic porous alumina is typically fabricated on an aluminum substrate using electrochemical anodizing (or anodization) [22–26]. In several acidic electrolyte solutions, the porous alumina fabricated by anodizing is self-ordered when prepared at the appropriate electrochemical conditions, including appropriate concentrations, temperatures, and voltages (or electrochemical potentials) [27–30].

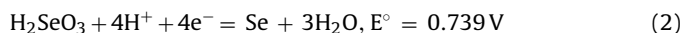
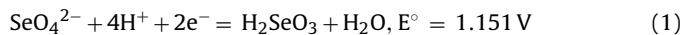
Sulfuric (H_2SO_4) [31], oxalic ($(\text{COOH})_2$) [7,32], and phosphoric (H_3PO_4) [33] acids are the three major electrolytes used for anodic porous alumina fabrication; many researchers have investigated the highly ordered anodic porous alumina formed by anodizing in these three electrolytes [34–36]. Malonic ($\text{HOOC}-\text{CH}_2-\text{COOH}$) [28,37–39] and tartaric ($\text{HOOC}(\text{CHOH})_2\text{COOH}$) [28,40] acids are also known self-ordering electrolytes, as reported previously. However, malonic and tartaric acids have seldom been

used for nanostructure fabrication because they do not perform as well with regards to self-ordering as the three major electrolytes. Chromic (H_2CrO_4) [41–43], formic (HCOOH) [44], malic ($\text{HOOC}-\text{CH}(\text{OH})-\text{CH}_2-\text{COOH}$) [27,45,46], citric ($\text{HOOC}-\text{CH}_2-\text{C}(\text{OH})(\text{COOH})-\text{CH}_2-\text{COOH}$) [27,47,48], glycolic ($\text{CH}_2\text{OH}-\text{COOH}$) [27], squaric (3,4-dihydroxy-3-cyclobutene-1,2-dione) [49], tartronic ($\text{HOOC}-\text{CH}(\text{OH})-\text{COOH}$) [50], and acetylenedicarboxylic ($\text{HOOC}-\text{C}\equiv\text{C}-\text{COOH}$) [51] acids have also been reported as electrolytes used to fabricate porous alumina that has characteristic nanostructure morphologies.

In addition to these acidic electrolytes, alkaline and neutral solutions used for porous alumina fabrication were reported by several research groups. Takahashi et al. reported that a porous anodic oxide film could be formed by anodizing in an $\text{H}_3\text{BO}_3/\text{Na}_2\text{B}_4\text{O}_7$ neutral borate solution at a high temperature [52]. Baron-Wiechec et al. investigated aluminum anodizing in a borax ($\text{Na}_2\text{B}_4\text{O}_7$) solution at 333 K and successfully obtained porous alumina [53]. Noguchi et al. investigated the anodizing behavior of aluminum in propylenediamine and choline alkaline solutions containing ammonium fluoride, ammonium tartrate, ammonium carbonate, and ammonium tetraborate, and obtained anodic porous alumina with nanopores that were 10–150 nm in diameter [54]. However, it is difficult to form a highly ordered porous alumina by anodizing in these neutral and alkaline solutions. Therefore, acidic solutions, especially the three major electrolytes (sulfuric, oxalic, and sulfuric acids), are typically used for anodic porous alumina fabrication.

* Corresponding author. Tel.: +81 11 706 6340; fax: +81 11 706 6342.
E-mail address: kiku@eng.hokudai.ac.jp (T. Kikuchi).

In 2013, we first reported a new self-ordered anodic porous alumina fabrication method that used selenic acid (H_2SeO_4) anodizing [55]. Selenic acid is easily soluble in water, and is a strong diacid with dissociation constants of $\text{p}K_{a1} = -3.0$ and $\text{p}K_{a2} = 1.7$, which are the same as those of sulfuric acid. Selenic acid solution dissolves silver, gold, and palladium metals. Standard electrode potentials related to selenic acid are as follows:



In our previous study, self-ordered porous alumina was rapidly produced by 0.3 M selenic acid anodizing using a simple electrochemical setup, and the porous alumina obtained had nanopores on the scale of 10 nm at the center of each cell. The concentration of the selenic acid solution was fixed at the typical anodizing concentration of 0.3 M. Stirring vigorously at low temperature (273 K) during selenic acid anodizing was required to achieve self-ordering. The anodic porous alumina produced by anodizing in the solution was only self-ordered at 48 V. However, the details of the self-ordering behavior of the anodic porous alumina during selenic acid anodizing at different solution concentrations and voltages had not been studied so far, and further investigation will be required for highly ordered nanostructure applications.

In the present investigation, we report on the self-ordering behavior of anodic porous alumina fabricated by anodizing at various voltages in various concentrations of selenic acid solution. The anodic porous alumina fabricated by selenic acid anodizing was examined in details by scanning electron microscopy (SEM) and atomic force microscopy (AFM). We found that the regularity of the anodic porous alumina formed by selenic acid anodizing was greatly improved with increasing anodizing voltage and electrolyte concentration. This observed improvement expands the range of voltages that can be used for the fabrication of self-ordered anodic porous alumina as well as the range of ideal hexagonal cell sizes, and it therefore expands the applicability of anodic porous alumina.

2. Experimental

2.1. Pretreatment and selenic acid anodizing

Aluminum foils (99.99 wt%, 110 μm thick, Showa Aluminum Co., Japan, impurities: Fe 10 ppm, Si 9 ppm, and Cu 57 ppm) were used as the anodizing specimens. The specimens were cut into 20 mm x 20 mm pieces with a handle and then ultrasonically degreased in an ethanol solution for 10 min. After degreasing, the specimens were electropolished in a 13.6 M $\text{CH}_3\text{COOH}/2.56 \text{ M HClO}_4$ mixed solution at 280 K at a constant voltage of 28 V for 60 s. A large aluminum plate (99.99 wt%) was used as the counter electrode, and the solution was slowly stirred with a magnetic stirrer during electropolishing. The electropolished specimens were then washed with distilled water and dried in a desiccator.

Fig. 1 shows a schematic model of the selenic acid anodizing setup. An extremely simple two-electrode electrochemical cell with a low temperature water bath was used in the anodizing process. For the fabrication of anodic porous alumina, selenic acid (80.0 wt%, Kanto Chemical Co., Japan) was used as the anodizing electrolyte. The electropolished specimens were immersed in H_2SeO_4 solutions with concentrations in the range of 0.1 to 3.0 M at 273 K and were placed parallel to and 15 mm from a glassy carbon cathode (1 mm thick, Tokai Carbon Co., Japan). Using the anodizing electrolyte at the low temperature of 273 K is an effective way to fabricate a self-ordered anodic oxide without burning [55]. After placement in the solutions, the specimens anodized for 180 min at a constant voltage in the range of 37 to 51 V (direct current power supply PWR400H, Kikusui, Japan). During

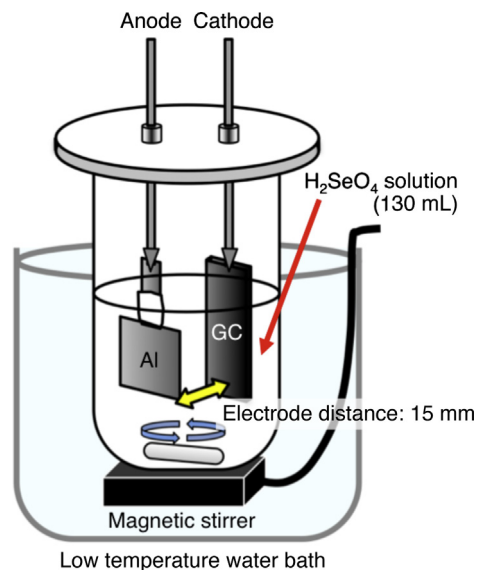


Fig. 1. Schematic representation of the experimental apparatus for the selenic acid anodizing. The solution was stirred vigorously during anodizing.

anodizing, the solutions were vigorously stirred with a magnetic stirrer and the current densities were recorded using a digital multimeter (DMM4040, Tektronix) connected to a computer. After anodizing, the specimens were quickly removed from the solution, washed with distilled water, and dried in a desiccator.

2.2. Second selenic acid anodizing

The aluminum specimen that was anodized at 46 V for 180 min in the 3.0 M H_2SeO_4 solution, as described above, was immersed in a 0.20 M $\text{CrO}_3/0.51 \text{ M H}_3\text{PO}_4$ solution at 353 K to dissolve selectively the anodic porous alumina. This specimen was then anodized again at a constant voltage of 46 V for 3 min in a 3.0 M H_2SeO_4 solution (two-step anodizing). Thus, the two-step anodizing process includes the first anodizing, the oxide dissolution, and the second anodizing. To widen the pores in the anodic porous alumina, the specimen was immersed in a 0.86 M H_3PO_4 solution at 293 K for 10 min.

2.3. Characterization of the anodic porous alumina

The surface morphologies of the specimens were examined after the first anodizing, after the oxide dissolution, and after the second anodizing using an SEM (JSM-6500F and JIB-4600F/HKD, JEOL, Japan, and Miniscope TM-1000, Hitachi, Japan) and an AFM (Nanocute, Hitachi, Japan, with the internal sensor type of cantilever). For the SEM observations of the anodic porous alumina, a platinum electro-conductive layer was sputter-coated on the specimens using a sputter coater (MSP-1S, Vacuum Device Co., Japan). To examine the vertical cross sections, two treated specimens were prepared: a) one group of specimens was mechanically cut. b) the other group of specimens was embedded in an epoxy resin, polished mechanically, and then immersed in a 0.25 M $\text{K}_3[\text{Fe}(\text{CN})_6]/4.17 \text{ M NaOH}$ solution at room temperature to clearly observe the anodic oxide.

3. Results and discussion

Fig. 2a shows the changes in the current density with anodizing time at several voltages in the 0.1 M H_2SeO_4 solution at 273 K. At 37 V, the current density increased rapidly to over 15 A m^{-2} and then decreased to 0.6 A m^{-2} during the initial 4 min. After this

Download English Version:

<https://daneshyari.com/en/article/185630>

Download Persian Version:

<https://daneshyari.com/article/185630>

[Daneshyari.com](https://daneshyari.com)