



Fabrication of self-ordered porous alumina via anodizing in sulfate solutions



Ryunosuke Kondo, Tatsuya Kikuchi*, Shungo Natsui, Ryosuke O. Suzuki

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

ARTICLE INFO

Article history:

Received 16 May 2016

Received in revised form

20 June 2016

Accepted 23 July 2016

Available online 26 July 2016

Keywords:

Aluminum

Anodizing

Sodium hydrogen sulfate

Porous materials

Self-ordering

Structural

ABSTRACT

Self-ordered porous alumina was fabricated via anodizing in an acid salt electrolyte solution, sodium hydrogen sulfate (NaHSO_4). High-purity aluminum specimens were anodized in a NaHSO_4 solution under various operating conditions with adjusted concentrations, temperatures, applied voltages, and times. Self-ordering was achieved via NaHSO_4 anodizing at appropriate applied voltages ranging from 20 to 28 V, and ordered cell arrangements with the cell size of 55–77 nm were successfully fabricated. Sulfur atoms originating from the electrolyte anions were incorporated into the ordered porous alumina. A honeycomb distribution consisting of a thick outer layer with a high concentration of sulfur and a very thin inner skeleton with a relatively low concentration sulfur was formed via NaHSO_4 anodizing. Our results suggested that there are now many electrolyte options for the fabrication of self-ordered porous alumina with a wide range of nanosizes.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Ordered porous alumina fabricated via electrochemical anodizing has a characteristic honeycomb structure with periodic nanoscale pores, and their fundamental behaviors and engineering were actively investigated for their use in challenging and novel nanomaterials, such as metamaterials [1], plasmonics [2], and surface-enhanced Raman scattering [3], and multifunctional materials [4]. The self-ordering of porous alumina can be achieved via anodizing in appropriate acidic electrolyte solutions under the corresponding appropriate applied voltage [5]. The size of each unit cell in the ordered porous alumina was determined by the applied voltage during self-ordering anodizing [6,7]. Although to date several acidic electrolytes, including sulfuric [8], selenic [9], phosphonic [10], phosphoric [11], etidronic [12], dicarboxylic, [13] and these mixture acids [14,15], have been reported for self-ordering electrolytes, new, additional electrolytes must be continuously discovered and examined to increase the self-ordering voltage and corresponding cell size.

Sulfuric acid anodizing is the most widely used approach for the formation of transparent porous alumina on aluminum substrates in many industrial applications. Ordered porous alumina with a cell size of 50–60 nm can be easily obtained via sulfuric acid anodizing at 19–25 V [6–8]. On the other hand, it is well known

that sulfuric acid is a highly toxic and corrosive acid, and its usage, transportation, and storage are restricted by law for safety reasons in most countries. Therefore, the discovery of more safety self-ordering electrolytes based on sulfuric acid is required for future anodizing applications. Sodium hydrogen sulfate (NaHSO_4) is a solid acid salt that is produced by sodium hydroxide and sulfuric acid, which is widely used as safe chemicals for food additives, surface finishing, and pH adjusting. It is interesting to study aluminum anodizing in such an acid salt electrolyte solution regarding the increasing the cell size and the safety of the anodizing science and technology.

In the present work, we described the self-ordering of porous alumina with increasing cell sizes fabricated via NaHSO_4 anodizing. Nanocharacterization of the ordered porous alumina was investigated via high-resolution electron microscopy and elemental analysis.

2. Experimental

High-purity aluminum plates (99.999 wt%, 0.25–1.0 mm thick, GoodFellow) were degreased in ethanol for 10 min and then electropolished in a 13.6 M $\text{CH}_3\text{COOH}/2.56$ M HClO_4 (78 vol% $\text{CH}_3\text{COOH}/22$ vol% 70% HClO_4) solution at 280 K and 28 V for 1 min. The electropolished specimens were anodized in a 0.25–2.0 M NaHSO_4 solution (273–313 K, $\text{pH}=0.45$ –1.1 at 293 K in 2.0–0.25 M NaHSO_4) at a constant voltage of 17–29 V for up to 24 h. A

* Corresponding author.

E-mail address: kiku@eng.hokudai.ac.jp (T. Kikuchi).

platinum plate was used as the cathode, and the electrolyte solutions were vigorously stirred with a cross-head stir bar during anodizing. The current density was measured by a digital multimeter (DMM4040, Tektronix) during constant voltage anodizing. After anodizing, the specimens were immersed in a 0.2 M CrO_3 /0.51 M H_3PO_4 solution at 353 K to selectively dissolve the anodic oxide on the aluminum substrate. Finally, the exposed aluminum surface was anodized again in a 0.25 M NaHSO_4 solution to form ordered porous alumina (two-step anodizing) [16,17].

The anodized specimens were examined by field emission scanning electron microscopy (FE-SEM, JSM-6500F and JIB-4600F/HKD, JEOL) and image-aberration-corrected scanning transmission electron microscopy (STEM, Titan G2 60-300, 300 kV, FEI). For the SEM observations, a thin platinum electroconductive layer was coated onto the specimens. For the STEM observations, ordered porous alumina fabricated via two-step anodizing was lifted off of the aluminum substrate in a 0.5 M SnCl_4 solution, was pasted on a molybdenum single-hole TEM grid, and was thinned by an argon ion beam using a precision ion polishing system (PIPS, Gatan). The elemental distribution in the porous alumina was examined by STEM-energy dispersive X-ray spectrometry (EDS). The extent of the self-ordering behavior was evaluated by fast Fourier transform (FFT) using the Image-J software package (Wayne Rasband,

National Institutes of Health, USA) [18,19].

3. Results and discussion

Fig. 1a shows the changes in the current density, j , with anodizing time, t , during anodizing in a 0.25 M NaHSO_4 solution (293 K) at various constant voltages of $U = 20$ –27 V for 60 min. Plateau current densities corresponding to a steady growth of anodic oxide were measured after the initial 5-min-anodizing at $U = 20$ –26 V, and the plateau current increased with anodizing voltage due to the rapid growth rate under the applied high voltage. However, the current density increased rapidly in the initial stage of anodizing at an excess applied voltage of 27 V due to the oxide burning phenomenon with non-uniform anodic alumina growth and oxygen gas evolution. These electrochemical behaviors were typically obtained via constant voltage anodizing under the formation of porous alumina on the aluminum substrate. The SEM images of the nanostructured aluminum surface exposed by selective oxide dissolution after anodizing are shown in Fig. 1b. A disordered aluminum dimple array was formed on the surface at a low applied voltage of 20 V (i.e., low current density), and the resulting FFT image exhibited a halo pattern based on the

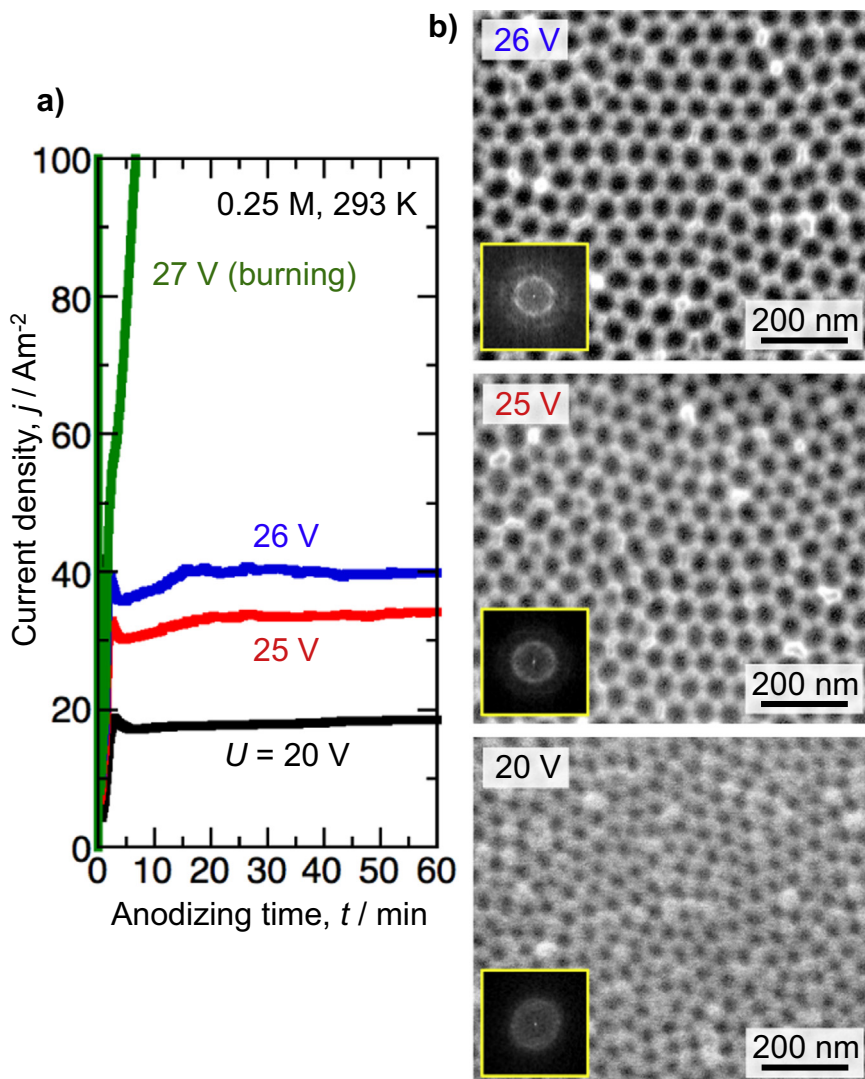


Fig. 1. a) Changes in the current density, j , with anodizing time, t , during anodizing in a 0.25 M NaHSO_4 solution (293 K) at different applied voltages ranging from 20 to 27 V. b) SEM images of the nanostructured aluminum surface after anodizing and selective oxide dissolution. The insert figure shows the resulting FFT image obtained from the aluminum dimple array.

Download English Version:

<https://daneshyari.com/en/article/1641100>

Download Persian Version:

<https://daneshyari.com/article/1641100>

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