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Superhydrophilicity of a nanofiber-covered aluminum surface fabricated via pyrophosphoric acid anodizing

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ABSTRACT

A superhydrophilic aluminum surface covered by numerous alumina nanofibers was fabricated via pyrophosphoric acid anodizing. High-density anodic alumina nanofibers grow on the bottom of a honeycomb oxide via anodizing in concentrated pyrophosphoric acid. The water contact angle on the nanofiber-covered aluminum surface decreased with time after a 4 μL droplet was placed on the surface, and a superhydrophilic behavior with a contact angle measuring 2.2° was observed within 2 s; this contact angle is considerably lower than those observed for electropolished and porous alumina-covered aluminum surfaces. There was no dependence of the superhydrophilicity on the density of alumina nanofibers fabricated via different constant voltage anodizing conditions. The superhydrophilic property of the surface covered by anodic alumina nanofibers was maintained during an exposure test for 359 h. The quick-drying and snow-sliding behaviors of the superhydrophilic aluminum covered with anodic alumina nanofibers were demonstrated.

1. Introduction

Aluminum anodizing is a simple electrochemical technique that is used to form thick anodic oxide films on an aluminum surface and has been widely investigated in the fields of surface science and engineering for corrosion protection, electronic devices, and optical materials [1–7]. Anodic oxide films fabricated via aluminum anodizing can be typically classified into the following two groups: barrier type oxide films formed in neutral solutions and porous type oxide films (porous alumina) formed in acidic and alkaline solutions [1,2,8–20]. Typically, anodizing in acidic solutions, such as sulfuric (H_2SO_4), oxalic ($(COOH)_2$), and phosphoric acid (H_3PO_4), causes the formation of porous alumina which consists of numerous nanoscale hexagonal cells measuring several tens or hundreds of nanometers in diameter with a nanopore at the center of each cell [21–27]. There has been interest in the characteristic nanostructure of porous alumina for their chemical and physical properties [28–32].

Recently, the fabrication of third-generation anodic oxide, anodic alumina nanofibers, which are different from the nanofeatures of barrier and porous oxides, has been reported by several research groups [33–36]. The fabrication processes for the alumina nanofibers are based on the typical anodizing in acidic solutions for the formation of porous alumina and the subsequent selective chemical etching of the porous alumina. High-aspect-ratio alumina nanofibers that are several tens or hundreds of nanometers in diameter can be fabricated via these processes, and the aluminum surface that is covered by the alumina nanofibers exhibits unique hydrophilic and hydrophobic behaviors. However, the fabrication of alumina nanofibers is based on multiple steps including long-term anodizing and chemical etching. In addition, the nanostructural features of alumina nanofibers, including their length, density, and uniformity, could not be controlled accurately in the previous investigations. Therefore, the development of a simple and rapid anodizing process is required for the formation of anodic alumina nanofibers on an aluminum substrate.

We have demonstrated the fabrication of anodic alumina nanofibers via a simple anodizing technique in a new electrolyte, pyrophosphoric acid ($H_4P_2O_7$) [37]. Pyrophosphoric acid anodizing readily creates ultra-high density ($10^{10}/cm^2$) alumina nanofibers with single nanometer-scale diameters [38]. Structural control of the alumina nanofibers, such as the length and density, can be achieved by an electrochemical approach during the anodizing. Well-defined, high-density, and highly ordered alumina nanofibers with a 37–75 nm periodic spacing have successfully been fabricated via novel two distinct anodizing processes [39]. In these investigations to characterize the alumina nanofibers, we found that an aluminum surface covered by high-density alumina fibers

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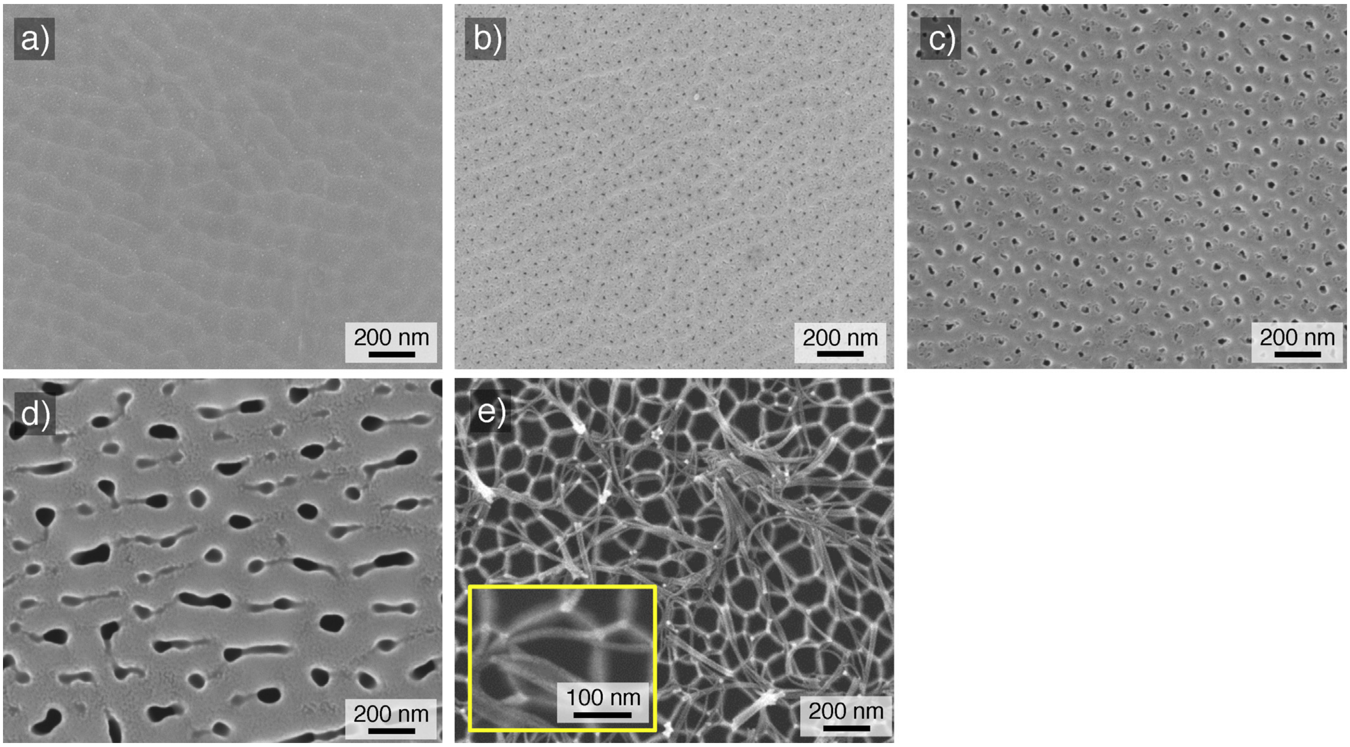

Fig. 1. SEM images of the surface of the a) electropolished aluminum specimen and specimens anodized in b) sulfuric acid, c) oxalic acid, d) phosphoric acid, and e) pyrophosphoric acid solutions. The insert figure shows a high magnification image.

exhibited ultra-fast superhydrophilic behavior with a contact angle near zero within 1 s after the distilled water drop was placed on the surface [37]. Because this novel aluminum surface covered by numerous alumina nanofibers is of great interest for various surface science and engineering endeavors, the superhydrophilic behavior of the aluminum surface should be further investigated.

In the present investigation, we studied the superhydrophilicity of the nanofiber-covered aluminum surface fabricated via pyrophosphoric acid anodizing. The effect of surface nanofeatures on the hydrophilic behavior was determined by microscopy observations and wettability measurements, and the applications of this surface for quick-drying and snow-sliding materials were demonstrated.

2. Experimental

High purity aluminum plates (99.99 wt%, 20 mm × 40 mm, 400 μm thick, Nippon Light Metal, Japan) were used as the starting materials. The aluminum specimens were ultrasonically degreased in ethanol for 10 min and then were electropolished in a 13.6 M CH_3COOH/2.56 M $HClO_4$ mixture (78 vol% CH_3COOH/22 vol% 70% $HClO_4$, T = 280 K) at a constant voltage of 28 V for 1 min. A large aluminum plate was used as the cathode for electropolishing.

The electropolished specimens were immersed in a concentrated pyrophosphoric acid solution (74.0–78.0 wt%, T = 293 K, Kanto Chemical, Japan) and were anodized at constant cell voltages of U = 25–75 V for up to t_a = 60 min. A high purity platinum plate was used as the cathode for anodizing, and the pyrophosphoric acid solution was slowly stirred with a magnetic stirrer during anodizing. A constant voltage was applied to the electrodes using a direct current power supply (PWR-400H, Kikusui, Japan) connected to a PC. The current density was monitored by a digital multimeter (DMM4040, Tektronix) during the constant voltage anodizing. The electrolyte solutions were maintained at a constant temperature using a water bath (UCT-1000, AS ONE, Japan). After anodizing, the specimens were immediately removed from the pyrophosphoric acid solution and then washed with distilled water and dried in a desiccator. For a comparison of the hydrophilic behaviors, the electropolished aluminum specimens were also anodized under the typical anodizing conditions for the formation of several types of porous alumina, in a) a 0.5 M sulfuric acid at 25 V and 283 K, b) a 0.3 M oxalic acid at 50 V and 293 K, and c) a 0.3 M phosphoric acid at 160 V and 273 K.

The nanomorphology of the anodized specimens was examined by field emission scanning electron microscopy (FE-SEM, JIB-4600F/HKD and JSM-6500F, JEOL, Japan) and scanning transmission electron microscopy (STEM, Titan G2 60-300, FEI). For the SEM observations, a thin platinum conductive layer was coated on the anodized specimens by a sputter coater (MSP-1S, Vacuum Device, Japan). For the STEM observations, a thin film specimen was obtained through the two steps: the specimen was pasted onto a molybdenum single-hole grid by an epoxy resin and was then thinned by a precision ion polishing system (PIPS, Gatan). The distribution of oxygen and phosphorus in the anodic oxide was examined by STEM-energy dispersive X-ray spectrometry (EDS).

The water contact angles on the aluminum surface anodized via each anodizing condition were measured by an optical contact angle meter (DM-501, Kyowa Interface Science, Japan). For the wettability measurements, the volume of distilled water placed on the surface of the specimens was adjusted to a relatively large amount of 4 μL to evaluate the superhydrophilic behavior in the initial stage of the measurements. The contact angle of the droplet was measured from 100 ms to 2 s just after the water drop was placed on the surface.

3. Results and discussion

For the formation of various anodic oxides on the aluminum surface, the electropolished aluminum specimens were anodized for t_a = 60 min in the following electrolyte solutions: sulfuric acid,