



Superhydrophilic and superhydrophobic aluminum alloys fabricated via pyrophosphoric acid anodizing and fluorinated SAM modification



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ABSTRACT

The fabrication of superhydrophilic and superhydrophobic aluminum alloys was achieved by pyrophosphoric acid anodizing and SAM (self-assembled monolayer) modification. The anodizing of three kinds of aluminum alloys, including 3004, 1N30, and 8021, in a concentrated pyrophosphoric acid solution resulted in the formation of numerous anodic alumina nanofibers. In addition, insoluble intermetallic compounds contained in the alloy matrix were exposed to the surface with increasing anodizing time, and nanofiber-tangled intermetallic particles also formed on the surface during anodizing. These anodized aluminum alloys exhibited a superhydrophilic behavior measuring less than 4° in the contact angle, and this superhydrophilicity was maintained via the long-term anodizing process. The nanofiber-covered aluminum alloys were immersed in fluorinated phosphonic acid SAM/ethanol solutions, thereby modifying SAMs on the anodic alumina nanofibers. The contact angle of the SAM-modified aluminum alloys increased with the immersion time and temperature of the SAM solution, and the surface was drastically shifted to superhydrophobicity, measuring more than 150° , from superhydrophilicity. However, exceeding 10 min in the anodizing process caused the contact angle to decrease and the gradual disappearance of hydrophobicity due to the formation of many hydrophilic intermetallic particles on the surface. The short-term pyrophosphoric acid anodizing and subsequent SAM modification are useful for the formation of various superhydrophilic and superhydrophobic aluminum alloys.

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1. Introduction

Aluminum and its alloys are widely used in various industrial applications, such as vehicles, aircrafts, trains, cans, electric and electronic products, and renewable energy technologies, due to their lightness, mechanical strength, reflectivity, conductivity, and corrosion resistance. Because the water wettability on the aluminum surface is one of the main important factors determining chemical and physical properties such as chemical reactivity, adhesiveness, and antifouling, the control of water wettability on the aluminum surface is one of the recent challenging topics for various industrial applications [1–3]. For example, hydrophilic presensitized plates for offset printing, hydrophilic aluminum plate-fin heat exchangers, and hydrophobic yogurt-repelling aluminum lids for yogurt pots are well-known applications through the wettability control of the aluminum surface. Fabrication of superhydrophilic (less than 10° in the water contact angle)

and superhydrophobic (more than 150°) aluminum surfaces has been heavily investigated for novel applications [4–9].

Wettability of material surfaces can typically be controlled via the formation of micro- and nano-structures on the surface [10]. Various surface finishing techniques such as photolithography [11], plasma treatment [12], chemical etching [13], electrodeposition [14], sol-gel methods [15], and laser irradiation [16] were demonstrated for the control of wettability to date. However, more simple and cost-effective processes for the fabrication of superhydrophilic and superhydrophobic aluminum surfaces must be developed for industrial applications.

Recently, we reported the control of wettability on a high-purity aluminum surface covered by anodic alumina nanofibers via pyrophosphoric acid ($H_4P_2O_7$) anodizing [17–20]. Anodizing of aluminum in a concentrated pyrophosphoric acid solution causes the growth of numerous anodic alumina nanofibers measuring less than 10 nm in diameter on the aluminum surface. The nanofiber-covered aluminum surface, fabricated in appropriate operating conditions, exhibits a rapid superhydrophilic behavior measuring 2.2° in the water contact angle within 2 s. This superhydrophilic aluminum surface possesses the potential for unique applications

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such as quick-drying and snow-sliding functions. Although this superhydrophilic aluminum surface can be obtained through the simple and short-term anodizing technique, we still have following two problems: i) The wettability of the aluminum surface must also be controlled to superhydrophobic regions ($>150^\circ$), and ii) commercially available aluminum alloys must be used for various industrial applications.

In the present investigation, we demonstrate the fabrication of superhydrophilic and superhydrophobic aluminum alloys through pyrophosphoric acid anodizing and subsequent modification of fluorinated phosphonic acid self-assembled monolayers (SAMs). We found that anodizing of various aluminum alloys in a pyrophosphoric acid solution established a superhydrophilic surface measuring less than 4° in the contact angle, and subsequent fluorinated SAM modification created a superhydrophobic surface measuring more than 150° . The superhydrophilicity and superhydrophobicity of the aluminum alloys could be achieved by the formation of anodic alumina nanofibers. These alumina nanofibers can also be fabricated by long-term anodizing in other acidic electrolyte solutions or selective chemical etching of the porous alumina after anodizing [21–24]. However, our pyrophosphoric acid anodizing easily creates anodic alumina nanofibers in a short time, and the nanomorphology of alumina nanofibers can be accurately controlled [17–20]. Growth behavior of the anodic alumina nanofibers formed on the aluminum alloys, superhydrophilicity of the nanofiber-covered surface, and superhydrophobicity after SAM modification are discussed in detail.

2. Experimental

2.1. Pre-treatment of aluminum alloys

Three types of commercially available aluminum alloys (250–300 μm thick plate, Toyo Aluminum, Japan) were used as the anodizing specimens, and the chemical compositions of the alloys are shown in Table 1 (JIS H 4160). 3004 aluminum is an Al–Mn alloy with 1.0–1.5 wt% Mn and 0.8–1.3 wt% Mg as well as small amounts of Cu, Zn, Fe, and Si. 1N30 aluminum is industrially pure aluminum with small amounts of Fe and Si. 8021 aluminum is an Al–Fe alloy including 1.2–1.7 wt% Fe as well as small amounts of other additional elements. These aluminum alloys are widely used for food and pharmaceutical packaging, batteries, building materials, and other household items. In addition to these three alloys, high-purity aluminum plates (99.999 wt%, 0.25 mm thick, GoodFellow, UK) were also used for comparing water wettability.

The aluminum specimens were cut into 20 mm \times 20 mm pieces with a handle and were ultrasonically degreased in ethanol for 10 min at room temperature. After ultrasonication, the specimens were chemically polished in a 2.5 M NaOH solution at 333 K for 5 min, and then were immersed in a 4.0 M HNO₃ solution at room temperature for 30 s to remove the smut formed on the surface.

2.2. Pyrophosphoric acid anodizing

The chemically polished specimens were used as an anode, and a platinum plate (21 mm \times 25 mm, 99.95 wt%, Furuya Metal, Japan)

was used as a cathode for pyrophosphoric acid anodizing. These electrodes were set 20 mm apart in parallel and were immersed in an electrochemical cell (inner diameter: 56 mm) filled by a concentrated pyrophosphoric acid solution (100 mL, 74.0 wt%, $T_a = 293$ K, Kanto Chemical, Japan). The aluminum specimens were then anodized at a constant cell voltage of $U_a = 25\text{--}75$ V for up to $t_a = 60$ min. A direct power supply (PWR-400 M, Kikusui, Japan) was used to apply the constant voltage. The pyrophosphoric acid solution was maintained at a constant temperature using a water bath (UCT-1000A, AS ONE, Japan) during anodizing and was slowly stirred with a magnetic stirrer. After anodizing, the specimens were quickly removed from the pyrophosphoric acid solution, washed with distilled water, and dried in a desiccator.

2.3. Modification of fluorinated phosphonic acid SAMs

Two types of fluorinated phosphonic acid SAMs with different chain lengths were used for the modification of the anodic oxide surface: a) 3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctylphosphonic acid (FOPA, C₈H₆F₁₃O₃P, Sigma-Aldrich, USA) and b) 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorododecylphosphonic acid (FDDPA, C₁₂H₆F₂₁O₃P, Sigma-Aldrich). Phosphonic acid SAMs are widely used for the formation of stable and dense layers on metal oxide surfaces such as Al₂O₃ and TiO₂. In addition, because the critical surface tension of the -CF₃ groups is 6 mNm⁻¹, the surface modified with fluorinated phosphonic acid SAMs may exhibit a highly hydrophobic behavior. The anodized specimens were immersed in a glass bottle filled by a 0.5 mM SAM/ethanol solution for up to $t_{im} = 48$ h. The glass bottle was sealed with a cap after immersion, and then was placed in an incubator (Heratherm IMC18, Thermo Fisher Scientific, USA, and AVO-200NS, AS ONE, Japan) at $T_{im} = 293\text{--}323$ K. After SAM modification, the specimens were washed with ethanol and dried in a desiccator.

2.4. Characterization

The nanomorphologies of the surface of the anodized specimens were examined by field-emission scanning electron microscopy (FE-SEM, JSM-6500F, JEOL, Japan). The elemental distribution of the surface was analyzed by a field emission electron probe microanalysis (FE-EPMA, JXA-8530F, JEOL). For the SEM observations and EPMA, a thin platinum electro-conductive layer was coated on the anodized specimens using a sputter coater (MSP-1S, Vacuum Device, Japan). The presence of fluorinated SAMs formed on the surface was detected by X-ray photoelectron spectroscopy (XPS, JPS-9200, JEOL).

The water contact angle on the specimens was measured by an optical contact angle meter (DM-501, Kyowa Interface Science, Japan). The distilled water droplets (4 μL in water volume for hydrophilic measurements, and 2 μL for hydrophobic measurements) were placed on the specimens using a needle, and the contact angles of the droplets were measured by a charge-coupled device (CCD) camera 2 s after the water droplets were removed from the needle. The time-dependent changes of the contact angle after the dropping were also observed for up to 60 s.

3. Results and discussion

Chemically polished 5N aluminum and 3004 aluminum alloy were anodized in a pyrophosphoric acid solution (293 K) at 75 V to compare growth behaviors of anodic alumina nanofibers. Fig. 1 shows SEM images of the surface of the 5N aluminum specimen anodized for a) $t_a = 2$ min, b) 4 min, c) 10 min, and d) 30 min, and Fig. 1a through 1c were obtained from a slightly declined angle to observe the nanostructures in detail. A unique labyrinthine

Table 1
Chemical composition of three types of aluminum alloys (wt%) used in our investigation.

	Cu	Mg	Mn	Zn	Fe	Si	Al
3004	≤ 0.25	0.8–1.3	1.0–1.5	≤ 0.25	≤ 0.7	≤ 0.30	bal.
1N30	≤ 0.10	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.7 in all		≥ 99.30
8021	≤ 0.05	–	–	≤ 0.10	1.2–1.7	≤ 0.15	bal.

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