

Fabrication of Superhydrophobic Aluminum Alloy Surface with Hierarchical Pore Nanostructure for Anti-Corrosion

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Aluminum and its alloys have been widely used in various fields because of low weight, high strength, good conductivity, and low price. It is well known that aluminum alloys that cause natural oxide film can inhibit corrosion in wet, salty environments. However, these oxides are so thin that corrosion occurs in a variety of environments. To prevent this problem, an electrochemical anodizing technique was applied to the aluminum alloy surface to form a thick layer of oxide and a unique oxide shape, such as a hierarchical pore structure simultaneously combining large and small pores. The shape of the structures was implemented using stepwise anodization voltages such as 40 V for mild anodizing and 80 V for hard anodizing, respectively. To maximize water repellency, it is crucial to the role of surface structures shape. And a hydrophobic thin film was coated by 1H, 1H, 2H, 2H-Perfluorodecyltrichlorosilane (FDTS) to minimize surface energy of the structure surface. Thus, such nanoengineered superhydrophobic surface exhibited a high water contact angle and excellent corrosion resistance such as low corrosion current density and inhibition efficiency.

Keywords: *Stepwise anodizing, Hierarchical pore nanostructures, Superhydrophobic coating, Anti-corrosion*

1. Introduction

As is well-known, aluminum and its alloys are the important materials because of their low weight, excellent machinability, high strength, and easy accessibility. Accordingly, they have achieved a wide range of applications for the industries, especially in the fields of shipbuilding, aerospace, and machine manufacturing. The most important feature of aluminum and its alloy is their excellent corrosion resistance owing to the presence of a thin and naturally formed protective oxide film on its surface [1,2]. Nevertheless, aluminum and its alloys are vulnerable in a wet environment and the water containing chloride ions [3].

Superhydrophobic aluminum surfaces with remarkable anti-corrosion have been recently reported in some research. Superhydrophobic surfaces, with a water contact angle (CA) greater than 150°, is one of the novel methods for protection against corrosion in a variety of environment. Generally, the superhydrophobic surface can be prepared by two steps. The first is to fabricate micro- and/or nano-scale rough structures and then introduce low surface energy material coating. Among the previous surface treatment research, electrochemical anodization processes,

which are a simple process and low-cost, have been fabricated and designed for modifying superhydrophobic surfaces by modulation of hierarchical micro/nano structures and surface shape via roughness [4-7].

In this work, we aimed to design non-wetting functional films on the anodized aluminum surfaces by stepwise anodization combining with the anodization voltage between mild anodization (MA) and hard anodization (HA) and varying the PW duration then was applied to aluminum 5052 alloy to designed hierarchical micro-/nano-structure. To obtaining a superhydrophobic surfaces, it was coated to self-assembly monolayer (SAM) on top of hierarchical nanostructures [8]. Finally, the electrochemical tests were carried out to examine corrosion protection properties. Therefore, it was possible to verify that superhydrophobic aluminum alloys are effective in corrosion protection.

2. Experimental Methods

Before anodizing, the aluminum 5052 alloy sheets (Al 5052) in the size of 20 mm × 30 mm × 1 mm were degreased ultrasonically with acetone, ethanol, and deionized (DI) water, sequentially. Subsequently, they were electropolished in a 1:4 by volume mixture of perchloric acid (HClO₄) and ethanol (C₂H₅OH) at 20 V for 1 minute.

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Table 1 Fabrication process conditions for stepwise anodization

Sample	First anodizing	AAO removal	Second anodization		Pore widening	Third anodization	
	Time (hour)	Time (hour)	Step	Time (min)	Time (min)	Step	Time (min)
a	6	10	MA	30	30	HA	0.5
b	6	10	MA	30	40	HA	0.5
c	6	10	MA	30	50	HA	0.5
d	6	10	MA	30	60	HA	0.5

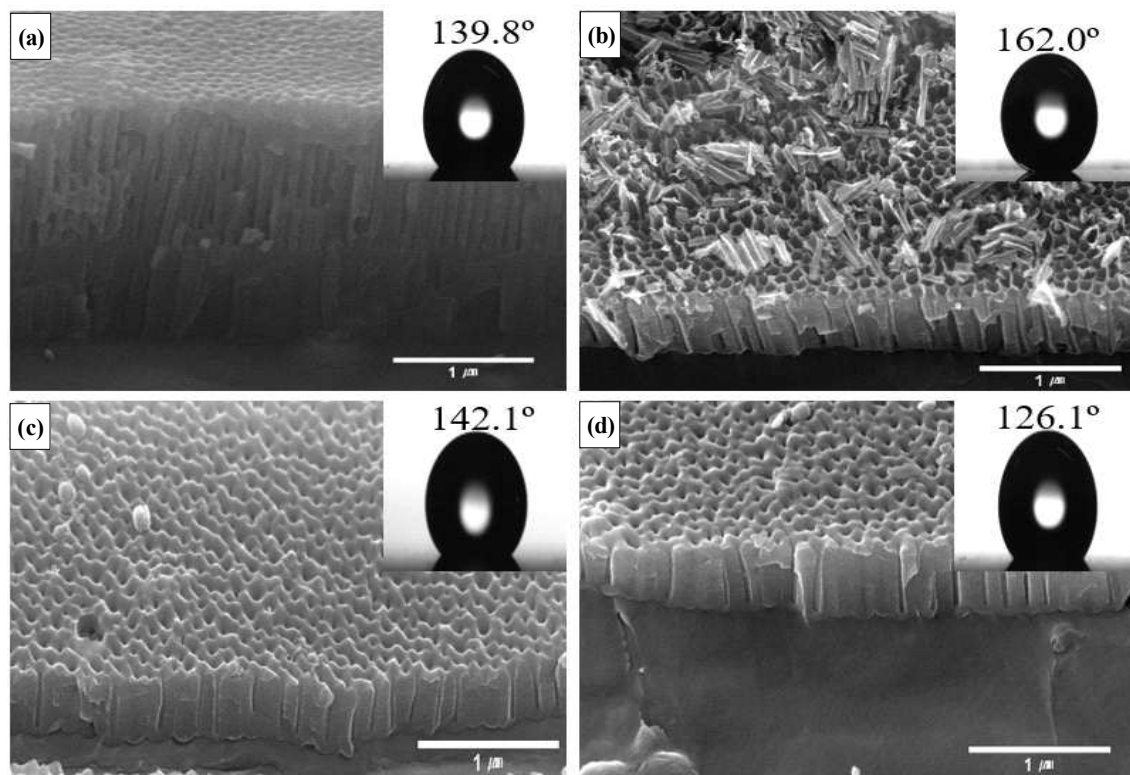


Fig. 1 FE-SEM image of Al 5052 cross-sectional morphology with different intermediate PW time of (a) 30 min, (b) 40 min, (c) 50 min and (d) 60 min. The inset referring to water contact angles after being modified by stepwise anodization and coated with FDTS.

The electropolished aluminum alloy was used as a working electrode (anode), and a platinum sheet was employed as a counter electrode (cathode). The two electrodes were separated by a distance of about 5 cm. The first anodization was performed in 0.3 M oxalic acid solution at 0 °C for 6 hours with appreciate magnetic stirring under the applied voltage of 40 V. The anodic aluminum oxide (AAO) layer formed by the first anodization step was removed by soaking in a mixture solution of 1.8 wt% chromic acid and 6 wt% phosphoric acid at 65 °C for 10 hours. Then, the second anodization step was employed by the same condition as the first anodization step. The second anodizing step involved both the mild anodization (MA) and hard anodization (HA) modes [9]. The MA mode was

applied at 40 V for 30 minutes and the HA mode was applied at 80 V for 30 seconds. To make pores wider, the AAO layers soaked in 0.1 M phosphoric acid at 30 °C for various times (30, 40, 50, and 60 minutes). And then, the same conditions used in the second anodizing step to attempt fabrication of hierarchical nanostructures, as listed in Table 1. Before modifying AAO layers coated with a self-assembled monolayer (SAM) of 1H, 1H, 2H, 2H-Perfluorodecyltrichlorosilane (FDTS), the samples were cleaned with O₂ plasma for 15 minutes, and then were dried in air and baked at 150 °C for 10 minutes. And then, the samples were coated with FDTS for 24 hours in vacuum [8,10].

Table 2 Electrochemical parameter derived from the polarization curves

Sample	E_{corr} (mV)	I_{corr} (A/cm ²)	IE (%)
Control	-914	2.19×10^{-5}	0
a	165	3.69×10^{-9}	99.98
b	223	1.18×10^{-9}	99.99
c	-883	7.37×10^{-7}	96.63
d	-891	6.13×10^{-6}	72.01

The resultant AAO morphologies were examined by a field emission scanning electron microscope (FE-SEM). The wettability properties of AAO surfaces were investigated by measuring apparent contact angles with a contact angle of the sessile water droplet (~3.5 μL) at room temperature. All the contact angle measurements were carried out at five-point on each sample. The corrosion resistance property of the superhydrophobic surface was evaluated with potentiodynamic polarization (PDP) in 3.5 wt% NaCl solution. The three-electrode system consists of an Ag/AgCl electrode as the reference electrode, a platinum mesh as the counter electrode and the AAO as the working electrode. The potential scan was taken from -2000 mV ~ 2000 mV at scan rate of 1 mV/s. All electrochemical tests are conducted at room temperature.

3. Results

3.1 Fabrication of superhydrophobic surface

The cross-sectional morphology and wettability of Al 5052 substrates after stepwise anodization step via MA→PW→HA with intermediate PW in phosphoric acid for the different time was investigated in Fig. 1. To study the effect of the PW time immersed in phosphoric acid, the PW time was varied from 30 minutes to 60 minutes. Apparently, hierarchical nanopore structures were observed by controlling both the anodization voltage and the PW duration. In this case, a PW time of 40 minutes exhibited a hierarchical nanopore structure with a pillar-like shape. Moreover, its wettability changed remarkably with the structural morphology. As a reference, AAO films with stable outlayer morphology by conducting the PW process for 30, 50, and 60 minutes showed $139 \pm 0.24^\circ$, $142 \pm 0.55^\circ$, and $126 \pm 0.27^\circ$, displaying the hydrophobic surfaces (Fig 1a, c and d). On the other hand, when the PW process for 40 minutes, the CA revealed the greatest value of $162 \pm 2.04^\circ$ (Fig. 1b). Obviously, a nano-scale pillared-like structure became AAO with varying the PW time, which led to the increasingly rough surface.

3.2 Corrosion behavior with electrochemical analysis

The anti-corrosion behavior of superhydrophobic surface to protect aluminum 5052 alloy from corrosion in 3.5 wt% NaCl solution was characterized by polarization curves in the absence and the presence of the superhydrophobic surface as shown in Fig. 2. The electrochemical corrosion parameters, such as corrosion potential (E_{corr}), current density (I_{corr}) and inhibition efficiency (IE) are listed in Table 2. The E_{corr} was -914 mV for the untreated Al 5052, 165 mV for AAO with PW time of 30 minutes, 223 mV for AAO with PW time of 40 minutes, -883 mV for AAO with PW time of 50 minutes, and -891 mV for AAO with PW time of 60 minutes. It is clear that the I_{corr} decreased drastically and E_{corr} shifted to a positive direction in the presence of the superhydrophobic. The corrosion current density (I_{corr}) of the untreated Al and that of AAO coated by FDTS are obtained by the polarization curves to the E_{corr} . The inhibition efficiency (IE) is calculated according to the following equation (1) [11]:

$$IE = \frac{i - i_0}{i} \times 100 \tag{1}$$

where i and i_0 mean the corrosion current density of the bare and superhydrophobic surface, respectively. The

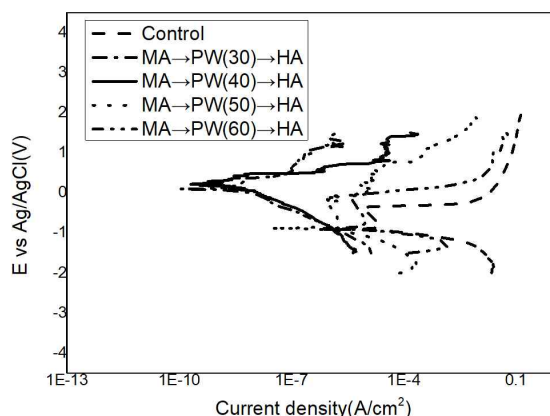


Fig. 2 Electrochemical polarization curves of bare and superhydrophobic Al 5052 in 3.5 wt% NaCl solution.

IE was 99.98%, 99.99%, 96.63%, and 72.01% as increased the PW time, respectively. The AAO with the greatest IE showed the largest contact angle. In addition, the superhydrophobic coating surface exhibited positive results, where the E_{corr} shifts positively for about 223 mV when the anodized aluminum 5052 alloys after SAM coating for producing superhydrophobic surface.

4. Discussion

In the case of the MA→PW→HA, the CA of all AAOs displayed more than 120° after being modified by employing stepwise anodization and PW step, which all demonstrated the hydrophobic surface. Surface roughness and surface energy are the key factors in water repellency on the superhydrophobic surface. The surface energy with a solid is determined by the surface chemistry, which in turn depends on its chemical composition. Additionally, a low surface energy material coating on modified AAO investigated the beneficial effect in controlling superhydrophobicity [12,13]. So, the hierarchical nanopore structures had a great impact on surface wettability. According to Wenzel-Cassie equation (2) [14]:

$$\cos \theta = r_f f_{SL} \cos \theta_0 - 1 + f_{SL} \quad (2)$$

Where θ_0 is Young's contact angle on a smooth surface, f_{SL} is the fraction of a solid-liquid wet surface and r_f is the roughness of the wetted solid surface which unity for the chemically homogenous surface. This equation indicated the CA and surface roughness had got the same tendency, which explained the greater value of r_f with the greatest value of roughness on a hierarchical surface. Moreover, superhydrophobic coatings on Al 5052 with pillared-like hierarchical nanostructure have shown remarkable corrosion resistance. As you can see in the polarization curves, the positive shift of the E_{corr} could be linked to an improvement in the superhydrophobic coating and structural morphology form on the Al 5052. It suggests that the superhydrophobic coating retards the dissolution of AAO between the interface of the AAO surface and seawater. The trapped air by superhydrophobic coating also prevents Al substrates from corrosion, e.g., chloride ions in seawater [15]. So, such nano-scale surface roughness with the controllability of the structural dimensions and shapes has been a critical parameter of the superhydrophobic surface on the corrosion resistance.

5. Conclusions

In conclusion, the superhydrophobic surface on aluminum 5052 alloys is created by electrochemical stepwise anodization process and low surface energy coating for examining anti-corrosion. Stepwise anodization fabricates nanopore hierarchical structure with roughness as revealed by FE-SEM image. The anodic aluminum 5052 alloy oxide covered with superhydrophobic coating can reach to 162°. The analysis of electrochemical polarization test shows that the aluminum 5052 corrosion resistance is effectively enhanced by the formation of the superhydrophobic film on modified aluminum 5052. It can be used that the various production of superhydrophobic nanoengineering materials with marine industry applications because of their excellent corrosion resistance property.

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