



Superhydrophobic aluminum alloy surface: Fabrication, structure, and corrosion resistance



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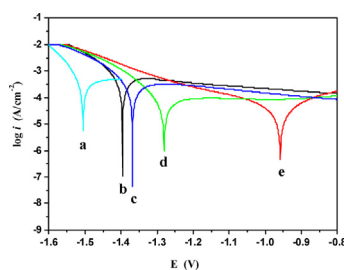
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HIGHLIGHTS

- The superhydrophobic surface is fabricated by a simple and environment-friendly method.
- The superhydrophobic aluminum alloy surface presents binary-scale structure.
- The corrosion rate decreases with the increase of the water contact angle.
- The superhydrophobic aluminum alloy has better corrosion resistance.

GRAPHICAL ABSTRACT

The corrosion potential (E_{corr}) of the aluminum alloy positively increases while the corrosion current density (i_{corr}) decreases with the increase of the water contact angle, which indicates that the instantaneous corrosion rate of aluminum alloy decreases with the increase of the water contact angle. Consequently, it can be found that the aluminum alloy with higher water contact angle has better corrosion resistance, and the superhydrophobic aluminum alloy has excellent corrosion resistance.



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ABSTRACT

A superhydrophobic aluminum alloy surface was successfully fabricated by a simple and environment-friendly method with boiling water treatment and stearic acid modification. The formation procedure, phase structure, morphology, composition, and corrosion resistance of the superhydrophobic aluminum alloy surface were investigated in this research. Results show that a superhydrophobic surface with a contact angle of 154.1° can be obtained when the aluminum alloy was treated in the boiling water for 30 s and modified with 5 mmol/L of stearic acid for 24 h at room temperature. The superhydrophobic aluminum alloy surface presents binary structures with both pillars and hollows. The corrosion resistance of the aluminum alloy enhances with the increase of the water contact angle, and the superhydrophobic aluminum alloy has the best corrosion resistance as compared to the other aluminum alloys.

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1. Introduction

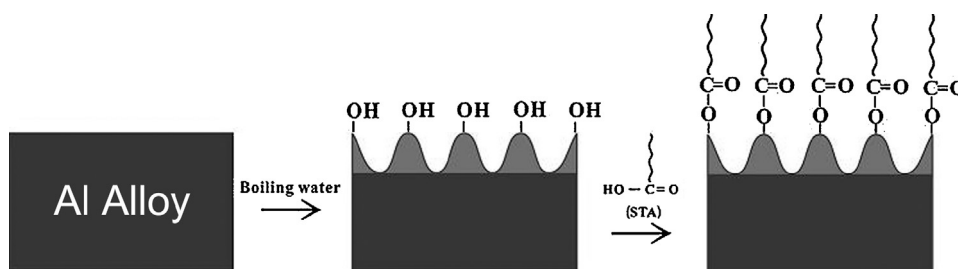
Wettability is one of the fundamental properties of a solid surface, which plays an important role in daily life, industry, and agriculture [1]. The surface with a water contact angle of more than 150° that repels water extremely is called a superhydrophobic

surface. Such surfaces have attracted considerable interest due to their great importance in both the fundamental research and potential for industrial applications [2–5]. Conventionally, superhydrophobic surfaces can be produced mainly in two ways: one is to create a rough structure on a hydrophobic surface ($CA > 90^\circ$), and the other is to modify a rough surface by materials with low surface free energy [6–8]. Currently, superhydrophobic surfaces can be achieved by a combination of low surface energy materials with micro- and nano-structure.

Aluminum and its alloys possess much predominance performance, such as high-specific strength, excellent heat and electrical

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Scheme 1. The fabrication procedure of the superhydrophobic aluminum alloy surface.

conductivities, and low-specific weight, so they are quite important metal engineering materials for applications in aerospace, aircraft, and national defense. Grounded on the practical or potential applications of superhydrophobic materials in anticorrosion [9,10], fluid drag reduction [11,12], no-loss transportation [13], and so on, the fabrication of the superhydrophobic surfaces on aluminum and its alloys have attracted more and more attention from researchers around the world. Some work has been reported on designing rough superhydrophobic surfaces on aluminum, which includes the conventional electrochemical machining [14–17] and chemical etching method [18–20]. However, the electrochemical machining and chemical etching methods require the acid corrosive procedure, while sulfuric acid, oxalic acid, and phosphoric acid are often used. These acids have certain hazards to the environment and the health of the operator. Thereupon, there is need to probe environmentally friendly method for the fabrication of superhydrophobic aluminum alloy surfaces. In this research, superhydrophobic aluminum alloy surfaces are fabricated by a simple and environmentally friendly method with boiling water treatment and stearic acid modification. Various surface roughness and morphology are achieved by careful control of the treatment parameters in the boiling water and stearic acid, and the resulting superhydrophobic surfaces have improved the corrosion resistance of the aluminum alloys. The relationship between the wettability, phase structure, morphology, chemical composition, corrosion resistance, and surface chemistry is discussed in detail.

2. Experimental

2.1. Materials

Aluminum alloy plates (6063Al in engineering materials with a size of 20 mm × 10 mm × 2 mm, weight composition: Si (0.20–0.60%), Fe (0.35%), Cu (0.10%), Mn (0.10%), Mg (0.45–0.90%), Cr (0.10%), Zn (0.10%), Ti (0.10%), other impurities (0.15%), and Al (the remaining element)). Stearic acid (STA) and N,N-dicyclohexylcarbodiimide (DCC) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. Acetone, *n*-hexane, etc., were from Tianjin Benchmark Chemical Reagent Co., Ltd. (China).

2.2. Fabrication of the superhydrophobic aluminum alloy surface

The superhydrophobic aluminum alloy surface was fabricated by a facile and environmentally friendly method. Firstly, aluminum alloy plates were polished mechanically using 800[#], 1200[#], and 1500[#] abrasive paper in turn, and then washed ultrasonically using absolute methanol, acetone, and distilled water for about 10 min, respectively. Second, the aluminum alloy plates were treated with the boiling water to roughen the surfaces. Finally, the aluminum alloy plates were modified with STA in *n*-hexane solution together with 2 mmol/L of DCC at room temperature, followed by washing with *n*-hexane, deionized water, and then dried in air. DCC is used here as an effective dehydration reagent and which can facilitate

the formation of the covalent bond between carboxyl groups and hydroxyl groups. The schematic process for fabrication is described in Scheme 1.

2.3. Surface characterization

The water contact angles were measured with a horizontal microscope with a protractor eyepiece (DSA 100, Kruss, Germany) at room temperature, while the size of applied water droplet was 5 μ L. Droplet was placed at five positions for one sample and the average value was adopted as the contact angle.

Morphology of the sample was observed by a field emission type of scanning electron microscope (FE-SEM, JSM-6701F, Japan).

The phase structure of the sample was characterized by X-ray diffractometer (XRD, XRD-7000LX, Shimadzu, Japan) equipped with graphite monochromatized Cu K α radiation.

The chemical state of the atoms in the aluminum alloy surfaces was analyzed on a multi-functional X-ray photoelectron spectroscope (XPS, PHI-5702, Perkin-Elmer, USA). The Al K α line was used as the excitation source. The binding energy of 284.5 eV of C1s in hydrocarbon was used as a reference.

The electrochemical measurements were carried out in a three-electrode cell. The aluminum alloy plate with a size of 10 mm × 10 mm was used as the working electrode. Measurements were performed in 3.5 wt% NaCl solution at room temperature using a computer-controlled electrochemical workstation (CHI660D, CH Instruments Inc.). Scan was conducted with a constant rate of 10 mV/s. Potentiodynamic anodic polarization curves were established and the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using the Tafel extrapolation method.

3. Results and discussion

3.1. Preparation of the superhydrophobic aluminum alloy surface

The superhydrophobic aluminum alloy surface was fabricated by a simple and environment-friendly method. Namely, the aluminum alloy was treated with the boiling water and then modified with STA. The whole preparation and modification procedure are monitored with the surface wettability, and the change of the water contact angles at the aluminum alloy surfaces after the different treatment steps is shown in Fig. 1.

It can be found from Fig. 1 that the contact angles on the aluminum alloy surfaces change remarkably after every disposal steps, demonstrating that the aluminum alloy surface wettability varies upon each disposal step. In specific, the original aluminum alloy surface with native oxidized top layer shows hydrophilic with a water contact angle of about 45°. By contrast, the contact angle reduces to about 30° after the aluminum alloy surface is burnished with abrasive paper (see as burnished surface in Fig. 1), while the water contact angle increases to around 82.1° after the aluminum alloy is cleaned ultrasonically with absolute methanol, acetone

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