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Fabrication of superhydrophobic aluminium alloy surface with excellent corrosion resistance by a facile and environment-friendly method

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ABSTRACT

This work develops a facile and environment-friendly method for preparing the superhydrophobic aluminium alloy surface with excellent corrosion resistance. The superhydrophobic aluminium alloy surface is fabricated by the boiling water treatment and stearic acid (STA) modification. Results show that the boiling water treatment endows the aluminium alloy surface with a porous and rough structure, while STA modification chemically grafts the long hydrophobic alkyl chains onto the aluminium alloy surface. Just grounded on the micro- and nano-scale hierarchical structure along with the hydrophobic chemical composition, the superhydrophobic aluminium alloy surface is endued the excellent corrosion resistance.

1. Introduction

In recent years, the development of new materials based on bionic science has been widely carried out in various fields [1,2]. As one of bionic materials, the artificial superhydrophobic surfaces with water contact angles larger than 150°, inspired by the lotus effect, have also been developed and researched extensively [3,4]. Due to the outstanding water repellent property, the superhydrophobic surfaces have attracted significant interest from both fundamental research and industrial applications [5,6]. Such a unique wettability for superhydrophobic surfaces has shown wide potential applications, such as self-cleaning, anti-icing, corrosion resistance, drag-reduction, anti-bioadhesion, and so on [7–9].

Wettability at the solid surface is a very important property which is governed by both chemical composition and geometric microstructure [10–12]. Generally, the superhydrophobic surfaces can be produced in two types of technology ways: on one hand, modifying of an appropriate rough surface with the low surface energy molecules or coatings. On the other hand, creation of a rough micro- and nanostructure at hydrophobic surfaces [13–15]. Up to now, artificial superhydrophobic surfaces have been fabricated by various techniques, such as sol–gel process, chemical etching, layer-by-layer assembly, electrostatic spinning, chemical vapor deposition, lithographic process, etc. [16–18]. Hydrophobicity is usually explained by the theories of Wenzel and Cassie–Baxter [19,20]. In Wenzel's model, the liquid fully penetrates the surface grooves, so-called homogeneous wetting, and the larger contact angle results from the increase of the hydrophobic surface roughness. While in the Cassie–Baxter model, the water rests on the structured air/solid interface, so the water droplets on the rough surface are easy to roll.

As we all know, the aluminium and its alloy is an important category of materials owing to its abundant in nature, easy to handle, and high technological value. Consequently, the aluminium and its alloy have wide range of industrial applications, especially in aerospace and household industries [21]. In dry and non-salty environments, aluminium develops a thin aluminium oxide layer (on the order of 20 Å), which can inhibit the further corrosion. Aluminium and its alloys, however, are reactive materials and are prone to corrosion in wet, salty environments for the oxide layer will be penetrated and further corrosion ensues [22,23]. This corrosion behavior prevents aluminium and its alloys from being widely used in wet, water, and salty environments.

The corrosion resistance can be improved by introducing the anticorrosive coatings on the surface of aluminium and its alloys. E.g., preparing the chromate-based coatings or anodizing the surfaces [24,25]. Chromate-based coatings can provide highly effective corrosion protection, but environmental regulations are increasingly restricting their use, while the anodization will increase the weight of the aluminium and its alloys. Given the strong water

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repulsive property of the superhydrophobic surfaces, it may be a promising technology for slowing the breakdown of the native aluminium oxide layer and thereby retarding corrosion of the aluminium layer underneath by fabricating the superhydrophobic coatings or surfaces on the aluminium and its alloys. As a result, the anticorrosion performance of aluminium and its alloys may be improved because the superhydrophobic surfaces can inhibit the contact of a surface with water, environmental humidity, and corrosive medium.

Up to now, a few methods have been reported for preparing the superhydrophobic surface on aluminium alloy with the outstanding corrosion resistance. Zhang and co-worker reported a hierarchical micro/nanostructured superhydrophobic film on a PAO/Al substrate, and which provides a very effective corrosion-resistant coating for the underlying aluminium [26]. Yin et al. fabricated a superhydrophobic coating applied in corrosion protection on the surface of aluminium alloy by chemical etching and surface modification [27]. Barkhudarov obtained a superhydrophobic films as corrosion inhibitors on aluminium surfaces from a precursor solution containing mixed alkoxides 3,3,3-trifluoropropyl-trimethoxysilane and tetramethyl orthosilicate [28].

However, in these cases, either special equipment/complex process control is required, or caustic or costly reagents, for instance, HNO_3, HF, H_2O_2 or fluoride, etc., are needed. Consequently, these methods/procedures may concern problem as environment pollution, high cost, and so on. Therefore, a simple, inexpensive, and environment-friendly fabrication method is quite needed since it is very advantageous for industrial large-scale production. Herein, we report a novel method for the fabrication of superhydrophobic surfaces on the aluminium alloy by treating the aluminium alloy in the boiling water and ethanol–water solution containing stearic acid, respectively. The procedure was fairly facile to carry out and no special technique or equipment is required. Moreover, only the ordinary reagents, such as the boiling water, ethanol, stearic acid, etc., are used in the procedure. Therefore, the method is also environment-friendly and inexpensive, while the as-fabricated superhydrophobic aluminum alloy surface has excellent corrosion resistance.

2. Materials and methods

2.1. Materials

Aluminium alloy sheet (brand LD6063, commercially available engineering materials) with a size of 20 mm × 10 mm × 2 mm was purchased from the market. Stearic acid (STA) was purchased from Sinopharm Group Chemical Reagent Co., Ltd. Ethanol and acetone, were from Tianjin Benchmark Chemical Reagent Co., Ltd. (China).

2.2. Fabrication of the superhydrophobic aluminium alloy surface

The superhydrophobic aluminium alloy surface was fabricated by a facile and environment-friendly method. Firstly, the aluminium alloy sheet was polished with $800^{\#}$, $1200^{\#}$, and $1500^{\#}$ sandpaper in turn, and then cleaned ultrasonically with acetone and deionized water, respectively. Second, the aluminium alloy sheet was treated in the boiling water. Finally, the sheet was immersed in an ethanol–water solution (volume ratio of 1:1) containing 10 mmol/L of stearic acid (STA) at 60 °C. The resulting sheet was cleaned with ethanol and deionized water in order to remove any physical adsorbed impurities, and then dried in air at room temperature. Thus, the aluminium alloy surface with superhydrophobic property is fabricated.

2.3. Sample characterization

2.3.1. Contact angle measurements

The water contact angle was measured with 8 μL deionized water droplet at room temperature using a horizontal microscope with a protractor eyepiece (DSA 100, Kruss, Germany). At least five parallel measurements were made for each sample, and the value of average contact angles is reported. In the rolling angle measurement, a water droplet was placed on the structured superhydrophobic aluminium alloy surface, and the measuring plane of the sample was tilted until the droplet started to slide. The value of the reported sliding angle is the average of the tilting angles of the measuring plane at which the droplet began to roll. The photograph of water droplet was observed with a digital camera, and the volume of the deionized water droplet was 10 μL.

2.3.2. SEM measurements

The microstructure of the aluminium alloy surface was observed using a field emission type of scanning electron microscope (FE-SEM, JSM-6701F, Japan).

2.3.3. Infrared spectroscopy

The chemical composition at the aluminium alloy surface was examined by charactering the power scraped from the surface with Fourier transform infrared spectroscopy (FTIR, VER-TEX 70, Bruker, Germany) via KBr pellet technique.

2.3.4. Electrochemical experiments

The polarization curves of electrochemical experiments were obtained with a computer-controlled electrochemical workstation (CHI660D, CH Instruments Inc.) in 3.5 wt% NaCl solution at room temperature. The experiment was performed in a three-electrode cell system with platinum electrode as a auxiliary electrode, untreated aluminium alloy sheet/superhydrophobic aluminium alloy sheet as a working electrode, and a saturated calomel electrode (SCE) as a reference electrode. The working electrode was set in a homemade Teflon holder with a circular window, and the area was 1 cm^2. Polarization curves were recorded at a sweep rate of 10 mV s^{-1} from −1600 to −500 mV. Each electrochemical test was repeated for three times to make sure good repeatability.

3. Results and discussion

3.1. Fabrication of the superhydrophobic aluminium alloy surface

The superhydrophobic aluminium alloy surface was fabricated by the treatment of the aluminium alloy sheet with sandpaper, boiling water, and STA modification in turn. No caustic reagents were used in the preparation procedure, and the fabrication work is very easy to put in practice. So the method for the fabrication is quite facile and environment-friendly.

The whole fabrication procedure is monitored by evaluating the surface wettability and morphology, and Figs. 1 and 2 show changes of the water contact angle and morphology at aluminium alloy surfaces after different treatment steps, respectively.

It can be found from Fig. 1 that the contact angles on the aluminium alloy surfaces change remarkably after each disposal step, demonstrating that the surface wettability varies gradually. In specific, the untreated aluminium alloy surface shows hydrophilic with a water contact angle of 45°, while the contact angle reduces to about 30° after the aluminium alloy surface is polished with sandpaper. The water contact angle increases to around 84° after the aluminium alloy is cleaned ultrasonically, and which may result from the following reason: there takes place the reaction between the aluminium alloy and methanol under ultrasonic. Consequently,