Development of stable superhydrophobic coatings on aluminum surface for corrosion-resistant, self-cleaning, and anti-icing applications

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ABSTRACT

Aluminum (Al) has been widely used in numerous applications, but it is prone to contamination or damage under harsh working environments. In this paper, a superhydrophobic coating (SHPC) on the Al surface was fabricated via a simple and cost effective method using anodization in sulfuric acid electrolyte followed by surface modification with inexpensive myristic acid. The as-prepared SHPC with hierarchical micro-nanostructure exhibited good superhydrophobicity with a static water contact angle (CA) of $155.2 \pm 0.5°$ and a sliding angle (SA) of $3.5 \pm 1.3°$. The SHPC possessed both good mechanical and chemical stabilities: it retained a CA as high as $151.1 \pm 0.1°$ after mechanical sandblasting for 60 s and was stable after dripping test using both acidic and alkaline solutions. Besides, after exposure to UV/water condensation cycles for 7 days, the coating remained superhydrophobic, indicating excellent weathering resistance. The prepared SHPC also demonstrated excellent self-cleaning and anti-icing performance. Ice adhesion strength as low as 0.065 ± 0.022 MPa was obtained for the optimized coating. Electrochemical measurement showed that there is a two-order of magnitude of reduction of the corrosion current density (J_{corr}) and the protection efficiency ($P\%$) of the as-prepared SHPC has reached up to 99.75%.

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1. Introduction

Aluminum (Al) and its alloys are important engineering materials owing to its abundance in nature, good ductility, low specific weight and excellent electrical conductivity. They have been widely used in many areas, especially in sports, aerospace, transportation and civilian industries. Al is known to develop a thin natural oxide layer in dry and non-salty environments, which could prevent itself from further corrosion. However, it is highly prone to corrosion in humid and salty environments [1], which will cause damage or malfunction of facilities and loss of esthetic values. Therefore, it is very important to form a surface layer on Al to protect it from a wide spectrum of mechanical and chemical attacks. One of the approaches is through transforming the hydrophilic nature of Al surface to be superhydrophobic.

Superhydrophobic surfaces with static water contact angles (CAs) higher than 150° and sliding angles (SAs) lower than 10° have attracted a great deal of interest in both scientific research and practical

applications because of their unique properties, including water repellency [2], self-cleaning [3,4], oil–water separation [5], anti-icing [6] and anti-corrosion [7]. The key to constructing superhydrophobic surface is to create a rough hierarchical micro-nanostructure on a low energy surface. In regards the broad applications of superhydrophobic surfaces in outdoor equipment, researchers have developed a great number of methods, including chemical etching [8], sol–gel [9], template [10], hydrothermal synthesis [11], electrospinning [12] and electrochemical processes [13].

Although there are numerous techniques to construct superhydrophobic surfaces, few products have been available for practical applications mainly due to their weak mechanical and poor chemical stabilities. It is important to note that most artificial superhydrophobic surfaces are easily damaged by even gentle physical rubbing, or finger scratching and so on. Besides, some superhydrophobic layers have weak adhesion with substrates, making it easy for them to be peeled off [14]. With respect to chemical stability, many superhydrophobic surfaces may lose their superhydrophobicity rapidly after exposure to harsh conditions, such as wet environment, strong acidic or alkali solutions. UV irradiation can accelerate their aging which leads to performance degradation and shortening of lifetime. To date, a variety of mechanically robust, chemically stable and UV resistant superhydrophobic surfaces have been reported. Wang et al. fabricated superhydrophobic sponges and fabrics with strong mechanical

robustness by in situ growth of transition-metal oxides and metallic nanocrystals [15]. Li et al. obtained superhydrophobic cotton fabrics with good abrasion and laundering stability through the repeated graft-on-graft strategy [16]. Wu et al. created mechanically robust superhydrophobic coatings on glass substrates and glass fiber reinforced epoxy composites using sol–gel method [17]. Lai et al. produced a transparent superhydrophobic TiO_2-based coating with good chemical stability on indium tin oxide (ITO) glass [18]. Pan et al. prepared good UV blocking superhydrophobic cotton fabric using sol–gel and self-assembly method [19]. Xiu et al. obtained inorganic superhydrophobic silica coating with improved UV stability via sol–gel processing [20]. However, these researches were mainly carried out on glass, fabric and sponge substrates. To the best of our knowledge, very few publications have been available on the investigation of mechanically and chemically stable [21], UV resistant superhydrophobic surfaces on Al surfaces.

Currently, a number of approaches have been reported to fabricate superhydrophobic surfaces on Al and its alloys with outstanding corrosion resistance. Zhang et al. prepared a hierarchical superhydrophobic film which provides an effective corrosion-resistant coating for the underlying Al on PAO/Al substrates [22]. Barkhudarov et al. created superhydrophobic films as corrosion inhibitors on Al surfaces from a precursor solution containing mixed alkoxides 3,3,3-trifluoropropyl-trimethoxysilane and tetramethyl orthosilicate via a variation of the aerogel thin film process [23]. Yin et al. produced a superhydrophobic coating on Al alloy for corrosion protection by chemical etching followed by surface modification [24]. However, the researchers mainly focused on the improvement of corrosion potential (E_{corr}) and decrease of corrosion current density (J_{corr}), they did not pay much attention to the protection efficiency (P%) of the SHPCs for Al substrates.

Ice is prone to accumulation on Al surfaces in tough freezing weather, which can cause serious accidents and economic losses [25]. It might be easy to correlate icephobicity with superhydrophobicity because it seems that the water repellence would be a common requirement for it. However, not all the superhydrophobic surfaces can display good anti-icing property on Al surfaces [26,27]. Besides, the durability of anti-icing property is an important consideration for any practical application. Kulinich et al. reported that superhydrophobic Al surfaces whose surface asperities were gradually damaged and even lost the superhydrophobicity during icing/de-icing cycles, showing that the anti-icing performance of the samples was significantly deteriorated [28,29]. So it is necessary to create SHPCs on Al surfaces which are endowed with excellent enduring anti-icing property.

For practical applications, the outdoor surfaces are usually polluted by contaminants and dusts. So far, although there have been lots of reports on producing self-cleaning SHPCs, little detailed research is available to quantify their self-cleaning efficiency. This can be done by the color contrast which is directly related to the amount of artificial dirt on the surface [30].

Summarizing the above analysis, it is very important to construct a stable and corrosion-resistant SHPC with excellent anti-icing property and self-cleaning effect on the Al surface for its wide applications. However, systematic work about all the properties together on the superhydrophobic Al surfaces has been rarely reported. Besides, most reported methods are still subjected to certain limited conditions involving low efficiency, complicated procedure and high cost of production [31,32]. In this work, a facile and low-cost method is used to construct SHPCs on Al surfaces. The fabrication process contains two steps: construction of rough hierarchical micro-nanostructure with nanotubes and chemical modification with inexpensive myristic acid. The as-prepared SHPC has a CA as high as $155.2 \pm 0.5°$ and a SA as low as $3.5 \pm 1.3°$. The mechanical and chemical stabilities of the SHPC have been evaluated by micro-sandblasting test and dripping test using solutions with different pH values. The SHPC also shows excellent weathering resistance and highly improved corrosion resistance after exposure to the UV/water condensation cycles for 7 days and

immersion in 3.5 wt.% NaCl solution. Furthermore, the low ice adhesion strength and dirt accumulation results demonstrate good anti-icing and self-cleaning performance of the as-prepared SHPC.

2. Experimental

2.1. Materials

The Al plates (purity: 99.9%, thickness: 0.05 mm) were purchased from Art Friend & Buona Vista Pte Ltd., Singapore. Myristic acid [$CH_3(CH_2)_{12}COOH$, purity: 95%], sodium hydroxide, nitric acid, sulfuric acid, hydrochloric acid and sodium chloride were supplied by Sigma-Aldrich, USA. Anhydrous ethanol was provided by EMD Millipore Corporation, Germany. In this experiment, all reagents were analytical grade and deionized (DI) water was used to prepare the aqueous solutions.

2.2. Sample preparation

First, the Al plates were mechanically polished using 1000 grid emery papers to remove the native oxide on the surfaces. Next, they were ultrasonically degreased in sequence using 5 wt.% NaOH and 5 wt.% HNO_3 solutions for 2 min, respectively, and DI water for 5 min before drying in air. A cleaned Al plate of 2.5 cm × 2.5 cm size as the anode and two lead (Pb) plates as the double cathodes were separated by a distance of 2.5 cm in a 15 wt.% H_2SO_4 electrolyte solution. The anodic oxidation was carried out with vigorously magnetic stirring under different voltages from 10 V to 22 V for 1 h. During the process, the temperature was kept at 25 °C using a water bath. After the anodization, the samples were thoroughly rinsed and ultrasonically cleaned with DI water and then dried. And then, the samples were modified with molten myristic acid at 70 °C for 30 min followed by immersing into anhydrous ethanol for 2 min and ultrasonically treated in DI water for 5 min to remove the excessive acid. Finally, the sample was heated at 80 °C for 1 h in the oven. The samples with myristic acid modification were denoted as MA-x and the anodized Al samples without surface modification used as reference were denoted as AAO-x, where x represents the value of anodization voltage. The schematic fabrication process is shown in Fig. 1.

2.3. Sample characterization

The CA and SA were measured with a contact angle measurement device (OCA20, DataPhysics Corporation, Germany). All samples were measured five times on different positions with 4 μL water droplets at ambient temperature. The surface morphology and chemical composition were characterized by a field emission scanning electron microscope (FESEM, JEOL JSM-6340F, Japan). The surface roughness was measured by an atomic force microscope (AFM, Asylum Research Cipher S, Oxford Instruments Company, USA) with a scan size of 10 μm × 10 μm. The mechanical stability of the obtained samples was evaluated using a home-designed micro-sandblaster tester. The chemical stability was analyzed by dripping water with different pH values on the surface for 5 s. The pH was adjusted by different amount of HCl or NaOH.

The weathering resistance was tested by a UV/Condensation weathering instrument (ATLAS material testing technology LLC, USA) according to ASTM G154-12a for 7 days. The procedure contains UV exposure for 4 h and water spray and condensation for 4 h sequently. During the UV process, eight UV lamps (295–400 nm) with power intensity of 0.77 W/m² each were used.

The electrochemical corrosion measurement was performed in 3.5 wt.% NaCl solution (pH = 6.0) at ambient temperature using an electrochemical workstation (CHI 750C, Shanghai Chenhua Instrument Corporation). The sample with an exposed area of 1 cm² was used as the working electrode (WE). The saturated calomel electrode (SCE)