



Fabrication of superhydrophobic surface with improved corrosion inhibition on 6061 aluminum alloy substrate

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ABSTRACT

This work has developed a simple and low-cost method to render 6061 aluminum alloy surface superhydrophobicity and excellent corrosion inhibition. The superhydrophobic aluminum alloy surface has been fabricated by hydrochloric acid etching, potassium permanganate passivation and fluoroalkyl-silane modification. Meanwhile, the effect of the etching and passivation time on the wettability and corrosion inhibition of the fabricated surface has also been investigated. Results show that with the etching time of 6 min and passivation time of 180 min the fabricated micro/nano-scale terrace-like hierarchical structures accompanying with the nanoscale coral-like network bulge structures after being modified can result in superhydrophobicity with a water contact angle (CA) of 155.7°. Moreover, an extremely weak adhesive force to droplets as well as an outstanding self-cleaning behavior of the superhydrophobic surface has also been proved. Finally, corrosion inhibition in seawater of the as-prepared aluminum alloy surface is characterized by potentiodynamic polarization curves and electrochemical impedance spectroscopy. Evidently, the fabricated superhydrophobic surface attained an improved corrosion inhibition efficiency of 83.37% compared with the traditional two-step processing consisting of etching and modification, which will extend the further applications of aluminum alloy especially in marine engineering fields.

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1. Introduction

As is well-known, aluminum and its alloys are irreplaceable engineering materials owing to their easy accessibility, excellent machinability, high fatigue strength and low price. Accordingly, they have achieved extensive industrial applications, especially in the fields of shipbuilding, oceanography engineering, aerospace and machine manufacturing [1,2]. Nevertheless, aluminum and its alloys are more vulnerable to penetrating and peeling corrosion destruction of the naturally formed protective oxide film in

wet environment and the water containing chloride ions [3,4]. Consequently, their lifespan and application fields are severely restricted. As yet, corrosive inhibition coatings can be introduced to slow down corrosion rate of aluminum and its alloys, such as brush-plating coating [5,6], electroplating coating [7,8] and magnetron sputtering ion coating [9,10]. Among these protective coatings, however, some are environment polluting, costly and hard to control. For this reason, the way to develop a simple and low-cost corrosion inhibition method of aluminum and its alloys has gained growing popularity among researchers.

In recent years, inspired by the water repelling behavior of lotus leaf, fabricating the superhydrophobic coating on aluminum and its alloys surfaces can provide a promising method to inhibit corrosion by isolating the contact with corrosive medium. Generally, the superhydrophobic surface with a CA larger than 150° and low adhesive force to droplets can be prepared by two steps. The first is to fabricate micro/nano-scale rough structures and then introduce the modified superhydrophobic coating [11–13]. In our previous research, we have fabricated some simple, low-cost

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and environment-friendly superhydrophobic surfaces by preparation of some hierarchical micro/nano-scale structures and surface modification, which exhibited a composite surface-air-water contacting interface with excellent repelling water medium behavior [14,15].

The traditional two-step processing to make superhydrophobic aluminum and its alloys surfaces including an etching processing and then modification has made gratifying achievements [16–19]. For example, Escobar et al. have fabricated the superhydrophobic aluminum surface via ethanol solution of hydrochloric acid etching and lauric acid modification [20]. Feng et al. have fabricated superhydrophobic LD6063 aluminum alloy surface via boiling water etching and stearic acid modification [21]. Ji et al. have fabricated a hierarchical superhydrophobic and superoleophobic A1100 aluminum surface with a good repelling property to diiodomethane, hexadecane and water through hydrochloric acid etching and a vapor deposition silanization coating [22]. However, few works were mentioned about corrosion inhibition behavior of the fabricated surfaces in seawater despite of their superhydrophobicity.

Surface passivation processing can change substrate surface activity and turn the electrode potential to a positive direction, which can reduce the dissolution rate and corrosion rate. Hence in this paper, by using a simple and low-cost etching, passivation and modification processing, we have fabricated a more superhydrophobic 6061 aluminum alloy surface with enhanced corrosion resistance in seawater compared with traditional two-step processing. To begin with, the etching and passivation time has been optimized to obtain the superhydrophobic micro/nano-scale rough structures. Moreover, after the micro/nano-scale rough structures being silanized, the superhydrophobic surface with excellent self-cleaning effect can be controlled. Finally, the electrochemical tests have been conducted to investigate corrosion inhibition of the fabricated superhydrophobic 6061 aluminum alloy surface.

2. Materials and methods

2.1. Materials

Aluminum alloy sheet (6061, commercially available engineering materials) with the main compositions of 96.1 wt% aluminum, 1.2 wt% magnesium and 0.8 wt% silicon was from Shanghai Haocheng Metal Co., Ltd., China. Trichloro (1H,1H,2H,2H-heptadecafluorodecyl) silane (>96%) was purchased from Tokyo Chemical Industry Co., Ltd., Japan. The other experimental chemicals used with an analytical grade were purchased from Shanghai Chemical Reagent Co., Ltd., China.

2.2. Procedures

Aluminum alloy sheets in size of 10 mm × 10 mm × 1 mm were first polished manually with #600, #1000 and #1200 metallographic abrasive paper in sequence and cleaned with deionized (DI) water and ethanol in ultrasonic bath. Secondly, after being dried with high purity following N₂, aluminum alloy sheets were etched at room temperature in 4 M hydrochloric acid solution for 1, 2, 3, 4, 5, 6, 7 and 8 min, respectively. After etching processing, the sheets were immediately ultrasonically rinsed with DI water. Thirdly, aluminum alloy sheets needed for passivated processing were immersed in 0.1 M potassium permanganate solution for 60, 120, 180 and 240 min, respectively. Finally, aluminum alloy sheets were modified by immersing in the ethanol solution of 20 mM trichloro (1H,1H,2H,2H-heptadecafluorodecyl) silane for more than 10 h and then dried in an oven at 100 °C for 2 h before further testing.

2.3. Characterization

CA was measured with 4 μL of distilled pure droplets at ambient temperature by using an OCA20 system equipped with a CCD camera and SCA 20 software (Dataphysics GmbH, Germany). Average CA for each sample was measured repeatedly for five times. Microstructures of the fabricated surface were observed via an Environmental Scanning Electron Microscopy (FESEM, FEI Quanta 200 FEG, America). Element composition was analyzed by Oxford Instruments Inca X-Max energy dispersive X-ray spectrometer (EDX). Potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) of electrochemical tests were obtained via an electrochemical workstation (CHI660D, Chen Hua Instrument Co., Ltd., China) in 3.2 wt% sterile seawater, which must be boiled for 30 min in advance. The experiment was conducted in a standard three-electrode system with the treated 6061 aluminum alloy sheet (exposing area of 1 cm²) as a working electrode, the Pt net as a counter electrode and the saturated calomel electrode (potential of +241 mV versus NHE at 25 °C) as a reference electrode. The potential was taken between –1600 and –400 mV versus SCE at a scan rate of 1 mV s⁻¹ in the potentiodynamic polarization measurements. EIS was tested in the frequency range between 10 mHz and 100 kHz with a sine-wave amplitude of 10 mV under open circuit conditions. Before electrochemical tests, 30 min of immersion time was given to ensure the steady state. All the electrochemical tests were repeated for three times to achieve a suitable repeatability.

In this paper, samples with different processing were labeled as follows: “E” referred to an etching processing in 4 M hydrochloric acid solution and the following figure was the etching time (in minutes), “P” referred to a passivation processing in 0.1 M potassium permanganate solution and the following figure was the passivation time (in minutes), and “M” referred to a modification processing in the ethanol solution of 20 mM trichloro (1H,1H,2H,2H-heptadecafluorodecyl) silane for 12 h. For example, E6P180M meant that the 6061 aluminum alloy sample was etched for 6 min at first, then passivated for 180 min, at last modified.

3. Results and discussion

3.1. Fabrication of superhydrophobic surface

The surface morphology, wettability and thickness of 6061 aluminum alloy substrates after being successively polished with P600, P1000 and P1200 metallographic abrasive paper and then etched in hydrochloric acid solution for different time was investigated in Fig. 1. All the data averaged after measured five times at different positions of samples at ambient temperature. Fig. 1a exhibited a relatively flat polished surface combining with some scratch defects in a fixed direction just as the yellow arrows showed. Meanwhile, the polished sample achieved an average CA of 108° and a thickness of 1 mm after modification. Fig. 1b–f revealed the surface morphology with the etching time of 1, 2, 3, 4 and 5 min, respectively. Obviously, a growing number of etching pits with micro/nano-scale terrace-like hierarchical structures became increasingly large on aluminum alloy substrates with the etching time prolonging, which led to the increasingly rough etching surfaces. Moreover, CA of the above five samples respectively increased to 114.4°, 120.8°, 127°, 133° and 143.6° after being modified, which all demonstrated the hydrophobic surfaces. However, the thickness still maintained at about 1 mm for all these samples. With the etching time extending to 6 min, the already formed etching pits interconnected all over the surface, as shown in Fig. 1g. Besides, it had presented a superhydrophobic surface with the maximal CA of 153.5° but a falling ratio of thickness by 10%.

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