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Micro-nano textured superhydrophobic 5083 aluminum alloy as a barrier against marine corrosion and sulfate-reducing bacteria adhesion

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ABSTRACT

Corrosion attack and undesired bio-adhesion are thorny issues threatening and restricting the service performance and security of the widely used structural 5083 aluminum alloys (AA5083) materials in maritime fields. In this paper, we employed a facile ammonia etching approach followed by 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (PFDTES) modification to fabricate micro-nano textured superhydrophobic AA5083 surface as an effective layer for corrosion inhibition and bio-adhesion suppression. The dual-scale surface morphology and roughness were revealed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) were employed to depict the chemical components of the micro-nano textured AA5083 surface. X-ray photoelectron spectroscopy (XPS) was employed to confirm the presence of functional groups of fluorinated carbon with low surface energy. The self-cleaning ability and corrosion resistance of the fabricated surfaces were investigated, suggesting an excellent water-proofing and anti-corrosion performance. Moreover, sulfate-reducing bacteria (SRB) was chosen as a typical bacteria to evaluate and demonstrate the anti-adhesion property of the as-fabricated superhydrophobic AA5083 surface. The present study therefore demonstrates that achieving superhydrophobicity on AA5083 substrate is expected to possess quite potential applications in marine corrosion and bio-fouling fields.

1. Introduction

Given the excellent comprehensive physical and mechanical properties, 5083 aluminum alloys (AA5083) are expected to be structural materials for oceanographic ships, coastal constructions, warships and offshore platforms etc. However, AA5083 show high susceptibility to localized corrosion attack when exposed to marine chloride environments [1,2], restricting their large-scale marine applications. What is worse, the undesired marine bio-fouling, *viz*. the bio-adhesion, deposits and growth of marine organisms such as microorganisms, barnacles and seaweeds on submerged surfaces, is a globally ubiquitous problem of maritime industries [3-6]. As a consequence, marine corrosion and bio-fouling seriously threaten the service performance and security of structural AA5083 materials.

Recent years, nature-inspired [7–11] biomimetic superhydrophobic surface arouses tremendous attention due to its potential applications such as self-cleaning [12,13], oil-water separation [14–16], drag reduction [17,18], water collection [19,20], anti-icing/frosting [21,22] etc. And more importantly, owing to the typical Cassie contacts and fascinating water repellence properties, metallic superhydrophobic surfaces are viewed as one of the most promising protective materials against marine corrosion attack. Heretofore, some artificial superhydrophobic surfaces have been developed to enhance the corrosion resistance of various metallic or alloy substrates, such as copper [23], zinc [24], aluminum [25], carbon steel [26], Mg alloys [27] etc. For instance, Wan et al. [28] fabricated superhydrophobic surface on copper substrate and demonstrated the superior corrosion resistance and long-term stability. Li et al. [29] prepared superhydrophobic

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AZ61 Mg surface with peony-like microstructures and presented a significantly decreasing of the corrosion current density. Karthik et al. [30] reported the fabrication and anticorrosive performance of superhydrophobic aluminum surface, presenting a remarkable improvement of charge transfer resistance with 2 orders of magnitude higher than pristine substrate. According to the relevant literatures, it is believed that the transformation from hydrophilic to superhydrophobic on aluminum substrates are expected to be a promising strategy towards marine corrosion inhibition and bio-fouling suppression.

To date, the achieving of superhydrophobicity on aluminum alloy substrates have not received due attention. In view of the key role of aluminum alloys in marine environmental applications, it is highly desirable and necessary to impart excellent corrosion resistant and anti-bioadhesion ability to aluminum alloys. Nevertheless, there are quite limited reports about the design and fabrication of superhydrophobic surface on aluminum alloy substrates up to now, especially the extensively used AA5083. Furthermore, there has no reports about the detailed investigation of superhydrophobic AA5083 surface for corrosion protection and bio-adhesion control.

Thus, in this paper, facile etching-textured superhydrophobic AA5083 with micro-nano hierarchical structure was fabricated through ammonia etching and 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (PFDTES) modification. The surface morphologies, chemical compositions and wettability behavior of sanded AA5083 and superhydrophobic AA5083 were investigated. The corrosion resistance was evaluated and analyzed by electrochemical impedance spectra. In addition, as an extensively marine existed microorganisms, sulfate-reducing bacteria (SRB) was chosen as a typical bacteria to evaluate the anti-bioadhesion performance of the as-fabricated superhydrophobic AA5083. This research work demonstrates the micro-nano textured superhydrophobic AA5083 surface can be employed as an effective barrier toward marine corrosion inhibition and SRB-adhesion suppression.

2. Experimental section

2.1. Materials and reagents

5083 Aluminum alloy (AA5083, Composition: 4.0∼4.9% Mg, 0.4∼1.0% Mn, 0.4% Si, 0.1% Cu, 0.25% Zn, 0.15% Ti, 0.05–0.25% Cr, 0.1–0.4% Fe and the balance is Al) with 0.3 mm thickness was used as substrates. 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (PFDTES, $C_{16}F_{17}H_{19}O_3Si$, 96%) was purchased from Shanghai Macklin Biochemical Co., Ltd. DAPI solution (10 μg/mL) was bought from Beijing Solarbio Science & Technology Co., Ltd. All other reagents (anhydrous ethanol, ammonia water, glutaraldehyde solution etc.) are purchased from Sinopharm Chemical Regeant Co., Ltd. with analytical grade and utilized as received. The deionized water with 18.0 MΩ·cm resistivity was employed during the whole experiments.

2.2. Fabrication of superhydrophobic AA5083

AA5083 specimen was firstly sanded with SiC paper (200, 400, 800, 1200, 2000 grade) successively. Then the substrate was ultrasonically cleaned in anhydrous alcohol and deionized water for 10 min respectively. The cleaned specimen was then promptly transferred into a 100 mL Teflon-lined hydrothermal reactor with 2 vol.% aqueous solution of ammonia and heated at 90 °C for 5 h. After the reaction, the sample was taken out and rinsed thoroughly using anhydrous alcohol. Then the specimen was immersed in 1 vol.% PFDTES/anhydrous alcohol solution for 10 min, followed by heating in drying oven for 10 min under 120 °C.

2.3. Characterizations

The surface topographies were recorded using field-emission scanning electron microscopy (FE-SEM, Hitachi S-3400 N, Japan) equipped with an energy dispersive spectroscopy (EDS) under a vacuum environment at 15 kV. The roughness and 3D images of the sanded AA5083 and superhydrophobic AA5083 surfaces were determined through an atomic force microscopy (AFM, Multimode 8 Bruker, Germany).

Water contact angle (WCA) measurements about superhydrophobic AA5083 surface was determined by Dataphysics OCA25 (Germany) at room temperature. In typical process, a 4 uL water droplet was carefully placed upon the as-prepared superhydrophobic surface. The CA value was the average of five different positions. The X-ray diffraction (XRD) pattern of micro-nano textured AA5083 surface was recorded with an Ultima IV diffractometer (Rigaku, Japan) with the 2θ ranging from 10° to 80° X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) was employed at a chamber pressure below 10^{-8} Torr to reveal the chemical components of the superhydrophobic AA5083 surface. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

2.4. Electrochemical experiments

The electrochemical experiments were carried out by immersing the specimens in a 3.5 wt.% NaCl aqueous solution using Zennium Pro (Zahner, Germany). In a typical process, a standard three-electrode system was used to perform the electrochemical tests equipped with an Ag/AgCl reference electrode, a platinum mesh as the counter electrode and the specimens as the working electrode. The electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential (OCP) in the frequency range of 10^5 Hz to 10^{-2} Hz. Before every electrochemical test, the samples (with 1 cm^2 area exposure) were immersed in solution for more than 60 min to stabilize. The EIS results were analyzed through fitting data *via* ZsimpWin software.

2.5. Sulfate-reducing bacteria (SRB) cultivation and bioadhesion tests

The SRB seed was isolated from marine sludge (Bohai Sea, China). The purified seawater employed in this experiment was collected from Huiquan Bay (Qingdao, China). In a typical cultivation process, SRB cultures were inoculated in sterile Postgate's culture (PGC) medium with a pH = 7 (adjusted by 0.05 M sodium hydroxide). The medium contains 0.5 g dipotassium hydrogen phosphate, 1.0 g ammonium chloride, 0.06 g calcium chloride, 0.06 g magnesium sulphate, 0.3 g sodium citrate, 1.0 g yeast extract, and 6 mL sodium lactate (70%) in 1 L aged seawater. The as-prepared solution was degassed by purging with high-purity nitrogen and then autoclaved at 121 °C for 20 min. After cooling, the culture solution was inoculated with bacteria at room temperature. The SRB culture was then sealed and stored in sterilized glass bottles at 30 °C in a temperature incubator.

The sterilized (ultraviolet radiation, 30 min) sanded AA5083 and superhydrophobic AA5083 specimens were vertically suspended into the 3-day-old culture medium for a certain period of time. After the bioadhesion tests, the samples were taken out gently and treated with sterilized 5% glutaraldehyde/PBS for 30 min. Then, the specimens were stained with acridine orange solution (AO, 10 μg/mL). After the staining, the SRB adhesion was observed under a fluorescence microscopy (Olympus BX-51). The SRB coverage of different samples were analyzed using software ImageJ.