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Preparation of multifunctional Al-Mg alloy surface with hierarchical micro/nanostructures by selective chemical etching processes

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ABSTRACT

A superamphiphobic aluminum magnesium alloy surface with enhanced anticorrosion behavior has been prepared in this work via a simple and low-cost method. By successively polishing, etching and boiling treatments, the multifunctional hierarchical binary structures composed of the labyrinth-like concave-convex microstructures and twisty nanoflakes have been prepared. Results indicate that a superhydrophobic contact angle of 160.5° and superoleophobic contact angle larger than 150° as well as low adhesive property to liquids are achieved after such structures being modified with fluoroalkyl-silane. Furthermore, the anticorrosion behaviors in seawater of as-prepared samples are characterized by electrochemical tests including the impedance spectroscopies, equivalent circuits fittings and polarization curves. It is found that the hierarchical micro/nanostructures accompanying with the modified coating are proved to possess the maximal coating coverage rate of 90.0% larger than microstructures of 85.9%, nanostructures of 83.8% and bare polished surface of 67.1% suggesting the optimal anticorrosion. Finally, a great potential application in concentrators for surface-enhanced Raman scattering (SERS) analysis of toxic and pollutive ions on the superamphiphobic surface is also confirmed. This work has wider significance in extending further applications of alloys in engineering and environmental detecting fields.

1. Introduction

Recent years have seen a gradually increased application of Aluminum magnesium alloys (Al-Mg alloys) in engineering fields due to their excellent physical, chemical and mechanical properties of bright color, high specific intensity, good workability, corrosion resistance, no low temperature brittleness and magnetism, high electrical and thermal conductivity [1–5]. Especially in shipbuilding and marine engineering fields, Al-Mg alloys are widely used for structural parts, shell structures, welding structures, pressure vessels and transport pan cans [6,7]. The reactive Cl^- abundant in seawater, however, can preferential adsorb and destroy the protective coatings on alloys surfaces leading to the pitting corrosion failure [8,9]. As a result, the application range as well as working life of this typical engineering material are seriously challenged.

The study for protecting Al-Mg alloys from corrosion in seawater is significant. Currently, the methods of protective coatings [10], surface oxidizations [11,12], mechanical alloyings [13–15], aged-hardening heat treatments [4,8] and corrosion inhibitors [16,17] have been adopted to improve their anticorrosion behaviors. Besides, Rasouli et al. have applied the friction stir processing to render AA5083 Al-Mg alloy an improved anticorrosion behavior [18]. Zazi et al. have fabricated a 5083-H321 Al-Mg alloy with a good repelling property to seawater through thermomechanical treatments [19]. Trdan et al. have investigated the effect of laser shock peening on the dislocation transitions, grain refinement as well as corrosion resistance of Al-Mg alloys [20]. Among these methods, however, electroplating with heavy metal ions is environmentally polluting. The micro-arc oxidation is under high voltage and strong current posing a potential safety risk. Samples are easily oxidized in mechanical alloying and the ball mill parts can cause samples pollution to some extent. While for laser engineering, it may be costly and uncontrollable. Hence, developing a simple and low-cost anticorrosion method for Al-Mg alloys is still a big challenge.

Recent years have seen some surface coating techniques of organic/inorganic hybrid nanocomposite membranes [21], conductive polyaniline anticorrosion coatings [22], chemical conversion coatings [23], superhydrophobic membranes [24] and self-assembled monomolecular films [25], among which the superhydrophobic surfaces with unique wettability can provide a promising method to repel corrosive mediums. Inspired by butterfly wings and rose petals with perfect wettability in nature, the

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preparation of micro/nanostructures and low surface energy coatings can achieve desired wettability on substrates surfaces. As far, various physical methods including high speed wire electrical discharge machining [26], electrospinning [27], laser machining [28] et al. and chemical methods including anodic oxidation [29], sol-gel [30], electrochemical etching [31], hydrothermal synthesis [32] and hybrid organic-inorganic coatings [33] et al. have been applied to prepare superior wetting aluminum alloys surfaces. However, the anticorrosion behaviors on such surfaces in seawater and oily corrosive mediums are seldom mentioned in above works. Even some works have reported the anticorrosion properties, but markedly decreased corrosion rates of substrates cannot be found.

In this work, a low-cost and simple method is developed to make Al-Mg alloys surfaces not merely superhydrophobicity but also superoleophobicity. The hierarchical binary structures with labyrinth-like tridimensional microstructures and twisty nanoflakes are firstly obtained by successively polishing, etching and boiling treatments. After fluoroalkyl-silane modification of the as-prepared surfaces, the superamphiphobicity is finally achieved. Moreover, the improved anticorrosion behaviors of the fabricated surfaces in seawater are electrochemically assessed. Finally, the fabricated surfaces are also proved to possess a great potential application in concentrators for SERS analysis of toxic and pollutive ions.

2. Experimental section

2.1. Materials

Experimental Al-Mg alloys plates (10 mm× 10 mm× 2 mm) with 95.7 wt% Al and 3.1 wt% Mg were used. 1H,1H,2H,2H-Perfluorodecyltrichlorosilane was purchased from Shanghai Aladdin Biological Technology Co., Ltd., China. Deionized water was obtained from a Millipore water purification system (MilliQ, specific resistivity of 18.25 MΩ.cm, S.A., Molsheim, France). Other chemicals reagents were of analytical grades from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Procedures

Al-Mg alloys plates were firstly ultrasonic cleaned with deionized water, acetone and ethanol after being successively polished with W40, W20, W10 and W3.5 abrasive papers (labeled as "**P**" processing). Then, the etching processing (labeled as "**E**" processing) was conducted by immersing the cleaned plates into 4 M hydrochloric acid solution for 18 min. After that, samples must be immediately cleaned with deionized water and then dried with high purity nitrogen. Thirdly, the boiling processing (labeled as "**B**" processing) was proceeded by putting the etched samples into boiling deionized water for 60 s and then dried with nitrogen. Finally, the fluoroalkyl-silane modification processing (labeled as "**F**" processing) was carried out by immersing the as-prepared samples into the ethanol solution of 20 mM 1H,1H,2H,2H-Perfluorodecyltrichlorosilane for 12 h and then heated at 100 °C for 2 h. All the processings were conducted at room temperature (about 5 °C, winter of Central China)

2.3. Characterization

The Field Emission Scanning Electron Microscope (FESEM, Ultra Plus-43-13) equipped with an energy dispersive X-ray spectrometer (EDX) were used to characterize the morphologies and compositions of the prepared Al-Mg alloys surfaces. An OCA20 system (Dataphysics GmbH, Germany) was employed to measure the static contact angle (θ_c) of a droplet (5 μL). And also the θ_c value for each surface was calculated by averaging the repeat tests for ten times. The Fourier-transform Infrared Spectrophotometer (FTIR, JASCO, Japan) was used to characterize the chemical composition of the modified surface. A three-dimensional noncontact surface profiler (NanoView-E1000, Korea) was used to characterize morphologic images and roughness of prepared surfaces. The electrochemical workstation (CHI660D, Shanghai Chen Hua Instrument Co., Ltd., China) was applied to conduct the electrochemical measurements of electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves in 3.5 wt% seawater. A standard three-electrode system including a Pt net counter electrode, a saturated calomel reference electrode and a working electrode of the treated sheet with exposing area of 1 cm^2 in seawater was applied in the electrochemical tests. SERS tests were conducted via a confocal microprobe Raman system (LabRam HR800) using a laser (632.85 nm) and an objective lens (50×, numerical aperture of 0.5).

3. Results and discussion

3.1. Preparation of superamphiphobic surface

FESEM images of the Al-Mg alloys surfaces processed with different steps are exhibited in Fig. 1. The morphologies with different magnifications of the bare polished surface are shown in Fig. 1a, which depicts a relatively smooth surface. However, different surface structures with equally distributed twisty flakes with ridge size of about 100 nm accompanying with some porous structures are clearly observed after the polished sample being immersed into boiling deionized water for 60 s, as shown in Fig. 1b. Actually, the substrate surface can react chemically with water under boiling conditions to generate $Al_2O_3{\cdot}xH_2O$ ($Al + H_2O \rightarrow A1_2O_3{\cdot}xH_2O + H_2\uparrow$), which further reacts with water leading to the formation of boehmite crystals. Meanwhile, hydrogen and bubbles can physically attack the dissolvable boehmite as well as substrate surface resulting in the development of rough nanoflakes and caverns. Fig. 1c shows the surface morphologies with different magnifications of the polished sample after being immersed into HCl solution for 18 min. Obviously, the roughly hierarchical labyrinth-like convex/concave structures with the ridge size of about 2 μm is attained. As a common crystal metal, Al-Mg alloys inherently contain many high-energy dislocations and line defects, which can be preferentially attacked and dissolved in etchant than any other sites. The hierarchical microstructures can just gradually form on substrate surface due to the above selective etching effect. Different from the above angular etching structures in Fig. 1c, the labyrinth-like convex/concave microstructures covered with the twisty nanoflakes are finally achieved with the further immersing treatment in boiling deionized water for 60 s, as depicted in Fig. 1d. These typical binary hierarchical micro/nanostructures will present a great perspective in superamphiphobicity realization on Al-Mg alloys surfaces.

Generally, alkylsilane modification on a surface is an effective method to prepare low surface energy coating for an enhanced surface wettability. Herein, the Al-Mg alloys surfaces with different treatments have been modified with fluoroalkyl-silane and also the corresponding wettability have been characterized by θ_c values (5 μL), as shown in Fig. 2. Clearly, θ_c changes significantly with various processing steps suggesting different wettabilities. The bare surface only with polished (P) treatment exhibits hydrophilicity with a θ_c of about 32.6°. After modification treatment of the polished sample (P-F), a largely increased θ_c of about 101.9° is observed. By contrasting the θ_c values on Al-Mg alloys surfaces processed with P-E-F (149.6°), P-B-F (129.5°) and P-E-B-F steps (160.5° along with a low sliding angle of 5.1°), it is found that the binary hierarchical micro/nanostructures can gain the optimal surface wettability, followed by microstructures, and finally nanos-