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Fabrication of the Superhydrophobic Surface on Magnesium Alloy and Its Corrosion Resistance

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The superhydrophobic surface was fabricated on the AZ31 alloy by the combination of the hydrothermal treatment method and post modification with stearic acid. The superhydrophobic surface showed a static water contact angle of 157.6°. The characteristics of the coatings were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The corrosion resistance of the superhydrophobic coatings was investigated by potentiodynamic polarization test and electrochemical impedance spectroscopy (EIS). The results revealed that the superhydrophobic coatings, characterized by petal-like structure significantly improved the corrosion resistance of the AZ31 alloy.

1. Introduction

Magnesium alloys are prime candidates for applications in the automotive, electronics and biomedical fields. However, magnesium alloys possess a lower corrosion resistance, hence restricting their use on a larger scale. Therefore, an improvement in corrosion resistance is of critical importance for magnesium alloys.

Up to now, numerous surface treatments have been adopted to enhance the corrosion resistance of magnesium alloys, including chemical conversion coatings[1–3], polymer coatings[4,5], microarc oxidation (MAO)[6,7], and silane coatings[8]. Among the above mentioned methods, some preparations are subject to special equipments or techniques, severe processing conditions, and even require toxic reagent. Therefore, it is imperative to introduce a sufficient corrosion protection strategy, maximizing the utility of magnesium and its alloys by means of a simple, facile, and chromium-free method.

Recently, due to the remarkable feature, such as self-cleaning, antibiofouling and anticorrosion, superhydrophobic surface has been proposed as corrosion resistance film[9–11]. Thus far, many methods have been developed to fabricate superhydrophobic surface such as electroless plating[12], chemical vapor deposition[13–15], anodic oxidation[16], electroless galvanic deposition[17], sol-gel processing[18–21], electrospinning[22,23], solution-immersion process[24–26], chemical etching[27–29], and self-assembly technique[30]. However, some methods may pollute the environment because of the use of strong acids[31]. In addition, some reagents used are expensive and the process is complex[32]. Therefore, a highly low-cost, environmentally-friendly method to fabricate the superhydrophobic surfaces is needed.

In this work, we tried to fabricate the superhydrophobic surface on magnesium alloy substrate to improve the corrosion resistance via a combination of a simple hydrothermal treatment method and post-modification with stearic acid (SA) in dimethyl formamide (DMF)/water mixture. SA is an endogenous long-chain saturated fatty acid and is nontoxic and biocompatible[33,34]. A hydroxide layer with a hierarchical structure was first obtained on the AZ31 substrate by the hydrothermal treatment process. The massive hydroxyl groups on the hydroxide layer make it easier for SA modification. The results showed that the obtained superhydrophobic properties of the hybrid coating are due to the synergistic action of the rough morphology and the hydrophobic groups. Furthermore, the improvement in corrosion resistance of magnesium alloys is notable and it provides the possibility of use in many industrial applications.

2. Experimental

2.1. Pretreatment of AZ31 alloys

AZ31 magnesium alloy was used for this study. The substrate surface was grinded with SiC papers up to 2000 grit to ensure the

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same surface roughness. The substrate surfaces were then ultrasonically cleaned in ethyl alcohol and dried under a steam of air.

2.2. Preparation of the superhydrophobic coating on AZ31 alloys

The superhydrophobic coatings were prepared on the AZ31 alloy by a two-step process. Firstly, the coating of $Mg(OH)_2$ was synthesized on the AZ31 alloy by the hydrothermal treatment method with 5.66 wt% NaOH solution as the mineralizer. The substrates were held in the Teflon-lined autoclave for hydrothermal treatment at 120 °C for 8 h to form $Mg(OH)_2$ layer. Subsequently, the AZ31 samples with $Mg(OH)_2$ coatings were modified with SA ($CH_3(CH_2)_{16}COOH$) in a DMF/water mixture containing 0.01 mol/L SA at 99 °C for 0.5 h to form an organic coating. The volume ratio of DMF to water was 1:1. The substrates were finally rinsed with ethyl ethanol, and dried at room temperature for further characterization.

2.3. Surface characterization

The surface morphology, chemical composition and thickness of the coatings were observed using a field-emission scanning electronic microscope (FE-SEM, Hitachi S-4800). All of the samples for the SEM observation were sputtered with gold. The structures of the coatings were examined using an X-ray diffractometer (D/Max 2500PC) with a Cu target ($\lambda = 0.154$ nm). The obtained coatings were also probed using Fourier transform infrared spectroscopy (FT-IR, Nicolet iN10 MX) in the wavenumber range from 4000 to 700 cm^{-1} at room temperature. The water contact angle was measured using a JC2000C1 contact angle goniometer. The volume of water drops was 2 μL. Potentiodynamic polarization curves and electrochemical impedance spectra (EIS) were obtained in a cell with 3.5 wt% NaCl solution using a Princeton potentiostat (model 2273). A classical three-electrode system was used with the sample as the working electrode (1 cm^2), a saturated calomel electrode (SCE) as the reference electrode, and a platinum plate as the counter electrode. The samples were immersed in the medium for 20 min before the electrochemical tests. The polarization curves were recorded with a sweep rate of 2 mV/s. EIS measurements were acquired from 100 kHz down to 10 mHz using a 5 mV amplitude perturbation.

3. Results and Discussion

3.1. Structure and composition of the superhydrophobic surface

Surface micrographs of the samples after hydrothermal treatment for 8 h are shown in Fig. 1. As can be seen, the surface of the coating is made up of particles with porous nanostructure, which is composed of erect flakes. The erect flakes are the product of the hydrothermal treatment, which are the magnesium hydroxide flakes. The magnesium hydroxide flakes are about 50–80 nm in diameter; closely gather together while some larger flakes attach to the surface. The cross sectional view indicated that the coatings are dense, uniform, and have close association with the AZ31 substrate and cover completely the magnesium alloy substrate. The thickness of the coating of about 23.5 μm was calculated by taking the average of thickness of five places in the microgram. The reaction is listed in Reactions (1–5). Under high temperature and high pressure condition, the increased hydrogen production led to the increase of system pressure, which increased the degree of ionization of water. The AZ31 alloys will produce Mg^{2+}, which will react with OH^- coming from NaOH solution, and finally magnesium hydroxide was obtained on the surface of the AZ31 substrate.

$$H_2O_{(l)} \rightarrow H^+{}_{(aq)} + OH^-{}_{(aq)} \quad (1)$$

$$NaOH_{(l)} \rightarrow Na^+{}_{(aq)} + OH^-{}_{(aq)} \quad (2)$$

$$Mg_{(s)} \rightarrow Mg^{2+}{}_{(aq)} + 2e \quad (3)$$

$$2H^+{}_{(aq)} + 2e \rightarrow H_{2(g)} \quad (4)$$

$$Mg^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Mg(OH)_{2(s)} \quad (5)$$

Fig. 2 shows the micrographs of the magnesium alloy surface further treated with SA. It is obvious that the morphology of the surface was drastically changed as compared to the micrographs of the magnesium alloy treated only with NaOH solution in Fig. 1, and many petal-like clusters are present at the porous and rough magnesium hydroxides surface; the flakes of magnesium hydroxides were completely covered. The thickness of the SA coating was about 11 μm.

Fig. 3 displays the photographs of water droplets of 2 μL on the coated samples. As can be seen, the surface of the bare magnesium alloy is hydrophilic and the contact angle is about 90.5°. Due to capillary phenomenon, the surface became much more hydrophilic after the hydrothermal treatment and the contact angle is determined to be 21.9°. The surface modified with SA is superhydrophobic, where a water droplet deposited on the surface forms almost a round sphere with a high contact angle of 157.6° (Fig. 3(c)). Moreover, the water droplets barely stick to the surface and roll off easily, which indicates that the magnesium alloy acquired a superhydrophobic surface by using SA. We attribute the enhanced superhydrophobic behavior to the combination of the high surface roughness of microstructure as well as the low energy of SA.

The X-ray diffraction (XRD) patterns of the bare AZ31 substrate, AZ31 coated with $Mg(OH)_2$ coating and AZ31 coated with the composite coatings are shown in Fig. 4. The figure reveals the characteristic peaks of $Mg(OH)_2$ according to Powder Diffraction Standards (JCPDS file No. 75–1527) as for the hydrothermal treated

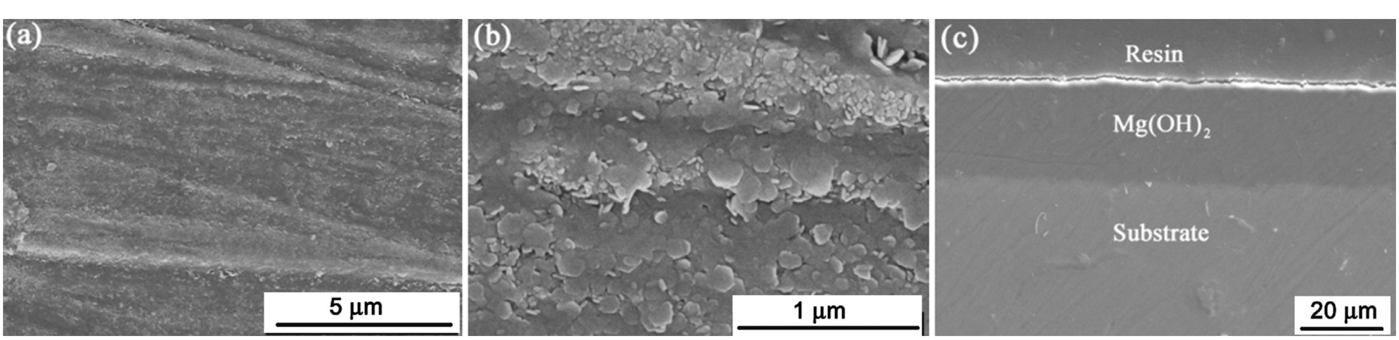

Fig. 1. Surface morphologies (a, b) and cross sectional view (c) of the coating after the hydrothermal treatment.