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Facile and fast fabrication of superhydrophobic surface on magnesium alloy

Zhongwei Wang, Qing Li*, Zuxin She, Funan Chen, Longqin Li, Xiaoxu Zhang, Peng Zhang

School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

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ABSTRACT

Superhydrophobic surface has many special functions and is widely investigated by researchers. Magnesium alloy is one of the lightest metal materials among the practice metals. It plays an important role in automobile, airplane and digital product for reducing devices weight. But due to the low standard potential, magnesium alloy has a high chemical activity and easily be corroded. That seriously impedes the application of magnesium alloy. In the process of fabrication a superhydrophobic surface on magnesium alloy, there are two ineluctable problems that must be solved: (1) high chemical activity and (2) the chemical activity is inhomogeneous on surface. In this study, we solved those problems by using the two characters to gain a rough surface on magnesium alloy and obtained a superhydrophobic surface after following modification process. The results show that the as-prepared superhydrophobic surface has obvious anti-corrosion effect in typically corrosive solution and naturally humid air. The delay-icing and self-cleaning effects are also investigated. The presented method is low-cost, fast and has great potential value in large-scale industry production.

1. Introduction

In recent years, a number of superhydrophobic surfaces were investigated by many researchers for their special functions, such as water-repellency, self-cleaning, anti-icing and anti-corrosion [1–5].

Magnesium alloy is one of the lightest metal materials, its specific gravity is approximately 2/3 and 1/4 that of aluminum and steel respectively, and has high strength-to-weight ratio. So magnesium alloy has been applied in automotive, aircraft, aerospace industries, and functional materials and so on [6–10]. Moreover, the more important thing is that with the shortage of energy source, the magnesium alloy would be used in more areas to meet the demand of lighting devices. The application of magnesium alloy would play an important role in saving energy, reducing carbon emission and more areas. However, due to low standard potential, magnesium alloy is easily corroded, which has further aggravated the large-scale use of magnesium alloy [11,12].

Preparing a superhydrophobic surface on magnesium alloy is a wonderful method to slow down the corrosive rates. Because the appearance of the electrolyte film on the metal surface would lead to the occurrence of atmospheric corrosion, the superhydrophobic surface could effectively restrain the formation of electrolyte film. On the other hand, the introduction of superhydrophobic surface may enlarge the application scope of the magnesium alloy. But in the process of preparing a superhydrophobic surface on magnesium alloy, there exists two ineluctable problems. One is the high chemical activity. Magnesium alloys could easily effected with many matters and be corroded, such as acid, alkali and saline solution. Up to now, most reported methods were applied on relatively inert and homogeneous substrates, such as silicon wafer, copper, zinc, aluminum, steel and glass [13]. Therefore most of methods in the present reports probably are impracticable due to possible side reactions. Another problem is that the chemical activity is inhomogeneous as the magnesium alloys are made up of at least two phases. For example, AZ91D magnesium alloy which has been widely used in automobile industries is mainly made of α phase (Mg) and β phase ($Mg_{17}Al_{12}$).

For above reasons, there are still limited reports about fabricating superhydrophobic surface on magnesium alloy. In the preparing methods side, some researchers used the methods which need high standard and expensive equipments to fabricate superhydrophobic surface on magnesium alloy, such as microarc oxidation treatment [14] and microwave plasma-enhanced chemical vapour deposition [15]. Although there were some facile methods, such as solution-immersion method [5,16,17], and electrodeposition [18,19], to prepare superhydrophobic surfaces on magnesium alloys. Those methods used relatively expensive regents, such as $AgNO_3$ [16] or fluoroalkylsilnane [5,17–19], especially the production and use of fluorinated regents may harm human body and the environment.

Etching method is a simple and effective way to gain a rough surface on metals. For example, Qian et al. [20] used dislocation-selective chemical etching to fabricate superhydrophobic surfaces on aluminum, copper and zinc. Lee et al. [21] used Copper Catalytic

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* Corresponding author. Tel.: +86 023 68252360; fax: +86 023 68254000.
E-mail address: liqingswu@163.com (Q. Li).

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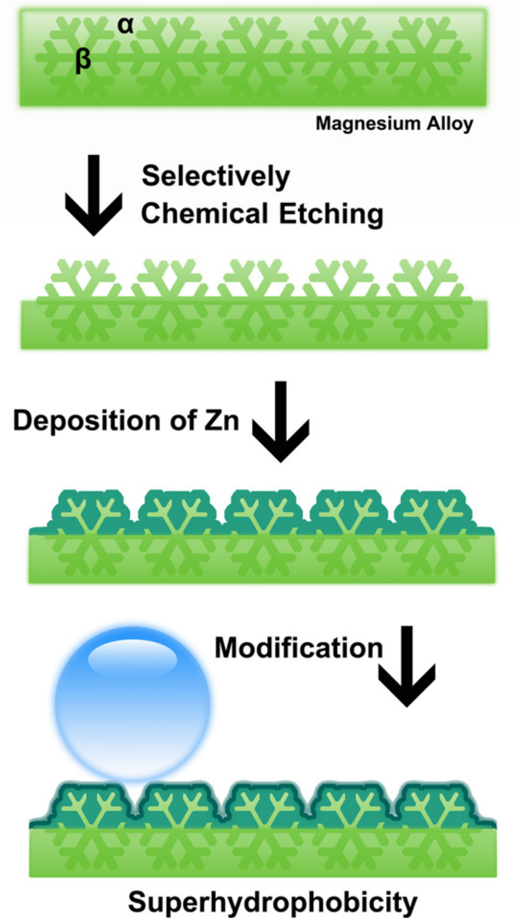

Scheme 1. Schematic illustration of fabricating superhydrophobic surface on AZ91D magnesium alloy.

Etching method to obtain a superhydrophobic surface on Si. Wang et al. [22] used H_2SO_4 and H_2O_2 to etch substrate and subsequently modified with stearic acid to gain a superhydrophobic surface on pure Mg. But the relationship between etching and hydrophobicity was not showed in paper. Fujii et al. [23] reported a method which used electro etching to gain a rough surface on Al sheet and subsequently deposited Al–Nb nanopillars, then used anodic treatment to obtain nanoporous anodic oxides and modified with fluoroalkyl phosphate to fabricate a superhydrophobic surface. But this method was relatively complex.

Etching is an efficacious method for gaining rough structures. But for magnesium alloy, its surface chemical activity is still high after etching. Herein we combine the above methods and design a facile method to fabricate a superhydrophobic surface on AZ91D magnesium alloy. The main experiments are exhibited in Scheme 1.

Firstly, the chemical etching method is used to obtain a rough surface. Although the magnesium alloy has a rough surface after chemical etching, the chemical activity was still at a high level. This would lead to the appearance of corrosion production and is disadvantageous to the sequent preparation. So we used the high activity to reduce Zn^{2+} to Zn and deposit it on the surface to protect the substrate from corrosion and maintain the rough structure. It is worthwhile to note that the main reason to choose Zn as protective layer is that the standard potential of Zn is the lowest in common metal coatings. So the driving force of electrochemical corrosion falls to the lowest. Another reason is that compared with other metal, Zn is appropriate for depositing on magnesium alloy, because the standard potential gap between Zn and Mg is moderate and the deposition could be easily controlled, and we could obtain an appropriate micro-structure for fabricating a superhydrophobic surface. At the same time, Zn is cost-saving and could be used for large-scale production.

2. Experiments

2.1. Materials

All solvents and chemicals except stearic acid (CR, Shanghai Chemical Reagent Co.) were purchased from Chengdu Kelong Chemical Reagent Co., China. The deionized water used was Milli-Q water (Milli Q, USA). AZ91D magnesium alloy was used for the investigation and was purchased from Chongqing Boao Mg-Al Manufacturing Co., Ltd. The AZ91D magnesium alloy was mainly composed of 8.77 wt% Al, 0.74 wt% Zn, 0.18 wt% Mn and Mg balance. The dimensions of samples are 35 mm × 18 mm × 4 mm.

2.2. Pretreatment of magnesium alloy

The substrate was metallographically grounded with No. 1500 SiC paper, rinsed with deionized water, ultrasonically degreased in acetone and dried in air, degreased in an alkaline solution containing 0.25 $g L^{-1}$ NaOH, 20 $g L^{-1}$ Na_2CO_3 and 0.5 $g L^{-1}$ $C_{12}H_{25}NaSO_4$ at 70 °C for 5 min, and then finally rinsed with hot and cool deionized water respectively.

2.3. Selectively chemical etching (SCE)

After pretreatment, the substrate was immersed in an optimal SCE solution which contained 50 $mL L^{-1}$ CH_3COOH, 15 $mL L^{-1}$ H_3PO_4 (85 wt%) and 5 $mL L^{-1}$ HNO_3 (65 wt%). Then the substrate was washed with deionized water.

2.4. Deposition of Zn

After SCE, magnesium alloy was dipped in a solution containing 120 $g L^{-1}$ $Na_2P_2O_7$ $10H_2O$, 30 $g L^{-1}$ $ZnSO_4$ $7H_2O$ and 5 $g L^{-1}$ Na_2CO_3 at 80 °C for deposition of Zn. After this process, the magnesium alloy was covered by the Zn coating.

2.5. Modification

In our study, the electrochemical deposition method was applied to adjust the microstructure to obtain an appropriate micro/nano structure and lower the surface energy. After deposition, the sample was immersed in a 0.01 $mol L^{-1}$ ethanolic stearic acid solution which contained 0.1 $g L^{-1}$ sodium acetate to enhance the electrical conductivity. Then a constant current power with voltage about 15 V was applied by direct current supply for 20 min. The anodic (magnesium alloy with Zn film) and two cathodic carbon electrodes were separated by a distance of 10 mm respectively. After that, the sample was dipped in water for several times to remove the sodium acetate. Then it was dried in air at 80 °C for 30 min. Finally, after natural cooling the superhydrophobic surface was obtained.

2.6. Characterization and tests

The water contact angle (CA) and slide angle (SA) for liquids were measured with 10 μL water droplets and an admeasuring apparatus (POWEREACH JC2000C1). Scanning electron microscopy images were obtained on a scanning electron microscope (SEM; HITACHI S-4800). The surfaces were also analyzed by X-ray diffractometer (XRD; Purkinje General Instrument XD-3) and Fourier transform infrared (FT-IR; Bruker TENSOR-27) spectra and energy dispersive X-ray spectroscopy. The pH value of corrosion solution