



# Fabrication of biomimetic hydrophobic films with corrosion resistance on magnesium alloy by immersion process

Yan Liu\*, Guolong Lu, Jindan Liu, Zhiwu Han, Zhenning Liu

Key Laboratory for Bionic Engineering (Ministry of Education), Jilin University, Changchun 130022, China

## ARTICLE INFO

### Article history:

Received 20 September 2012

Received in revised form 10 October 2012

Accepted 10 October 2012

Available online 29 October 2012

### Keywords:

Hydrophobic

Immersion process

Magnesium alloy

Biomimetic film

## ABSTRACT

Biomimetic hydrophobic films of crystalline CeO<sub>2</sub> were prepared on magnesium alloy by an immersion process with cerium nitrate solution and then modified with DTS (CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>Si(OCH<sub>3</sub>)<sub>3</sub>). The CeO<sub>2</sub> films fabricated with 20-min immersion yield a water contact angle of 137.5 ± 2°, while 20-min DTS treatment on top of CeO<sub>2</sub> can further enhance the water contact angle to 146.7 ± 2°. Then corrosion-resistant property of these prepared films against NaCl solution was investigated and elucidated using electrochemical measurements.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Biologic surface has ingenious structures and predominant functions, among which water-repellent ability is one of the most common characteristics. Such water-repellence is remarkably exhibited on lotus leaf. Lotus leaf is covered by many papillae with a diameter in the range of 3–10 μm, while these papillae are decorated with smaller protrusions of nanometer size [1]. Such special micro-nano-binary structure plays an important role in the wetting behavior of solids [2,3], which not only increases the surface roughness dramatically but also traps more air in the grooves underneath the liquid to reduce the contact area between the leaf and the liquid [4]. Thus water droplets on lotus leaf yield nearly spherical shape and roll off easily. In recent years, the super-hydrophobic biomimetic surfaces have been extensively studied due to the necessity of self-cleaning materials [5,6]. Many methods have been employed to fabricate a superhydrophobic surface such as template method [7], lithography [8], sublimation [9], electrochemical method [10], chemical etching [11], anodic oxidation [12], layer-by-layer method [13,14], bottom-up fabrication of nano-arrays [15], etc. Actually, all methods fall into two general strategies, one is roughening the surface of hydrophobic materials [16], and the other is forming a rough surface first and then modifying the rough surface with a special low surface energy material [17]. However, researchers usually prepare hydrophobic films on metallic and

inorganic materials with stable chemical property. Consequently, reactive metal and their alloy are rarely investigated.

Magnesium and its alloys exhibit low density, high specific strength and good castability and thus become important structural materials for automotive and aerospace industries. However, application of magnesium alloys is yet limited due to poor corrosion resistance. Many surface modification methods have been adopted to improve corrosion resistance of magnesium alloy such as electrochemical deposition [18,19], electroless plating [20,21], anodic oxidation [22], physical vapor deposition [23] and so on. A hydrophobic coating would be a promising approach to improve surface performance. Wang et al. [24] fabricated a superhydrophobic surface on a pure magnesium substrate through chemical etching followed by immersion in the 0.05 mol/L ethanolic solution of stearic acid (SA) at room temperature for about 1 h. Fang et al. [25] successfully fabricated the superhydrophobic coating on the surface of magnesium alloy AZ31 by chemical etching and surface modification. Jun et al. [26] created a stable biomimetic superhydrophobic surface on magnesium alloy fabricated by microarc oxidation pretreatment and followed by chemical modification based on lotus effect. Ishizaki et al. [27] fabricated the superhydrophobic surface on AZ91 magnesium alloy by immersion in a cerium nitrate aqueous solution and then were covered with FAS and TTST molecules. Li et al. [28] prepared magnesium thin films by bias magnetron sputtering.

Lanthanide metal has texture soft and bulk, ductility good, etc., The characteristics are beneficial to gain greater surface roughness on the forming film. However, cerium is the most active metal in lanthanide metal. Cerium coating in the air is easy to be oxidized to cerium oxide, this is a kind of self passivation process.

\* Corresponding author. Tel.: +86 431 5095760; fax: +86 431 5095575.  
E-mail address: [liuyan2000@jlu.edu.cn](mailto:liuyan2000@jlu.edu.cn) (Y. Liu).

In this report, biomimetic hydrophobic films of crystalline CeO<sub>2</sub> were prepared on magnesium alloy by electroless method. The CeO<sub>2</sub> films fabricated with 20-min immersion yield a water contact angle of  $137.5 \pm 2^\circ$ , while 20-min DTS treatment on top of CeO<sub>2</sub> can further enhance the water contact angle to  $146.7 \pm 2^\circ$ . Then corrosion-resistant property of these prepared films against NaCl solution was investigated and elucidated using electrochemical measurements.

## 2. Experimental

### 2.1. Preparation of super-hydrophobic films

AZ91D magnesium alloy was chosen as experimental material, whose chemical composition was 8.534% Al, 0.522% Zn, 0.208% Mn, 0.016% Si, 0.001% Ni, 0.002% Fe, with the rest being Mg. Raw material was cut into 10 mm × 10 mm pieces and polished to 1.5 μm mirror finish. The surface was first ground with No. 1000 SiC paper, followed by No. 1500, No. 2000, and finally 1.5 μm diamond suspension in oil. The polished specimens were degreased by sonicating in acetone for 10 min, and then methanol for 10 min with a final distilled water rinse. The cleaned magnesium alloy substrates were immersed in an acidic solution containing 0.1 M cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) (pH ~4.5) at room temperature for 10, 15, 20, 25, and 30 min, respectively. The solution was agitated with a magnetic stirrer at a rotation of 150 rpm during immersion. After immersion, samples were thoroughly washed with 95% ethanol. To prepare DTS-coated samples, post-Ce-coating samples were immersed in 60 mL of a toluene solution containing 600 μL of DTS (CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>Si(OCH<sub>3</sub>)<sub>3</sub>) for 5, 10, 20, and 30 min, respectively, and then washed with 95% ethanol.

### 2.2. Evaluation of corrosion resistance

Samples with hydrophobic coatings were immersed in 5 wt% NaCl solution for 60 min to evaluate corrosion-resistant property.

### 2.3. Surface characterization

Static water contact angles of the fabricated surfaces were estimated with a contact angle meter (JC2000A Powereach, China) based on a sessile drop measuring method with a water drop volume of 3 μL. Water droplet was dropped onto five different places of the as-prepared surface. Finally get their average value. Surface morphologies of obtained samples were observed by scanning electron microscope (JSM-5500LV, Japan Electronic). All electrochemical measurements (CS300, China) were performed in 3.5 wt% NaCl aqueous solution (pH 6.0) at room temperature.

## 3. Results and discussion

### 3.1. Effects of the hydrophobic property on AZ91D magnesium alloy

We first examined micro-morphologies of prepared samples using SEM. Fig. 1 shows SEM images of the sample surfaces after immersion in cerium nitrate solution for (a) 10, (b) 15, (c) 20, (d) 25, and (e) 30 min, respectively. After 10 min of immersion, the surface of the magnesium alloy (Fig. 1a) is almost fully covered by CeO<sub>2</sub>, but some microcracks are formed on the coating. These cracks may form due to oxidation of cerium during sample preparation or loss of water contained in the coating after samples have been withdrawn from the solution. Large cracks decrease after 15-min immersion (Fig. 1b) and almost disappear after 20-min immersion (Fig. 1c). This may be due to that increasing of

immersion time yields thicker film coated on magnesium alloy matrix and thus prevents large cracks. However, further increasing of immersion time causes an opposite effect, leading to more and more small cracks (Fig. 1d and e), probably because of the space crunch and loose contact in outlayers when the coating gets even thicker. In fact, after 30-min immersion, the outlayer of CeO<sub>2</sub> attaches to the substrate so weak that peeling of coating can be observed.

Subsequently, hydrophobic property of aforementioned samples was assessed by water contact angles. As shown in Fig. 2, the water contact angles of these samples at different electroless plating timepoints changes in a pattern that correlates with morphologies observed with SEM as shown in Fig. 1. First, the contact angle of the coating increases with longer immersion time and reaches its peak value of  $137.5 \pm 2^\circ$  at 20-min plating. Post-20-min plating, the contact angle drops. Thus 20-min appears to be the optimal time to generate desired surface roughness and appropriate hydrophobicity under our experiment conditions.

We then set out to test whether low surface energy material, such as DTS (CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>Si(OCH<sub>3</sub>)<sub>3</sub>), can further improve hydrophobicity. Fig. 3 shows SEM images of sample surfaces after immersion in DTS solution at room temperature for (a) 5, (b) 10, (c) 20, and (d) 30 min. After 5-min treatment of DTS, deposited samples form patches to partially cover the surface (Fig. 3a). In contrast, after 10-min treatment, samples are almost fully covered over the entire surface but the roughness is still not enough (Fig. 3b). Sample surfaces become more dense and rough when the treatment time increases and massive tiny crystals of 1–4 μm in length can be observed (Fig. 3c and d). However, the aggregation of these tiny crystals can lead to undesired irregular surface topography with nanoscale pores composed of valleys and hills (Fig. 3d). Therefore, we conclude that 20-min immersion yield the best result in forming a compact but relatively even coating of DTS.

Then hydrophobic property of these Ce-DTS-double-coated samples was evaluated by water contact angles. As shown in Fig. 4, the water contact angles of these samples correlates with the pattern observed with SEM as shown in Fig. 3. The contact angle of sample surfaces with 5-, 10-, and 20-min of DTS immersion at room temperature rises as immersion time increases and reaches the maximum value of  $146.7^\circ$  with 20-min immersion. Furthermore, the contact angle for the surface with 30-min DTS immersion drops to  $130.6 \pm 2^\circ$  due to over-dramatic morphology. Therefore DTS immersion yields the best hydrophobic property at 20 min under our conditions.

### 3.2. Effects of corrosion resistance property on AZ91D magnesium alloy

Next, corrosion resistance against NaCl solution was investigated by following the change of water contact angles after different length of corrosion within 5 wt% NaCl aqueous solution. Fig. 5 shows the average contact angle value of five different points on the same sample after a certain time of corrosion within 5 wt% NaCl solution. As demonstrated in Fig. 5, the average water contact angle of the prepared DTS hydrophobic surface quickly drops to around  $126 \pm 2^\circ$  within the first 60 min and then gradually decreases to  $115 \pm 2^\circ$  after 300-min corrosion. This could indicate that slow dissolve of DTS molecules and gradual degradation of nanostructure occurs on the sample surface. The average static contact angle is estimated to be  $60^\circ$  after 24-h immersion in 5 wt% NaCl solution, when the films of the DTS molecules and the nanostructure have almost been completely destroyed.

Download English Version:

<https://daneshyari.com/en/article/5354077>

Download Persian Version:

<https://daneshyari.com/article/5354077>

[Daneshyari.com](https://daneshyari.com)