Applied Surface Science 422 (2017) 566–573

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

# One-step hydrothermal process to fabricate superhydrophobic surface on magnesium alloy with enhanced corrosion resistance and self-cleaning performance

Libang Feng[a,*], Yali Zhu[a,b], Jing Wang[a], Xueting Shi[a]

[a] School of Mechatronic Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China
[b] Department of Mechanical and Electrical Engineering, Xi'an Railway Vocational & Technical Institute, Xi'an 710026, China

ARTICLE INFO

*Article history:*
Received 7 March 2017
Received in revised form 5 May 2017
Accepted 5 June 2017
Available online 7 June 2017

*Keywords:*
Magnesium alloy
Superhydrophobicity
One-step
Hydrothermal process
Anti-corrosion
Self-cleaning

ABSTRACT

Superhydrophobic surfaces can exhibit anti-corrosion, anti-fogging, and self-cleaning performance due to their high water repellence. It is significant for industrial fabricating of superhydrophobic surface with a simple and environment-friendly method. Herein, a facile, environment-friendly, and cost-effective one-step hydrothermal route is proposed to fabricate the superhydrophobic surface on magnesium alloy. The as-prepared superhydrophobic magnesium alloy surface presents the rough and hierarchical micro/nano-structure grafted with long hydrophobic alkyl chains via covalent bonds. Both electrochemical corrosion test and long term immersion in 3.5 wt.% of NaCl solution demonstrate that the superhydrophobic surface greatly improves the corrosion resistance of magnesium alloy. Meanwhile, the superhydrophobic magnesium alloy exhibits excellent self-cleaning performance. It is supposed that this facile method and remarkable properties of resultant superhydrophobic magnesium alloys have a promising future in expanding the application of magnesium alloys.



## 1. Introduction

The corrosion of metals can cause a tremendous economic loss each year [1–3], and it has attracted much attention of developing new methods and technology to slow down the corrosion rate of metals [4–7]. Among various metals, magnesium and its alloy have stimulated considerable interest in aerospace, automobile, machinery, computer, electronic industry, and so on, thanks to their excellent characteristics as low density, high specific strength, high ductility, good thermal/electrical conductivity, electromagnetic compatibility, good castability, and abundant availability [8,9]. However, due to the low standard potential and high chemical reactivity, magnesium is one of very active metals and it is susceptible to erode in an aqueous environment, moist atmosphere, or other corrosive media. And which has limited its large scale application in engineering fields. In order to improve the corrosion resistance and extend the application area of magnesium and its alloy, many strategies have been attempted, such as introducing rare earth elements [10], increasing the purity of alloy [11], using rapid solidification processing [12], introducing corrosive metal atoms [13], wet chemical etching [14], and so on.

Recently, many studies have shown that it is an effective method of constructing superhydrophobic surfaces on various metals to enhance their corrosion resistance since the superhydrophobic surfaces can hinder the close contact of a surface with the corrosive species [15–19]. So it may be a preferred method to improve the corrosion resistance by endowing magnesium and its alloy with the superhydrophobicity. Various methods have been reported for preparing the superhydrophobic surface on magnesium and its alloy. For example, chemical conversion film, electrodeposition, anodization, chemical vapor deposition, laser treating, micro-arc oxidation, wet chemical etching, electrospinning, and so on [20–26].

However, in most cases, the method is subject to certain limitations, such as special equipment, complex operations, caustic reagents (for instance, $HNO_3$, $H_2SO_4$, HF, $H_2O_2$, etc.), or expensive materials (namely, fluoride, etc.), and severe conditions. Consequently, these procedures/methods may cause a lot of problems as no universality, high cost, environment pollution, and so on [23–26]. Thus, it is quite needed of developing simple, inexpensive, versatile, and environment-friendly process for the fabrication of the superhydrophobic surfaces on magnesium alloys so as to promote the advantages for industrial large-scale application.

* Corresponding author.
*E-mail address:* lepond@hotmail.com (L. Feng).

http://dx.doi.org/10.1016/j.apsusc.2017.06.066
0169-4332/

Hydrothermal reaction is an efficient way for materials preparation and modification, and it has been used to prepare the superhydrophobic surfaces as well [27,28]. A few papers have been reported for the preparation of superhydrophobic surfaces on magnesium alloys. For example, Wang and co-workers [29] prepared the superhydrophobic magnesium alloy by the hydrothermal process and then modified the surfaces with fluoroalkylsilane, and results showed that the superhydrophobic surface had outstanding corrosion protection effect on magnesium alloy. Li et al. [30] also proposed a hydrothermal method to fabricate superhydrophobic surface on AZ91D magnesium alloy combining stearic acid modification. The as-prepared samples exhibited a considerable enhancement in corrosion resistance and superior anti-bacteria adhesion effect. However, two steps are involved in both routes for fabricating the superhydrophobic surfaces: the first step is to construct a rough-structured surface via hydrothermal process and then to modify surfaces with low-surface-energy substances. Moreover, the caustic NaOH or expensive fluoroalkylsilane is used in the fabrication procedures. To overcome the inherent disadvantage and simplify the procedure, herein, a facile, environment-friendly, and cost-effective method is developed for preparing superhydrophobic magnesium alloys via only one-step hydrothermal process. Furthermore, the as-prepared superhydrophobic surface greatly enhances the corrosion resistance of magnesium alloy. Meanwhile, the superhydrophobic magnesium alloys show excellent self-cleaning performance. The presented method is simple, low-cost, and environment-friendly, which is significant for industrial fabricating of superhydrophobic surfaces with excellent anti-corrosion and self-cleaning performance. Therefore, it is supposed to have a promising future in expanding the application of magnesium alloys.

## 2. Material and methods

### 2.1. Materials

Magnesium alloy (AZ91) plate was purchased from Qingdao Dexingsheng metal materials Co., Ltd. The chemical composition of AZ91 was 8.50–9.50% Al, 0.45–0.90% Zn, 0.17–0.40% Mn, 0.05% Si, 0.025% Cu, 0.001% Ni, 0.004% Fe, and Mg balance. Stearic acid (STA) was supplied by Shanghai Zhongqin Chemical Reagent Co., Ltd. Ethanol was purchased from Sinopharm Group Chemical Reagent Co., Ltd.

### 2.2. Fabrication of the superhydrophobic magnesium alloys

The fabricating process of the superhydrophobic magnesium alloy surface is shown in Scheme 1. After polished with abrasive paper and cleaned ultrasonically with acetone/deionized water, AZ91 plate was introduced into a Teflon-lined stainless steel autoclave filled with deionized water, ethanol, and STA. The volume ratio of ethanol to deionized water was kept at 1:1.4 while STA concentration was 50 mmol/L. Then the autoclave was sealed and maintained at 80 °C for 10 h. After the hydrothermal reaction finished, AZ91 plate was taken out and cleaned with ethanol for three times. Finally, the as-prepared sample was dried in air, and thus the superhydrophobic magnesium alloy was obtained.

### 2.3. Corrosion resistant performance evaluation

The corrosion resistant performance of as-fabricated superhydrophobic magnesium alloys was evaluated by both electrochemical corrosion test and long term immersion in 3.5 wt.% of NaCl solution.

Electrochemical corrosion test was performed on a computer-controlled electrochemistry workstation (CHI660D, CH Instruments Inc., China) by potentiodynamic polarization in a three-electrode system: working electrode, a platinum stick counter electrode, and a saturated calomel reference electrode. Dynamic measurement of polarization plots in a Tafel model was acquired at a scan rate of 1 mV/s at room temperature when samples were exposed to corrosive solution for a short period of 10 min.

Long-term durability of superhydrophobic magnesium alloys under continuous contact with saline water was carried out by immersing samples in 3.5 wt.% of NaCl solution at $25.0 \pm 0.5$ °C from 0 to 60 h. After a definite time of immersion, the sample was taken out, dried under a nitrogen stream, and retained in a vacuum oven at 30 °C for 2 h. Then, the wettability of the samples was measured.

### 2.4. Self-cleaning performance test

The self-cleaning performance of as-fabricated superhydrophobic magnesium alloys was evaluated by measuring the ability of the rolling water droplets taking away the simulating contaminant particles, while the cigarette ash, carbon powder, and chalk dust were used as the simulating contaminant particles. The self-cleaning test was carried out by deliberately spreading contaminants to form thick layers on the magnesium alloy surfaces. Then a water droplet with a volume of 10 μL was dripped gently onto the sample surfaces under a slope angle of 6° above horizontal.

### 2.5. Characterization

The wettability was evaluated by both static water contact angle (CA) and sliding angle (SA). In our research, the CA and SA for deionized water were measured with a 10 μL of droplet using a horizontal microscope with a protractor eyepiece (DSA 100, Kruss, Germany) at ambient temperature. The droplet was placed at five different spots for each sample surface and the average value was regarded as the contact angle. The error of the contact angle is ±1°. The sliding angle was measured by slowly tilting the level stage controlled with computer, and the tilted angle was adopted when the droplet began to roll in the downhill direction on the sample surfaces.

Scanning electron microscopy (FE-SEM, JSM-6701F, Japan) was used to observe the surface morphology. X-ray diffractometer (XRD, XRD-7000LX, Shimadzu, Japan) was used to characterize the phase structure. Fourier transform infrared spectra (FT-IR, VER-TEX 70, Germany) and energy dispersive X-ray spectroscopy (EDS, Inca X-Max, UK) were used to analyze the surface chemical composition.

## 3. Results and discussion

### 3.1. Surface morphology, structure, and wettability

The superhydrophobic magnesium alloys are fabricated by one-step hydrothermal method. SEM images of the untreated magnesium alloy substrate and superhydrophobic surface are shown in Fig. 1. The SEM image of untreated magnesium alloy surface (see as Fig. 1a) displays a relatively flat and smooth surface while only abrasive grooves are observed. The untreated substrate surface takes a static water contact angle of ca. 38.3°, indicating the hydrophilic nature of the alloy surface. Fig. 1b–d shows surface morphologies of magnesium alloy after hydrothermal treatment. It can be noted that great changes happen at the magnesium alloy surface after hydrothermal process. The low-magnification SEM image in Fig. 1b shows the surface is covered by a large number of bar-like and plate-like structure completely. It is clearly observed from the high magnification SEM images (Fig. 1c and Fig. 1d) that the as-prepared surface consists of many nano-plates. The plate length is between 1 μm and 5 μm while the plate thickness is about 50–100 nm. Moreover, it is worth noting from Fig. 1d that the plate is composed of several layers. Meanwhile, a great deal of gaps can