Journal of Colloid and Interface Science 505 (2017) 87–95

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

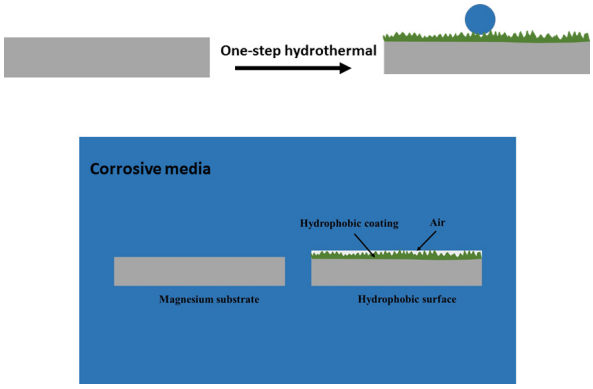
Regular Article

Formation of a hydrophobic and corrosion resistant coating on magnesium alloy via a one-step hydrothermal method

Tianxu Zheng [a,b], Yaobo Hu [a,b,*], Yuxin Zhang [a,*], Fusheng Pan [a,b]

[a] College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China
[b] National Engineering Research Center for Magnesium Alloys, Chongqing 400044, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 March 2017
Revised 24 May 2017
Accepted 25 May 2017
Available online 26 May 2017

Keywords:
Magnesium alloy
Hydrophobic
Corrosion resistance
EIS

ABSTRACT

A hydrophobic coating was fabricated on the surface of magnesium alloy using a simple one-step hydrothermal method with the use of environmentally friendly agent. Scanning electron microscopy, energy-dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and contact angle test were used to characterize the surfaces. Corrosion behavior in a 3.5 wt.% NaCl solution was evaluated using OCP time curves test, potentiodynamic polarization test and EIS analysis. The findings show that the substrate is covered by the coating of magnesium hydroxide and magnesium stearate, reaching a contact angle of around 146°. Corrosion behavior show huge improvement, the progress with increase of treatment time could be related to the increased growth rate of coating.

1. Introduction

Magnesium alloys as one of the lightest metal structural materials have great potential in automotive, aerospace and electronic products areas [1]. With its advantages of low density, high specific strength and abundant resources, magnesium alloys are particularly interested in the automotive industry facing the pressure of emission reduction and energy saving [2,3]. However, the corrosion resistance of magnesium alloys is poor due to the high chemical reactivity of magnesium and poor protection capacity of the natural oxides film, especially in an aggressive medium containing chloride anions [4–6]. This weakness of magnesium alloy counteracts the merits and restricts the wide spread applications.

* Corresponding authors at: College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China.
E-mail addresses: yaobohu@cqu.edu.cn (Y. Hu), zhangyuxin@cqu.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.jcis.2017.05.092
0021-9797/

Various methods have been used to address the poor corrosion resistance of magnesium alloys, such as alloying [7,8], heat treatment [9], surface modifications [10], and providing coatings [11–13]. In these methods, providing coatings is one of the effective and directive ways to prevent the contact of magnesium alloys and the corrosive medium. Inspired by the self-cleaning lotus leaf, the use of superhydrophobic surfaces with water contact angles larger than 150° and sliding angles smaller than 10° has been considered as one of the promising coating ways to enhance the anti-corrosion performance of the substrate due to the effective barrier to keep humid atmosphere or corrosion media away from contact and interaction with underlying substrates [14–18]. Herein, preparation of superhydrophobic surfaces is considered as a promising way to enhance the corrosion property of magnesium alloys.

The wettability of a surface is governed by surface structures and chemical compositions. To realize a superhydrophobic surface, the appropriate rough surface and low surface energy materials are needed [19,20]. Based on this principle, a significant body of work has been devoted to fabricate superhydrophobic surfaces in the past decades, and different techniques are applied, such as hydrothermal method, electrochemical deposition [21,22], chemical etching, microarc oxidation, anodic oxidation [23], and chemical vapor deposition [24–33]. Among these techniques, hydrothermal method is competitive owing to its benefits of easy control, simplicity, low cost, environmentally friendly and so on. The use of water as the only or main chemical during the hydrothermal treatment is more promising, which almost has no impact on the environment and makes the coating more stable as the substrate is involved in the reaction. This kind of approach has been reported in some published papers. For example, Ishizaki et al. report the successful fabrication of a superhydrophobic cerium oxide film on magnesium alloy surface. The degradation of the nanostructured cerium oxide film was also investigated [17]. Ishizaki et al. reported a two steps method containing the hydrothermal treatment to build rough structure and a followed modification with *n*-octadecyltrimethoxysilane [34]. In 2013, Ou et al. fabricated a superhydrophobic surface on magnesium via a one-step hydrothermal method, in which the mixed solution of water and low surface energy material was employed for the reaction [35]. However, the above mentioned method usually contained biological poison materials to achieve low surface energy.

In this paper, we report an environmentally friendly one-step hydrothermal method to fabricate a hydrophobic coating on magnesium alloys. The corrosion performance of the coating is characterized by electrochemical method. We show that this method provides a simple way to enhance the corrosion performance of magnesium alloys, it is hoped that this simple method without any environmental toxicity can accelerate the wide spread applications of magnesium alloys and may be in some help for other light alloys.

2. Material and methods

2.1. Materials and pretreatment

The AZ31 magnesium alloy sheet of 1 mm thickness was selected as substrate, with a chemical composition that was mainly Mg, 3 wt.% Al, 0.8 wt.% Zn and 0.2 wt.% Mn. All reagents used in this experiment were of analytical grade and were used without further purification. Firstly, the magnesium sheet was cut into disks with a diameter of 14 mm, following the mechanical abrasion with 800 grit SiC papers to get rid of the surface contamination. Next, the disks were cleaned ultrasonically in anhydrous ethanol and distilled water successively. Afterwards, the disks were degreased in 0.1 M sodium hydroxide solution for 10 min at 60 °C, subsequently picked and activated in 0.1 M hydrogen chloride solution for 2 min at ambient temperature. The disks were rinsed with plenty of distilled water between each step.

2.2. Hydrothermal treatment

The one-step hydrothermal fabrication was conducted as follows. First, the stainless Teflon-lined autoclave with 50 mL capacity was filled with 15 mL 0.01 M stearic acid ethanol solution, then 15 mL distilled water was added to the vessel. After the cleaned magnesium disks were introduced into the mixed solution, the autoclave was sealed and maintained at a temperature of 170 °C for 4 h to 12 h. The autoclave was cooled down to room temperature after the reaction. Finally, the obtained samples were taken out, rinsed with ethanol and distilled water subsequently, dried at room temperature.

2.3. Characterization

The surface and cross-sectional morphologies of the as-prepared samples were characterized by field emission scanning electron microscopy (JSM-7800F, JEOL, Japan) with an accelerate voltage of 8 kV. The composition of the coating was identified using X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo Fisher Scientific), powder X-ray diffraction (PANalytical X'Pert Powder), Fourier Transform Infrared Spectrometer (Nicolet iS5 FT-IR, USA) and Energy Dispersive Spectrometer (EDS, INCA Energy, Oxford Inc.). The CAs were measured using an optical angle meter (HARKE-SPCA, China) at the ambient temperature. The volume of test droplet is 5 μL. In order to get a reliable result, each contact angles were measured five times for each sample and then the average value was used with errors.

2.4. Electrochemical test

The anticorrosion performance was assessed by means of potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) tests employing a conventional three-electrode cell configuration. A platinum foil (15 mm × 15 mm × 3 mm) was used as counter-electrode, a saturated calomel electrode (SCE) was used as reference-electrode, and the disk samples were mounted into a PVDF holder, leaving a surface area of 1 cm^2 to form the working electrode. The electrolyte was 3.5 wt.% NaCl solution comprised of analytical-reagent grade sodium chloride and distilled water. The measurement of electrochemical polarization curves and EIS were carried out using a Zennium E electrochemical workstation. The open circuit potential time curves were recorded using a CHI 660E electrochemical workstation. The electrochemical polarization curves were at a scan rate of 10 mV s^{-1} in the range of ±300 mV versus the open circuit potential (OCP). EIS scans were acquired from 100 kHz to 0.01 Hz with an AC amplitude of 10 mV. The EIS experimental data were further analyzed by ZView software.

3. Results and discussion

3.1. Morphologies and composition of the coatings

Fig. 1 shows the typical surface and cross-sectional SEM images of the coatings on magnesium alloy surfaces after one-step hydrothermal treatment for 4 h, 8 h and 12 h. For simplicity, the coated samples (hydrothermal treatment after 4 h, 8 h, and 12 h respectively) are referred to H4, H8 and H12. Looking at Fig. 1, it is obvious that all the coating's surface is composed of hierarchical micro/ nanostructure. There is no significant difference in the