Corrosion Science 80 (2014) 177–183

Contents lists available at ScienceDirect

Corrosion Science

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

One-step method for the fabrication of superhydrophobic surface on magnesium alloy and its corrosion protection, antifouling performance

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ARTICLE INFO

Article history:
Received 21 May 2013
Accepted 19 November 2013
Available online 26 November 2013

Keywords:
A. Magnesium
A. Alloy
A. Organic coatings
B. Polarization
B. EIS
C. Microbiological corrosion

ABSTRACT

Inspired by the lotus leaf, various methods to fabricate artificial superhydrophobic surfaces have been developed. Our purpose is to create a simple, one-step and environment-friendly method to construct a superhydrophobic surface on a magnesium alloy substrate. The substrate was immersed in a solution containing ferric chloride ($FeCl_3 \cdot 6H_2O$), deionized water, tetradecanoic acid ($CH_3(CH_2)_{12}COOH$) and ethanol. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Fourier transformed infrared (FT-IR) were employed to characterize the substrate surface. The obtained surface showed a micron rough structure, a high contact angle (CA) of 165° ± 2° and desirable corrosion protection and antifouling properties.

1. Introduction

The phenomenon of superhydrophobicity which is known as "lotus effect" exists widely on the plant surfaces and the bodies of some animals and insects [1]. The design of artificial superhydrophobic surfaces with water contact angles of more than 150° is nature inspiredly. Over the past few decades, many efforts have been made to replicate the micro/nanostructures with their special water-repellent and self-cleaning properties [2]. Practical applications include the production of anti-biofouling paints [3], reducing fluid resistances [4], corrosion resistance [5], self-cleaning surfaces [6], stain resistant textiles [7], and anti-icing coating [8].

After decades of development, there are various methods to create the superhydrophobic surface such as chemical vapor deposition [9,10], chemical etching [11,12], sol–gel techniques [13–15], hydrothermal synthesis [16], physical vapor deposition [17], layer-by-layer self-assembly [18], and electrospinning [19]. Generally, the way to fabricate an artificial superhydrophobic surface involves two steps: the first step is to form a surface with a micro/nano-structured roughness and then to modify that surface using low-surface-energy substances [20–22]. For example, Ishizaki and co-workers fabricated a superhydrophobic surface on a magnesium alloy coated with nanostructured cerium oxide film and used fluoroalkylsilane (FAS) to enhance the surface hydrophobicity [23]. Wang et al. prepared a conformal silica shell on the surface of a ZnO nanorod by a bioinspired layer-by-layer deposition method and the ZnO/SiO_2 nanorod array was modified with an octadecyltrimethoxysilane self-assembled monolayer [24]. However, the fabrication of such micro/nanostructures usually requires special conditions, expensive materials and complicated procedures, limiting its widespread use. Furthermore, most existing methods involve the use of biological poison materials, such as FAS and rf-sputtered Teflon, to achieve a low energy surface.

Therefore, if both steps can be made in just one step, the process of preparing superhydrophobic surface would be simplified [21]. Organic acid solution immersion is one method to achieve surface roughness and surface energy reduction [21]. As long chain aliphatic acid having hydrophobic hydrocarbon side effects, so it reacts with substrates and also play a role in the surface modification. Because of this, tetradecanoic acid is to be taken as a model system. A surface treated with tetradecanoic acid is environment-friendly [25] and fulfils this purpose; the tetradecanoic acid is safe to use with its natural existence of long chain fatty acids.

Magnesium alloy is one of the lightest engineering materials. Due to its superior properties, such as low density, high weight ratios and good heat dissipation, it is expected to be an excellent material for reducing vehicle weight, increasing equipment strength and reducing fuel consumption [26–28]. However, the extremely drawback is low corrosion resistance and chemical stability in corrosive medium. A superhydrophobic coating would be a promising technology for improving corrosion protection because

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0010-938X/$ - see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.corsci.2013.11.026

it would inhibit the contact of a surface with environmental humidity. Jiang et al. fabricated a superhydrophobic surface on a Mg–Li alloy, followed by immersion and annealing processes using FAS [29].

In this paper, we report a simple, one-step and environment-friendly process for the formation of a tetradecanoic acid iron ($Fe(CH_3(CH_2)_{12}COO)_3$) superhydrophobic surface on AZ31 magnesium alloy. The coating with micron rough structure and high contact angle produces AZ31 magnesium alloy with desirable corrosion protection and antifouling properties.

2. Experimental section

2.1. Materials

All reagents were of analytical grade and used as received without further purification. Magnesium alloy AZ31, 1.5 mm think, was used as the substrate (composition: 2.98 wt% Al, 0.88 wt% Zn, 0.38 wt% Mn, 0.0135 wt% Si, 0.0027 wt% Fe, 0.002 wt% Ni, 0.001 wt% Cu, and the remaining is Mg).

2.2. Preparation of the magnesium alloy

In a typical process, preparation for the substrates was the following: magnesium alloy AZ31 substrates, 30 mm × 20 mm × 1.5 mm, were abraded with silicon carbide papers (from 600 # to 2000 #), and then ultrasonically degreased in absolute ethanol for 10 min, followed by ultrasonication with deionized water for 10 min. After that, the substrates were dried under atmospheric conditions.

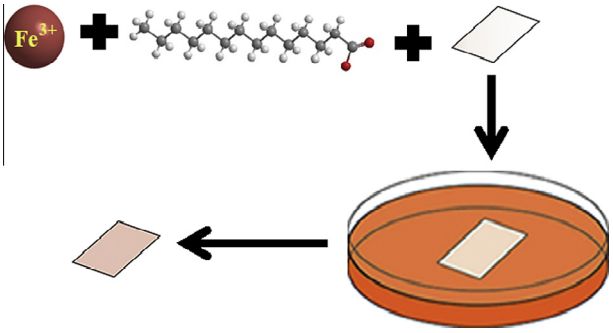
2.3. Formation of the superhydrophobic surface

The mixture of the solution is important for the formation of the superhydrophobic surface. Firstly, tetradecanoic acid (4.567 g) was dissolved in 100 ml of ethanol, and ferric trichloride hexahydrate (5.406 g) was dissolved in 100 ml of deionized water. Secondly, the ferric trichloride solution was added dropwise into the tetradecanoic acid ethanol solution while stirring magneticlly at room temperature.

After completion of the addition of the ferric trichloride solution, the mixed solution was stirred until it became uniform and transparent. Thirdly, the solution was placed in a 60 °C water bath. Subsequently, the cleaned magnesium alloy substrates were immersed in it. After 2 h, the substrates were taken out and thoroughly washed several times with ethanol and deionized water, respectively. Finally, the washed substrates were dried at 60 °C for 2 h allowing the surface ethanol to gradually volatilize (Scheme 1).

2.4. Characterization

Morphological analysis was performed using a scanning electron microscope (SEM, JEOL JSM-6480A). Static water contact angles of the surfaces were estimated with a FTA200 drop shape analysis system using a water drop volume of 2 μL. The average CA value was determined by measuring the same substrate at five different positions. The chemical state of the substrates surface was analyzed by X-ray photoelectron spectroscopy (XPS, PHI-5700, Perkin–Elmer, USA). The Al Kα radiation ($h\nu$ = 1486.6 eV) was used as the excitation source, and the binding energy 284.5 eV of C1s in hydrocarbon was used as the reference. Fourier-transform infrared (FT-IR) spectra were recorded with an AVATAR 360 FT-IR spectrophotometer. The electrochemical properties of the as-obtained substrate surface were determined in 3.5 wt% NaCl aqueous solution, using an electrochemical workstation (Princeton Applied Research, VMP3/Z), equipped with a standard three-electrode system with an Ag/AgCl reference electrode, a platinum mesh as the counter electrode, and the sample as the working electrode. The working electrode was set in a homemade holder of Teflon, which had a circular window of area 1 cm^2 exposed to the electrolytic solution. The potentiodynamic polarization curves were measured at a scanning rate of 1 mV s^{-1} from 400 to 800 mV. The electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 5 mV. All measurements were made at room temperature. Surface microbial adhesion was observed by scanning electron microscope. And the initial population of local natural water was measured by plate colony-counting methods.



Scheme 1. Schematic representation of the fabrication of tetradecanoic acid iron on the surface of AZ31 magnesium alloy.

3. Results and discussion

3.1. Morphology and wettability of the superhydrophobic surface

The morphology of the as-prepared superhydrophobic surface was studied from SEM images. The micrograph in Fig. 1a shows a large number of tufted microstructures evenly covering the substrate surface. And it can be seen there is a few microcracks on the surface (the yellow circle as shown in figure). The irregular arrangement of these micro clusters is composed of numerous nanosheets, 300–400 nm thick, length of 1–2 μm, with neighboring lamellae randomly overlapping and joining each other (Fig. 1b).

Fig. 1c suggests the as-prepared surface is hydrophobic. The wettability of the surface was studied in detail by water static contact angle measurements. According to the test results, the as-prepared surface is so hydrophobic that a water droplet deposited on the surface forms almost a round sphere with a high CA of 165° ± 2° (Fig. 1d), which is much higher than the untreated magnesium alloy surface (34° ± 2°). Moreover, the water droplets barely stick to the surface and roll off easily, which indicates that the magnesium alloy successfully acquired a superhydrophobic surface by our one-step process. We attribute the enhanced superhydrophobic behavior to the high surface roughness of micron structures.

3.2. Composition of the superhydrophobic surface

The chemical composition of the as-prepared surface was studied by XPS and FT-IR.

XPS analysis was used to determine the chemical composition and the nature of the chemical bonding on the as-prepared surface. From the full survey spectrum (Fig 2a), signals of O 1s, C 1s, and Fe 2p peaks are detected. The elemental composition obtained from XPS analysis atomic concentration ratio of Fe, C and O was found