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The fabrication and hydrophobic property of micro-nano patterned surface on magnesium alloy using combined sparking sculpture and etching route

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ABSTRACT

Magnesium alloy with micro-nano structure roughness surface, can serve as the loading reservoirs of medicine capsule and industrial lubricating oil, or mimic 'lotus leaf' hydrophobic surface, having the potential applications in medical implants, automobile, aerospace and electronic products, etc. Herein, we propose a novel strategy to design a micro-nano structure roughness surface on magnesium alloy using combined microarc sparking sculpture and etching in CrO_3 aqueous solution. A hydrophobic surface (as an applied example) was further fabricated by chemical decorating on the obtained patterned magnesium alloy surface to enhance the corrosion resistance. The results show that the combined micro-nano structure of 7–9 μm diameter big pores insetting with nano-scale fine pores was duplicated after etched the sparking sculptured 'over growth' oxide regions towards the magnesium substrate. The micro-nano structure surface was chemically decorated using $AgNO_3$ and stearic acid, which enables the contact angle increased from 60° to 146.8°. The increasing contact angle is mainly attributed to the micro-nano structure and the chemical composition. The hydrophobic surface of magnesium alloy improved the corrosion potential from −1.521 V of the bare magnesium to −1.274 V. Generally, the sparking sculpture and then etching route demonstrates a low-cost, high-efficacy method to fabricate a micro-nano structure hydrophobic surface on magnesium alloy. Furthermore, our research on the creating of micro-nano structure roughness surface and the hydrophobic treatment can be easily extended to the other metal materials.

1. Introduction

Magnesium alloy with micro-nano structure roughness surface, can serve as the loading reservoirs of medicine capsule and industrial lubricating oil, or mimic 'lotus leaf' hydrophobic surface, which are expected to extend the wide applications in medical implants, automobile, aerospace and electronic products [1–3], etc. Methods to fabricate the micro- or/and nano-scale structure were mainly composed of laser engraving [4] and mechanical machining. However, these methods always have some limitations, such as the high-cost special devices, the low efficiency when required for large area or special shape samples, etc. Herein, we propose a novel strategy to design a micro-nano structure roughness surface on magnesium alloy using combined microarc sparking sculpture and etching in CrO_3 aqueous solution.

Nevertheless, the corrosion resistance of the micro-nano structure roughness surface on magnesium alloy is still a challenge for practical application as the high metal reactivity of magnesium [5]. Up to now, many strategies have been developed to improve the corrosion resistance of magnesium alloy, such as alloying [6–8], protective coatings [8–12] and surface treatments [13–16]. Since the micro-nano structure exists on the surface, super-hydrophobic treatment is a considerable approach among the various methods. Hydrophobic surface prevents the water to contact with the substrate easily, so that the corrosion resistance of the metal enhanced. Moreover, the super-hydrophobic surface has self-cleaning [17–22] and antisticking [23,24] properties, which is of special interest in both academic and industries field.

In nature, many plant leaves have super-hydrophobic surface, such as the lotus leaf. The lotus leaf has a wax-like component

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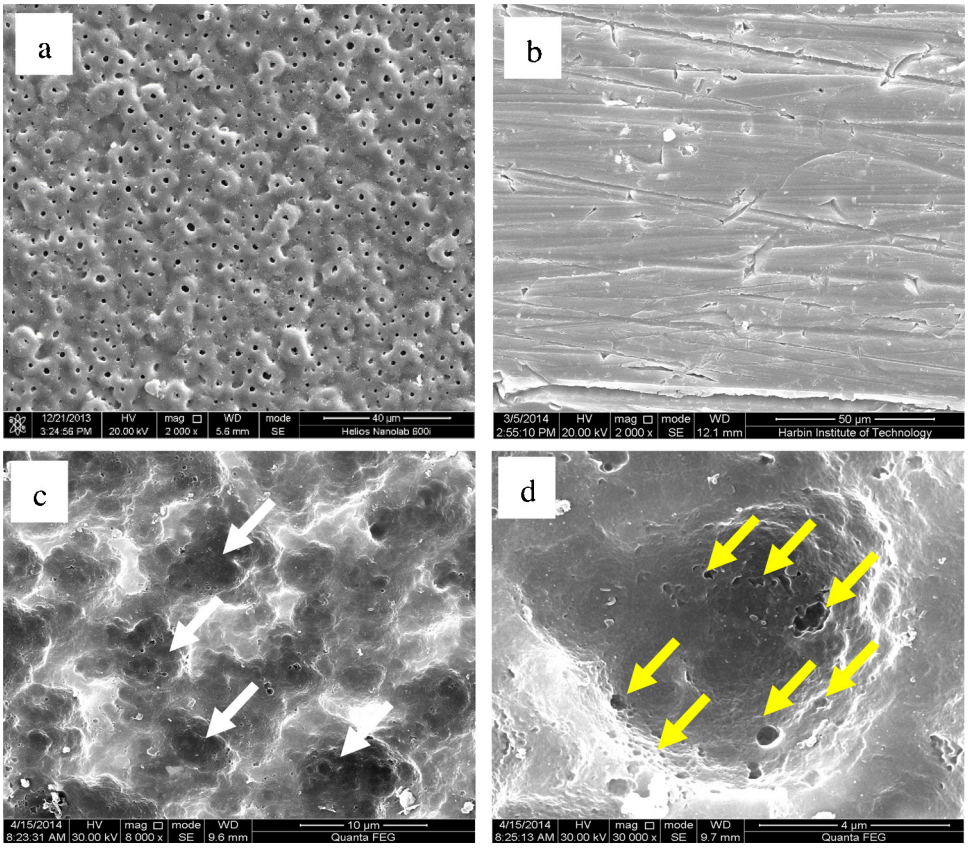

Fig. 1. SEM images of (a) the sample surface after MAO treatment; (b) bare magnesium immersed into CrO_3 solution for 2 h; (c) the micro-nano structure surface of the coated sample after etching; (d) the local magnified morphology of Fig. 1(c) (the white arrows show the microscale of the structure and the yellow arrows shows the nanoscale of the structure). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and a micro-, nano-scale roughness surface, in which the wax-like component provides hydrophobic to the leaf because of the low surface energy and the roughness surface enhances the hydrophobic degree [5]. Inspired by the structure of super-hydrophobic leaves, the micro-nano roughness surface and chemical composition to fabricate a low energy surface endow the water-repellent [25–30]. Thus far, various methods have been reported to fabricate the super-hydrophobic surface on magnesium alloys, including chemical etching [5,31–36], hydrothermal crystallization [37–39], polymer plating [40,41], chemical vapor deposition [42] and electrochemical machining [43–47], etc.

In this study, we propose a novel strategy to design a micro-nano structure roughness surface on magnesium alloy using combined microarc sparking sculpture and etching in CrO_3 aqueous solution. The produced micro-nano structure surface exhibits an apparently increasing hydrophobic property. To further enhance the hydrophobicity of the micro-nano structured magnesium surface, the samples were chemically decorated with the sequent steps: immersed and etched in 0.1 mol/L $AgNO_3$ aqueous solution for 90 s and then modified by 0.1 mol/L stearic acid ethanol solution ($CH_3(CH_2)_{16}COOH$) for 2 h. Meanwhile, the wettability and electrochemical tests were carried out to evaluate the hydrophobic properties and corrosion resistance of the surface treated samples.

2. Material and methods

2.1. Materials and sample preparation

The Φ10 mm × 1 mm round AZ31B magnesium alloy plates composed of 2.5–3.0 wt.% Al, 0.7–1.3 wt.% Zn, 0.2 wt.% Mn and Mg balance were used in this study. The plates were degreased with acetone in ultrasonic bath, abraded using SiC papers (from 400 to 2000 grades), rinsed with distilled water and dried in air at room temperature. The combined micro-nano structure of the magnesium alloy surface, with big pores insetting with nano-scale fine pores, was prepared by a duplex process of microarc sparking sculpture and etching in CrO_3 aqueous solution.

Firstly, the sparking sculptured 'over growth' oxide regions towards the magnesium substrate were formed by a microarc oxidation (MAO) method. The magnesium plates were used as the anodes and a stainless steel plate was used as a cathode in the electrolyte bath for microarc oxidation treatment. The electrolyte was prepared by the dissolution of reagent-grate chemicals of $Ca(H_2PO_4)_2$ (10 g/L), Na_2SiO_3 (15 g/L) and NaOH (10 g/L) into deionized water. Pulse frequency and duty cycle were fixed at 600 Hz and 8%. The temperature of the electrolyte was kept under 40 °C by a cooling system. The MAO ceramic coatings with a large number of the sparking sculptured 'over growth' oxide regions towards the magnesium substrate were produced at a constant voltage of 400 V for 5 min. The samples were rinsed in distilled water and dried in air at room temperature for the subsequent treatment of CrO_3 solution etching to strip the oxide coatings from magnesium alloy.

To obtain the micro-nano structure with big pores insetting with nano-scale fine pores on magnesium alloy surface, the coated samples with sparking sculptured 'over growth' oxide regions towards the magnesium substrate were firstly immersed into the 200 g/L CrO_3 aqueous solution for 2 h to strip the oxide coatings, especially etching the 'over growth' oxide regions to reproduce the micro-nano structured porous roughness surface on the magnesium alloy.

To further enhance the hydrophobicity of the micro-nano structured magnesium surface, the samples were chemically decorated with the sequent steps: etched in 0.1 mol/L of $AgNO_3$ aqueous solu-