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Fabrication of non-wetting surfaces on zinc surface as corrosion barrier

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ABSTRACT

Two kinds of non-wetting surfaces, super-hydrophobic surface (SHS) and slippery lubricant-infused porous surface (SLIPS), were fabricated on zinc surface with hydrothermal method. Their surface properties were characterized with FE-SEM, XRD, XPS and contact angle meter, and their corrosion protection performances were evaluated with electrochemical measurements. It was demonstrated that both kinds of surfaces present high corrosion resistance to the underlying zinc substrate for the air (or lubricant) layer trapped in film. In comparison with SHS, the SLIPS presents advantage in maintaining stability in corrosive medium. This research provides guidance for the selection of non-wetting surface in practical corrosion protection application.

1. Introduction

Zinc and zinc coating products are widely used in our daily life. However, zinc is easily corroded for its low potential. Surface modification is regarded as an effective corrosion protection strategy by hindering electrochemical reactions of underlying metal substrate. At present, numerous methods have been proposed for inhibition of zinc, such as conducting polymers [1–3], inhibitors [4–6], and so forth [7,8]. However, there are still many drawbacks along with these methods, such as high toxicity, complicated fabrication process. Thus, novel surface modification strategies are urgently required for corrosion protection of zinc.

Corrosion is a phenomenon that occurs on the metal/solution interface. The surface wettability can affect the corrosion process and mechanism of metal substrate [9]. Non-wetting surface is a potential strategy for metal corrosion protection [10–12]. As a typical non-wetting surface, super-hydrophobic surface (SHS) has attracted much attention for its potential application in our daily life, and it was proven to be an effective corrosion protection strategy for numerous kinds of metal [13–16]. Our previous studies demonstrated that the air layer can be trapped among microstructures of SHS for the capillary effect, and it is the essential contributor for the corrosion protection performance of SHS [17,18]. However, the air layer can be collapsed for the external wetting pressures during practical application [19]. Nepenthes pitcher plant provides an alternative idea to achieve non-wetting surface with capillary effect. It was reported that Nepenthes pitcher plant can lock-in a thin liquid layer with its porous micro-structures. The existence of liquid layer can repel the oil on the feet of insects, thereby causing insects to easily slide off the plant surface. Inspired by this idea, slippery lubricant-infused porous surface (SLIPS) was designed to exhibit non-wetting property to most kinds of liquid. Furthermore, SLIPS can withstand high drop impact pressure, and self-heal by capillary wicking upon damage. It can be expected that SLIPS is a potential strategy for corrosion inhibition of metal, and it may also present advantage in maintaining stability.

In this research, two kinds of non-wetting surfaces, SHS and SLIPS, were fabricated on zinc surface with hydrothermal method. Their surface properties were characterized with surface analysis techniques, and their corrosion protection performance and stability were evaluated and compared. Finally, the corrosion protection mechanisms of the two kinds of non-wetting surfaces were proposed. This research provides effective information about the performance comparison between the two typical kinds of non-wetting surfaces.

2. Experimental

2.1. Materials and reagents

Zinc foil with purity of ≥99.99 wt.% was purchased from Sinopharm Chemical Reagent Co., Ltd. The 1H,1H,2H,2H-perfluorodecyl-triethoxysilane (PFTEOS, 97%, Sigma-Aldrich), Perfluoropolyether (PFPE, Nascent™ FX-5200, Switzerland), and other chemical reagents with analytical grade were used as received, including ammonia, ethanol, and so forth.

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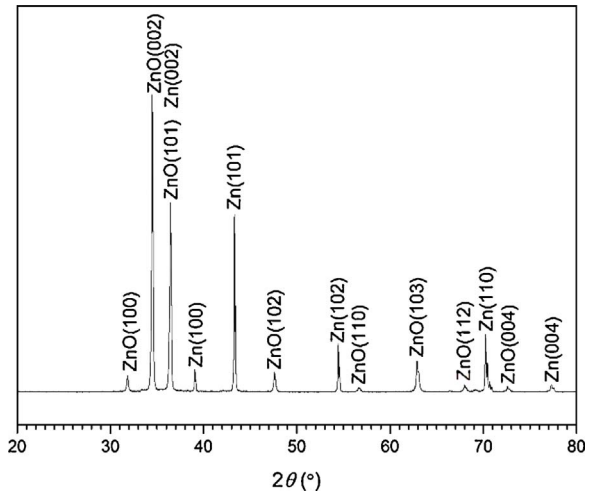

Fig. 1. XRD patterns of zinc foil after hydrothermal procedure.

2.2. Fabrication of SHS and SLIPS

To fabricate SHS, zinc foil was firstly abraded with emery paper (400 grade), degreased with ethanol, and then electrochemically polished in phosphoric acid/ethanol solution with volume rate of 37:63. The electrochemical polishing was performed under applied voltage of 20 V for 15 min at 5 °C in a two-electrode cell, in which, zinc sample is anode, and stainless is cathode. After the electrochemical polishing process, the sample was then transferred into a 100 mL Teflon-lined autoclave with 0.98 wt.% ammonia solution, and heated at 100 °C for 12 h. After hydrothermal process, the sample was immersed into 1 vol. % PFTEOS/ethanol solution, and then transferred into heating oven, and heated at 120 °C for 20 min.

SLIPS was fabricated on zinc foil by pouring lubricant PFPE over the SHS. The samples were then tilted with an angle of ~20° for 1 h to allow the excess lubricant to flow off.

2.3. Surface characterization

The morphology of sample was characterized with field emission scanning electron microscope (FE-SEM, Hitachi S4800). The X-ray diffraction (XRD) patterns of the sample were performed on an Ultima IV diffractometer (Rigaku, Japan) using Cu Kα radiation ($\lambda = 0.15418$ nm) with the 2θ ranging from 20° to 80°. The contact angles of 3 μL water droplet on bare and filmed zinc were measured with contact angle meter at ambient temperature. The x-ray photoelectron spectroscopy (XPS) measurement was carried out on a Thermo ESCALAB 250 photoelectron spectrometer equipped with an Al-anode at a total power dissipation of 150 W (15 kV, 10 mA), and the binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon.

2.4. Electrochemical experiments

Before electrochemical experiments, the zinc samples were mounted in the silicone with 10 mm × 10 mm area exposed for test. The open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and polarization curves were obtained with a computer-controlled electrochemical system (CHI 920C, CH Instruments Inc.) in 3.5 wt.% NaCl at ambient temperature. These experiments were performed in a three-electrode cell, in which, a platinum electrode is used as counter electrode, zinc sample as working electrode, and a silver/silver chloride (Ag/AgCl, 3 M KCl) electrode as reference electrode. EIS experiments were performed at open circuit potential with the amplitude of the perturbation voltage of 20 mV, and the test frequency range is from 10^5 to 10^{-2} Hz. The EIS results were analyzed by fitting the data using Zsimpwin software. Polarisation curves were performed by scanning the potential at a rate of 1 mV s^{-1}. Each test was repeated more than three times to verify the repeatability of results.

3. Results and discussion

3.1. Morphology, composition and wettability

XRD was utilized to characterize the composition of layer formed over zinc foil. According to the XRD patterns of zinc after hydrothermal procedure (Fig. 1), the peaks located at 62.9°, 47.6° and 34.4° are ascribed to (103), (102) and (002) planes of ZnO [PDF No. 36-1451], respectively. The peaks ascribed to (100), (101) and (102) planes of Zn [PDF No. 04-0831] can be observed from the XRD patterns. It is indicated that ZnO is the main composition of layer formed on zinc substrate after hydrothermal procedure.

Fig. 2 presents the micro-morphology of ZnO layer formed over zinc substrate. It can be found that ZnO arrays form over zinc surface (Fig. 2a). The amplified SEM picture (Fig. 2b) demonstrates that hexagonal rods with typical diameter of 0.5 μm grow along [001] direction over zinc substrate. During hydrothermal process, Zn can react with H_2O to form $Zn(OH)_2$, which can be further dehydrated to ZnO according to the Reactions (1) and (2).

$$Zn + 2H_2O = Zn(OH)_2 + H_2 \quad (1)$$

$$Zn(OH)_2 = ZnO + H_2O \quad (2)$$

Furthermore, Zn can also react with ammonia to form complex

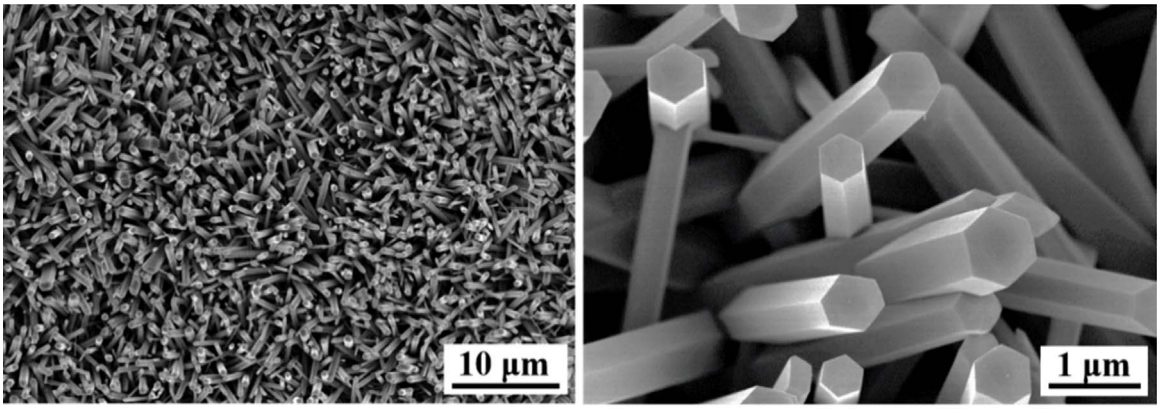

Fig. 2. Micro-morphology of ZnO film formed over zinc surface.