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One step phase separation process to fabricate superhydrophobic PVC films and its corrosion prevention for AZ91D magnesium alloy

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ABSTRACT

A one step, simple fabrication method to prepare independent superhydrophobic polyvinyl chloride (PVC) coating is reported in this paper. The rough surface structure and low surface energy could be simply obtained only by a phase separation process. The independent PVC superhydrophobic film was also applied on AZ91D magnesium alloy. Scanning electron microscopy (SEM), water contact angle measurements, electrochemical test and adhesion tests have been performed to characterize the surface morphology, wettability, anti-corrosion and adhesion strength of independent PVC film and superhydrophobic magnesium alloy respectively. The results indicated that whether it was the PVC film or superhydrophobic magnesium, they show static contact angles higher than 150°, excellent anti-corrosion effect and adhesion strength. We believed that the presented method could provide a straightforward and simple route to fabricate low-cost and anti-corrosion coating on various substrate materials. Moreover, this one step process may find potential application in the field of industry because of its simplicity and universality.

1. Introduction

In recent decades, the famous lotus effect, which is called superhydrophobic property with a water contact angle (CA) greater than 150° and a sliding angle (SA) less than 10°, was popularly reported [1–3]. The study of superhydrophobic materials has been receiving considerable attention for their special functions, such as water repellency [4], self-cleaning [5], anti-icing [6] and anti-corrosion [5]. Generally, superhydrophobic researches are divided in two types: one type is that fabricating superhydrophobic surface on substrate, which includes glass [7,8], silicon wafer [9,10], etc. and non-metal materials and copper [11], aluminum alloy [12], magnesium alloy [5,6], etc., in addition to metal materials. The other type is that preparing superhydrophobic coating or superhydrophobic and superoleophilic coating by using supermolecule or macromolecule to achieve superhydrophobicity [13–15]. Compared with the first type, the second one can be easily prepared without limitation of substrates and the used materials are easily obtained and are of low cost. Polyvinyl chloride (PVC), polystyrene (PS), and polypropylene (PP) are usually used to prepare superhydrophobic film due to their intrinsic hydrophobicity and low-cost. Kang et al. prepared superhydrophobic PVC surface [15]; Yuan et al. [13] and Aruna et al. [16] prepared superhydrophobic PS film; Patel and Chase obtained superhydrophobic PP film [17]. All the superhydrophobic polymer films were fabricated by non-solvent inducing phase separation method without further modification. However, so far most studies have focused on the preparation process of these independent superhydrophobic films. And research about the application of these films is extremely rare. Self-cleaning [5], anti-icing [6] and anti-corrosion [5,6] applications are well known to all researchers due to the excellent water repellency of superhydrophobic materials. Among them, anti-corrosion application, which can expand application scope, plays an important role, especially for metal materials [5,18,19].

Magnesium alloys, as one of important metallic engineering materials, have been applied in aerospace industries, aircraft and automobile for their low density, high strength-to-weight ratio, excellent machinability, good damping properties, fine electromagnetic interference shielding properties and easy recyclability [6,18,20,21]. However, low corrosion resistance limits their widespread application [18]. So it is significant to improve the anti-corrosion ability to widen the application of magnesium alloy.

In this paper, independent superhydrophobic PVC films were prepared via a facile solvent/non-solvent coating process without introducing low surface energy material. And this superhydrophobic film was applied on AZ91D magnesium surface by a dip-coating method. Research results indicated that the as-prepared superhydrophobic film behaved with excellent corrosion resistance and

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stable superhydrophobic performance in acid, alkali and salt corrosive solutions. And it also shows very good corrosion protection for AZ91D magnesium. This fabrication approach was low-cost and facile to carry out without using special reagents or complex equipments. It could be widely applicable and it is easy to prepare large-area superhydrophobic surface on various substrate materials for corrosion resistance.

2. Experimental

2.1. Materials

PVC (polyvinyl chloride) powder is obtained from No. 2 Chemical Corporation (SG5 type). PVC, THF (tetrahydrofuran) and other chemicals are purchased from Chongqing Boyi chemical manufacturing Co., Ltd. All chemicals are analytical reagent grade and used without further purification.

Specimens of AZ91D magnesium alloy (wt. fraction: Al 8.8%, Zn 0.74%, Mn 0.18%, balance Mg) were cut from an as-cast ingot with a size of 50 mm × 20 mm × 5 mm.

2.2. Preparation of superhydrophobic film

0.6 g PVC powder was dissolved in 15 mL THF at 30 °C for 40 min to obtain homogeneous PVC solution. Then different concentrations of ethanol ranging from 25% (v/v) to 70% (v/v) were added into the PVC–THF solutions by drops and continuous stirring for 30 min. The solution was then poured into cleaned glass Petri dishes and dried in fume cupboard for 24 h at 30 °C. Films with various amounts of PVC ranging from 400 mg to 1000 mg were also prepared in the same manner. All film samples were kept in desiccators until further use.

2.3. Preparation of superhydrophobic coating on ZA91D magnesium surface

AZ91D magnesium alloys were grounded with SiC sandpaper from 150 to 1500 mesh, washed with distilled water, and then ultrasonically cleaned in acetone for 5 min.

The fabrication of superhydrophobic coating mainly contains two steps: anodization (10 V, 15 min) of magnesium and dip coating of PVC–THF solutions (an approximate speed of 1.8 mm/s at room temperature).

The detailed fabrication method of superhydrophobic coating on magnesium alloys is shown in Scheme 1. It can be seen that three kinds of hydrophobic films with different layer of PVC were prepared on magnesium surface. In condition A, the magnesium surface after anodization is covered with a PVC film without phase separation and the surface morphology remains unchanged. The coating does not show superhydrophobicity (CA ≅ 93°). In condition B, porous and discontinuous nanostructure is formed on the former PVC film, and the superhydrophobicity is evidently improved from 93° (CA value) to 138°. But the water drop may adhere to the discontinuous location without forming a continuous air film between the water and PVC film. Then, in order to obtain superhydrophobic PVC coating, the third PVC film is prepared on the former coating as illustrated in condition B. In condition C, superhydrophobicity is successfully obtained by preparing a continuous and porous nanostructure. In this paper, the condition C was well studied.

2.4. Characterization and tests

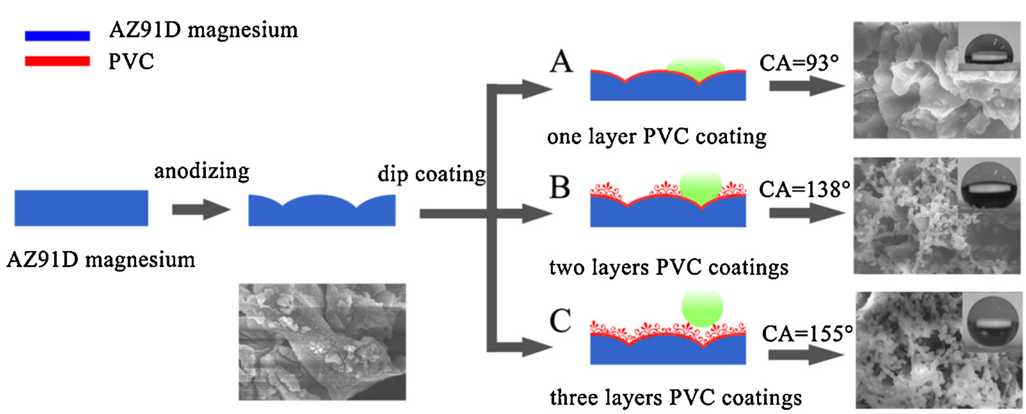
The water contact angle and sliding angle were measured with a water drop volume of 5 μL using an optical contact angle meter (POWEREACH JC2000C1) at room temperature. The values reported are averages of five measurements made on different positions of the sample surface. SEM images were obtained on a scanning electron microscope (SEM; HITACHI S-4800).

The corrosion resistance of superhydrophobic PVC coating for magnesium was evaluated by means of potentiodynamic polarization using a classical three electrodes cell with platinum as a counter electrode, saturated calomel electrode (SCE, +0.242 V vs. SHE) as reference electrode, and the samples with an exposed area of 1 cm^2 as working electrode, in four corrosive solutions at room temperature. The potentiodynamic polarization curves were performed by electrochemical workstation (CorrTest CS350) with a constant voltage scan rate of 1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were performed with CS350 Electrochemical Workstation. The employed amplitude of the sinusoidal signal was 10 mV, and the frequency range studied was from 10^5 to 10^{-2} Hz. The corrosive media for the electrochemical corrosion tests were neutral 3.5 wt.% NaCl solution, 0.6 mol L^{-1} Na_2SO_4, NaOH solution with a pH value of 13 and H_2SO_4 solution with a pH value of 3. All corrosion tests were normally repeated at least three times under the same conditions, checking that they presented reasonable reproducibility.

3. Results and discussion

3.1. The influence of non-solvent on structure and superhydrophobicity

The researches indicated that adding non-solvent into film-forming solution can cause enhanced phase separation, which could increase the corresponding surface roughness [13,22].



Scheme 1. The schematic diagram of fabricating superhydrophobic PVC on AZ91D magnesium surface.