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Facile transition from hydrophilicity to superhydrophilicity and superhydrophobicity on aluminum alloy surface by simple acid etching and polymer coating

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ABSTRACT

The transition from the hydrophilic surface to the superhydrophilic and superhydrophobic surface on aluminum alloy via hydrochloric acid etching and polymer coating was investigated by contact angle (CA) measurements and scanning electron microscope (SEM). The effects of etching and polymer coating on the surface were discussed. The results showed that a superhydrophilic surface was readily obtained after acid etching for 20 min and a superhydrophobic surface was readily fabricated by polypropylene (PP) coating after acid etching. When the etching time was 30 min, the CA was up to 157°. By contrast, two other polymers of polystyrene (PS) and polypropylene grafting maleic anhydride (PP-g-MAH) were used to coat the aluminum alloy surface after acid etching. The results showed that the CA was up to 159° by coating PP-g-MAH, while the CA was only 141° by coating PS. By modifying the surface with the silane coupling agent before PP coating, the durability and solvent resistance performance of the superhydrophobic surface was further improved. The micro–nano concave–convex structures of the superhydrophilic surface and the superhydrophobic surface were further confirmed by scanning electron microscope (SEM). Combined with the natural hydrophilicity of aluminum alloy, the rough micro–nano structures of the surface led to the superhydrophilicity of the aluminum alloy surface, while the rough surface structures led to the superhydrophobicity of the aluminum alloy surface by combination with the material of PP with the low surface free energy.

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1. Introduction

Recently, superhydrophilic surfaces with a water contact angle (WCA) below 10° and superhydrophobic surfaces with a WCA higher than 150° have attracted much interest, due to their conveniences in many fields, such as enhanced boiling heat transfer, self-cleaning and contamination inhibiting [1–9]. These widespread applications have motivated great efforts to improve the preparation techniques of superhydrophilic and superhydrophobic surfaces. In general, the wettability of a solid surface is strongly influenced by the chemical composition and its geometric structure [10]. So far, many methods have been used

for fabricating superhydrophilic and superhydrophobic surfaces by changing the chemical composition and the geometric structure in recent years [11–24]. Among these methods, surface roughness has been focused on designing superhydrophobicity or superhydrophilicity [25–31]. Generally, a superhydrophilic surface can be obtained by improving the roughness of a hydrophilic surface, while a superhydrophobic surface can be realized by improving the roughness of a hydrophobic surface or modifying a rough surface by materials with low surface free energy [2,32]. Therefore, the roughness is crucial for the preparation of superhydrophilic and superhydrophobic surfaces. So far, many methods have also been developed to fabricate rough surfaces [33–37].

If the WCA of a surface is lower than 90°, the surface is described as a hydrophilic surface, which has relatively high surface energy. In a contrast, if that of a surface is higher than 90°, the surface is described as a hydrophobic surface, which has low surface energy. For smooth surfaces, WCA can be represented by the Young's equation and the surface with lower surface energy has higher

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WCA [38]. For rough surfaces, the wetting state can be described by the Wenzel model, which assumes that the liquid is in intimate contact everywhere with the rough surface, and completely fill any surface structures [39,40]. According to the equation of Wenzel,

$$\cos \theta_c = \frac{r(\gamma_{SG} - \gamma_{SL})}{\gamma_{LG}} = r \cos \theta \quad (1)$$

where r is the roughness factor of a rough surface, θ is the WCA of a smooth surface, and θ_c is the CA of rough surface. When θ is lower than 90° , θ_c will decrease with the increment of r . In other words, the roughness factor (r) in the Wenzel equation can enhance the natural state of the material, and gives hydrophilic surfaces a lower contact angle and hydrophobic surfaces a larger contact angle. When the roughness factor is enough large, superhydrophilic or superhydrophobic surfaces could be obtained. Therefore, both of superhydrophilic surfaces and superhydrophobic surfaces could be explained by the Wenzel model. On the other hand, the Cassie–Baxter model introduces another new wetting state and assumes that the liquid is in partial contact with the rough surface [41]. At this time, the liquid may span across surface structures and leaving trapped air. Both the Cassie–Baxter and Wenzel states can cause high static contact angles on a hydrophobic surface, but only the Cassie–Baxter state can lead to a very low sliding angle. Therefore, a true superhydrophobic surface is much fit to the Cassie–Baxter state and could be calculated more precisely by the Cassie–Baxter equation [42,43].

Aluminum alloys have been applied extensively in our daily life because of their good performance. Therefore, the fabrication of superhydrophilic and superhydrophobic surfaces on aluminum alloys is of importance. Since the natural wettability of aluminum alloys is hydrophilic, a facile method for fabricating a superhydrophilic surface on aluminum alloys is to enhance the surface roughness, while a suitable method for fabricating a superhydrophobic surface on aluminum alloys is to modify a rough surface by materials with low surface free energy. Therefore, aluminum alloy surfaces with superhydrophilicity or superhydrophobicity must firstly be processed to obtain rough structures. Secondly, for obtaining superhydrophobic surfaces on aluminum alloys, the rough surfaces must be modified by materials with low surface free energy because of their natural hydrophilicity. Though some methods and low surface free energy materials have been applied to prepare the superhydrophobic surfaces on metal substrates [44–47], the existing problems, such as complicated processes, expensive materials and poor durability, severely hindered the extensive applications of superhydrophilic or superhydrophobic surfaces.

In this work, a facile and simple method of acid etching combining with coating polymer was used to prepare superhydrophilic and superhydrophobic surfaces on an aluminum alloy and realize the transition from the hydrophilicity to the superhydrophilicity and superhydrophobicity. Here, the rough surfaces were achieved by the simple acid etching method and then coated by polymers with low surface free energy. Both the different etching times and different polymer coatings were studied. The morphologies of the surfaces were observed by scanning electron microscope (SEM) and were used to elucidate the superhydrophilic or superhydrophobic mechanisms. In this work, the method for fabricating the superhydrophilic and superhydrophobic aluminum alloy surfaces is simple and the transition from the hydrophilicity to the superhydrophilicity and superhydrophobicity is readily realized. Moreover, the used materials are inexpensive. Thus, this method of acid etching and polymer coating is expected to be used extensively.

2. Experimental

2.1. Materials

Aluminum alloy (5B02) was kindly supplied by Zhuzhou Electric Locomotive Co., Ltd. PP (Q/SH 3045050) and PS (GB/T 12671–2008) were purchased from China Petrochemical Shanghai Petrochemical Industry Co., Ltd. PP-g-MAH with 1.5% grafting ratio was purchased from Dupont Company of America. Silane coupling agent (DL-171) was purchased from Hubei DeBang Chemical New Material Co., Ltd. Other chemicals were commercially available and used as received.

2.2. Preparation of superhydrophobic surface on aluminum alloy

The substrates used in our experiment were aluminum alloy plates (2.0 cm × 2.0 cm × 0.2 cm), which were ultrasonically cleaned successively in alcohol and deionized water baths after polishing with 600 mesh sand paper and dried for the following processing. In a typical acid etching experiment, a cleaned aluminum alloy plate was immersed into a hydrochloric acid solution with the concentration of 4 mol/L for some time at 20 °C. The etched aluminum alloy plate was then cleaned with deionized water and dried in a vacuum drying oven at 70 °C. The dried aluminum alloy plate was then immersed into the polymer/dimethylbenzene solution for 30 s at 80 °C for polymer coating. The coated aluminum alloy plate was taken out to dry in air at room temperature.

2.3. Characterizations

The macroscopic digital photographs were taken by a digital camera (PowerShot A700, Canon) at room temperature. The volume of a water droplet for macroscopic observation was 50 μL. The microscopic contact angles (CAs) were measured by an optical contact angle meter (OCA20) at room temperature. The volume of a water drop was 5 μL. The morphologies of the surface were observed by a scanning electron microscope (SEM) (S-3000N, Hitachi). To avoid the possible influence of sputtered Pt, all of the SEM observations of the surfaces were performed without sputtering Pt.

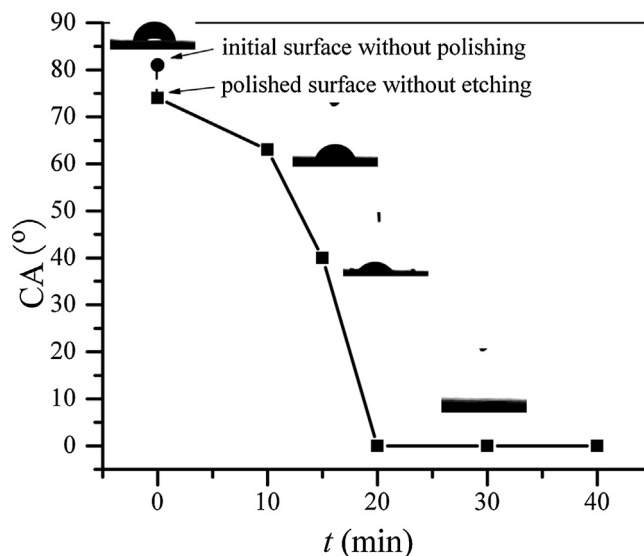


Fig. 1. The relationship of the surface CAs after polishing and etching with etching time (the insets are the CA images).

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