Research Article

Fabrication and Corrosion Resistance of Superhydrophobic Hydroxide Zinc Carbonate Film on Aluminum Substrates

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1. Introduction

Aluminum and aluminum alloys have been widely used in household and industrial fields such as marine, autoaviation, and aerospace industries, owing to their significant advantages, including high-specific strength, excellent heat and electric conductivities, and low-specific weight [1, 2]. Also, aluminum has high resistance to corrosion due to the presence of a thin, compact oxide film that spontaneously formed on the metal surface. However, aluminum is active and prone to corrosion in contact with water, especially in corrosive environment such as in aqueous solution containing Cl− ions [3], then it limits the scope of application of aluminum and aluminum alloy. So, it is necessary to enhance the corrosion resistance property of aluminum in corrosive environment which will greatly extend their applications as engineering materials.

In recent years, inspired by the nature, superhydrophobic surfaces with water contact angle of larger than 150° have attracted much attention due to their self-cleaning and water-repelling properties [4–6]. Investigation on the representative example of the natural superhydrophobic surface, lotus leaf, revealed that the superhydrophobicity stemmed from the cooperation of wax-like component on leaf surface and surface roughness at micro- and nanoscales [7]. In this way, people developed two strategies to fabricate artificial superhydrophobic surfaces: roughen the surface of hydrophobic materials or chemically modify a rough surface with low-surface-energy material [8–10]. Traditionally, superhydrophobic metallic surfaces were produced by introducing microstructured compounds modified with low surface energy material onto substrates [11]. Till now, various techniques have been employed to create rough surfaces with different microstructures, such as electrochemical deposition [12], anodization...
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[13], phase separation [14], sol-gel process [15], layer-by-layer assembly [16, 17], chemical etching method [9].

Taking advantage of the characteristics of water repellency and low adhesion, superhydrophobic treatments have been applied on various engineering material surfaces such as steel, copper, zinc, titanium, and magnesium to improve their anticorrosion performances by providing an effective barrier to keep water, moisture, and corrosive medium away from contacting and reacting with the metal [18–24]. For instance, Ishizaki et al. [20, 21] promoted rapid formation of superhydrophobic surfaces on magnesium alloy by modified microstructured cerium oxide film with fluoroalkylsilane and the anticorrosion resistance of magnesium was significantly improved by the superhydrophobic treatment. Hu et al. [22] fabricated a superhydrophobic TiO2 film with water contact angle greater than 170° on the Hastelloy substrate after modification with fluoroalkylsilane molecules. Zhang et al. [23] prepared superhydrophobic films on titanium as effective corrosion barriers via the combination of electrochemical oxidation and modification of perfluoroctyltriethoxysilane. Su et al. [24] discussed the tunable wettability of hydroxide zinc carbonate (HZC) film on zinc plates from superhydrophilic to superhydrophobic by altering the type of solvent, but no further study on anticorrosion properties was reported.

In this paper, we attempt to present a facile method for fabricating superhydrophobic surfaces through modulating different morphologies of hydroxide zinc carbonate (HZC) films deposited on aluminum substrate by altering deposition conditions. The transformation of morphologies and wettability of the sample after FAS modification were analyzed. The corrosion resistance property of the superhydrophobic sample was also investigated.

2. Experimental Section

2.1. Deposition of HZC Film on Aluminum Substrate. All chemicals were of analytical grade and used without further purification. The HZC films were fabricated through an in situ deposition process; 2 × 2 cm2 aluminum plates (99.5%) with a thickness of 1.5 mm were used as the substrates for the deposition. The substrates were immersed perpendicularly in 0.5 M zinc nitrate aqueous solution containing different molar ratios of urea in a 3-neck, round bottom flask equipped with a Teflon-coated magnetic stir bar and reflux condenser and stirred at 95°C for 1.5 h. Then the aluminum substrates were washed several times with deionized water, were blown dry, finally were placed in an oven at 80°C for 1 h.

2.2. Modification of the Surfaces. The coated aluminum substrates were immersed in 50 mL of absolute ethanol solution containing 1 mL of FAS (CH2(CF2)2(C2H5)2SiOCH3)3 for 24 h at room temperature. The samples were then thoroughly washed with absolute ethanol several times, were blown dry; finally were placed in an oven at 60°C for 1 h.

2.3. Characterization. The surface morphologies of the obtained samples were investigated using a scanning electron microscopy (NOVATM NanoSEM 230) at 5 kV. The samples were coated with a thin layer of gold before measurement. The sessile drop method was used for water contact angle (WCA) measurements of the as-prepared surfaces using a data-physics OCA20 contact angle system at ambient temperature. The water droplet size used for measurements was 5.0 μL. The average WCA value was obtained by measuring more than five different positions for the same sample. The crystal structure of the samples was characterized by X-ray diffraction (XRD) on PANalytical X’Pert Pro. MPD X-ray diffractometer with Ni filtered Cu Ka radiation of 1.542 Å at the scan rate of 0.08 °s⁻¹. The chemical bonding mode of the films fabricated on aluminum substrate was investigated by Fourier transform infrared spectrometer (FTIR) spectroscopy (Shimadzu IRAffinity-1), and the films were scratched from aluminum substrate and pressed into tablets with KBr. The chemical composition of the sample’s surface was characterized using X-ray photoelectron spectra (XPS) in a Kratos Axis Ultra DLD system, using Al Kα radiation as the exciting source. All binding energies in the spectra were corrected using standard binding energy of C 1s peak (284.6 eV) as reference. Electrochemical impedance spectroscopy (EIS) was performed on a CHI 604C electrochemical analyzer (Shanghai ChenHua Instrument, China) in 3.5 wt% NaCl aqueous solution at room temperature with a three-electrode system. An untreated or superhydrophobic aluminum plate was used as the working electrode, a platinum plate, and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The potentiodynamic polarization curves were subsequently measured with respect to the open circuit potential (OCP) at a scanning rate of 10 mV/s from –1100 to + 400 mV.

3. Results and Discussion

3.1. Morphology and Wettability of Sample. Figure 1 shows typical SEM images of (a) the untreated aluminum substrate and the sample surfaces after in situ deposition in zinc nitrate aqueous solution under different molar ratios between Zn(NO3)2·6H2O and CO(NH2)2: (b) 10:1; (c) 5:1; (d) 2:1; (e) 1:2; (f) 1:5. The wetting properties of the sample surfaces fabricated by in situ deposition in a zinc nitrate aqueous solution for 1.5 h followed by modification with FAS were evaluated by water contact angle measurements. It can be found from Figure 1(a) that the aluminum substrate was smooth and its water contact angle (WCA) was 88.1°, that is, the hydrophilic nature of aluminum substrate. There were different morphologies and WCAs after in situ immersion in the solution containing different molar ratios between Zn(NO3)2·6H2O and CO(NH2)2. When the molar ratio between Zn(NO3)2·6H2O and CO(NH2)2 was 10:1, the microstructure of the deposited film was microporous and the pore size ranged from 1 μm to 3 μm, and the WCA was 128.7° after modification, as shown in Figure 1(b). When the molar ratio was 5:1, the surface displayed rose petal-like microstructure composed of about 1 μm sized petals, and WCA was 137.3° after modification (Figure 1(c)). While the molar ratio was 2:1, the surface displayed block-shaped microstructure with the size of each block ranging 200–300 nm, and WCA was 156.2° after modification (Figure 1(d)).
When the molar ratios between Zn(NO$_3$)$_2$·6H$_2$O and CO(NH$_2$)$_2$ were 1:2 and 1:5, the surface displayed pinecone-like microstructure with the size of each pinecone of around 2 µm and 5 µm, respectively, and the corresponding WCA was 151.1° and 139.2° (Figures 1(e) and 1(f)). Obviously, the molar ratio between Zn(NO$_3$)$_2$·6H$_2$O and CO(NH$_2$)$_2$ had a great influence on the morphology and wettability of the sample surfaces.

It is well known that low surface energy combined with surface roughness contribute to the superhydrophobic property of the surface [25]. Cassie and Baxter [26] proposed an equation to describe the relationship between the WCA on a flat surface (θ) and a rough heterogeneous surface (θ$_r$) composed of solid and air:

$$\cos \theta_r = f_1 \cos \theta - f_2.$$  

(1)

In this equation, $f_1$ and $f_2$ are the fraction of solid surface and trapped air in the composite surface, respectively (i.e., $f_1 + f_2 = 1$). This equation predicts that the solid surface fraction $f_1$ is definitely important in determining the hydrophobicity of the heterogeneous surface; when the solid surface fraction $f_1$ is decreased, the WCA of rough surface can be increased, and at the limit when $f_1$ approaches zero, the surface contact angle approaches 180°. Substituting the WCA values on flat aluminum surface (88.1°) and superhydrophobic surface (156.2°) into (1), the value $f_1$ and $f_2$ of the heterogeneous aluminum surface can be calculated to be 0.082 and 0.918, respectively. This means that air occupies about 91.8% of the contact areas; when the heterogeneous aluminum surface contacts with the water droplet, air pockets trap between the solid and liquid (the composite...
solid-liquid-air interface) and the droplet will be suspended upon the asperity, thus leading to a significant increase of WCA [27]. In summary, the molar ratio of 2:1 between Zn(NO$_3$)$_2$·6H$_2$O and CO(NH$_2$)$_2$ was the best condition to create appropriate microstructure and roughness on the surface, and thus lay the morphological foundation for the excellent superhydrophobicity.

3.2. Sample Structure and Chemical Composition of the Superhydrophobic Surface. XRD was employed to analyze the chemical structure of the sample. The XRD pattern of powder deposited under the molar ratio of 2:1 was shown in Figure 2. All of the reflection peaks can be indexed to hydroxide zinc carbonate (HZC), Zn$_5$(OH)$_6$(CO$_3$)$_2$ (in Joint Committee on Powder Diffraction Standards, JCPDS card no. 19-1458). The formation of HZC crystals was initiated by the slow reaction between urea and water. With the hydrolysis of urea, carbonate and hydroxyl being slowly released, Zn ions in the aqueous solution undergo a homogeneous coprecipitation with released carbonate and hydroxyl and finally lead to the formation of HZC [28, 29].

The chemical composition and bonding states of the superhydrophobic films were investigated by FTIR and XPS analysis. The FTIR spectrum of Figure 1(d) sample was shown in Figure 3. A broad absorption band coming from –OH groups appears at around 3421 cm$^{-1}$. The absorption bands corresponding to the CO$_3^{2−}$ group can also be observed: the absorption bands at 1552 cm$^{-1}$ and 1382 cm$^{-1}$ can be assigned to the asymmetric stretching modes and the band at 829 cm$^{-1}$ should be attributed to the out-of-plane deformation mode [24]. The presence of the “Zn–OH” bonding can also be observed at 941 cm$^{-1}$ [30]. The bands at 2926 and 2854 cm$^{-1}$ should be attributed to asymmetric and symmetric stretching vibrations of C–H groups, respectively [31], while the band at 1041 cm$^{-1}$ can be assigned to C–F stretching of –CF$_2$ group [32], which, implying the long-chain alkyl group from FAS, is chemically absorbed on the surface.

The XPS spectrum of the superhydrophobic surface was shown in Figure 4. Peaks due to C 1s (284 eV), O 1s (530 eV), and F 1s (686 eV) were observed. The presence of the F 1s peak and C 1s peak (due to C–F) confirms that FAS molecules has been successfully self-assembled onto the HZC surface [33]. This is in good accordance with the results of FTIR. The analysis of FTIR and XPS reflects that the HZC film was covered with fluorine containing long-chain alkyl chemical species, inducing the low surface energy surface, which combined with rough microstructure of HZC film, to obtain excellent superhydrophobicity of the sample.

3.3. Electrochemical Impedance Analysis. Figure 5 shows the potentiodynamic polarization curves of (a) untreated aluminum and (b) superhydrophobic aluminum. As can be clearly seen in Figure 5, the corrosion potential, $E_{corr}$, of the superhydrophobic surface was positive than that of the
untreated aluminum. The shift of the $E_{\text{corr}}$ towards the positive direction could be linked to an improvement of the protective properties of the superhydrophobic film formed on aluminum substrate. The corrosion current density, $j_{\text{corr}}$, of the superhydrophobic surface on aluminum substrate ($7.53 \times 10^{-3}$ A/m$^2$) decreased by more than 1 order of magnitude as compared to that of the untreated one ($2.92 \times 10^{-2}$ A/m$^2$). These results indicate that the superhydrophobic film has good corrosion resistance.

4. Conclusions

In conclusion, superhydrophobic surfaces were successfully fabricated on aluminum by a two-step method. In the initial step, HZC films with different microstructures were fabricated on aluminum via a convenient in situ immersion in zinc nitrate aqueous solution by adjusting the molar ratios between Zn(NO$_3$)$_2$·6H$_2$O and CO(NH$_2$)$_2$. In the second step, the HZC surfaces were modified with FAS molecules. All FAS-modified HZC surfaces enhanced the water repellent property of the aluminum and obtained a greatest static contact angle of 156.2°, indicating excellent superhydrophobicity. Moreover, it is significant that the electrochemical measurements’ results revealed that the superhydrophobic aluminum has good corrosion resistance in corrosive medium.

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