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Short Communication

Study on Corrosion Resistance of Superhydrophobic Film Prepared on the Surface of 2024 Aluminum Alloy

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Superhydrophobic film was prepared on the surface of aluminum alloy by anodic oxidation, ammonium fluorotitanate sealing and perfluorooctanoic acid modification sequentially. The morphology and composition of the film were characterized and analyzed. Moreover, the surface wettability, stability and corrosion resistance of samples were tested. The results show that the density and corrosion resistance of porous anodic oxide film on aluminum alloy surface are improved after surface modification. After surface modification, the surface of anodic oxide film forms rough structure resulting in optimal superhydrophobicity performance with maximum droplet contact angle 155.6°. The superhydrophobic film has good corrosion resistance, while maintaining superhydrophobicity for a long time, which can effectively block the corrosive medium to inhibit the development of corrosion and provide stable corrosion protection for aluminum alloy.

Keywords: Superhydrophobic film; Corrosion resistance; Anodic oxidation; Sealing; Surface modification

1. INTRODUCTION

Aluminum alloy is widely used in many fields such as construction, machinery, chemical industry, shipbuilding and so on. In the conventional atmospheric environment, the corrosion resistance of aluminum alloy is relatively good. However, due to the presence of chloride ions and high humidity environment, aluminum alloy is prone to be corroded and seriously damaged in the marine atmospheric environment [1-5]. In order to prevent the corrosion caused by the adhesion of chloride ions and humid environment, the preparation of superhydrophobic film on the surface of aluminum alloy is effective and significant.

It is found that the superhydrophobic film can reduce the interfacial tension and hinder the direct contact between the corrosive medium and the substrate, thus showing better corrosion resistance. At present, the main methods to prepare superhydrophobic film include vapor deposition, etching, hydrothermal method, template method, electrochemical method and so on [6-10]. Anodic oxidation is considered as a simple and mature electrochemical method which is more suitable for preparation of superhydrophobic film on aluminum alloy surface compared with other methods [11-12]. However, the anodic oxidation film prepared on aluminum alloy surface is a porous film, which needs to be sealed or modified to present good superhydrophobic and corrosion resistance performance. Many researchers have reported some ways to improve superhydrophobic and corrosion resistance performance by sealing or surface modification method [13-17]. Compared with the single sealing or surface modification process, the technology combined with sealing and surface modification has more advantages and innovations. Therefore, in this study, superhydrophobic film was prepared on the surface of aluminum alloy by anodic oxidation, ammonium fluorotitanate sealing and perfluoro caprylic acid modification sequentially. The microstructure, surface composition, hydrophobic property and corrosion resistance of superhydrophobic film were studied.

2. EXPERIMENTAL

2.1 Materials

2024 aluminum alloy plate with thickness of 1 mm is chosen as the substrate. The samples are cut into 40 mm×24 mm and polished step by step with abrasive papers of different roughness. After the surface is smooth, the sample is cleaned by ultrasonic in deionized water for 3 min, and then immersed in 20% nitric acid solution for 30 s. Finally, the sample is washed and dried immediately in a drying oven.

2.2. Preparation of superhydrophobic film

The preparation of superhydrophobic film on 2024 aluminum alloy is divided into three steps: anodic oxidation, sealing and surface modification. The details are described as follows:

(1) Anodic oxidation: 98% sulfuric acid (24 mL/L) mixed with tartaric acid (80 g/L) is chosen as the electrolyte. The pretreated aluminum alloy sample is used as anode, and pure lead plate is used as cathode, respectively. The conditions of anodic oxidation process are as follows: electrolyte temperature 36 °C, anode current density 2 A/dm^2, oxidation time 50 min. The thickness of anodic oxide film on the surface of aluminum alloy is about 30 μm.

(2) Sealing: The anodized aluminum alloy sample is immersed in the solution with 45 g/L ammonium fluorotitanate at 50 ℃ for 20 min.

(3) Surface modification: After anodized and sealed, the aluminum alloy sample is immersed in 10% perfluorooctanoic acid alcohol solution at 30 ℃ for 30 min. After that, the sample is taken out and placed in a thermostatic drying oven to heat at 100 ℃ for 1 h to obtain a superhydrophobic film.

2.3 Performance Test

2.3.1 Surface morphology and composition

The surface morphology and composition of the aluminum alloy are characterized by ZEISS SUPRA55 scanning electron microscope and OXFORD X-MAX50 energy dispersive spectrometer respectively.

2.3.2 Surface wettability

JC-2000DM contact angle measuring instrument is used to measure the contact angle of water droplets of different film layers on aluminum alloy surface. In order to reduce the error, each sample is measured three times, and the measurement results are averaged. When the droplet contact angle is less than 90°, the surface is hydrophilic and easy to be wetted. When the droplet contact angle is greater than 90° and less than 150°, the surface is hydrophobic and not easy to be wetted. When the contact angle of water droplets is greater than 150°, the surface is superhydrophobic and difficult to be wetted.

2.3.3 Electrochemical test

The electrochemical test is carried out on the PARSTAT2273 electrochemical workstation using a standard three-electrode system: saturated calomel electrode as the reference electrode, platinum plate as the auxiliary electrode and test plate as the working electrode. The electrolyte was 3.5% sodium chloride solution, and the parameters of polarization curve test are set as follows: scanning potential ranges from -250 mV~+250 mV with scanning rate 1 mV/s. The corrosion potential (E_{corr}) and the corrosion current density (J_{corr}) are obtained by fitting the polarization curve with the software of electrochemical workstation, and the protection efficiency (η) of aluminum alloy by different anodic oxide films is calculated. The protection efficiency is defined as the difference between the corrosion current of aluminum alloy and the corrosion current of oxide film divided by the corrosion current of aluminum alloy.

2.3.4 Immersion corrosion test

The stability of superhydrophobic film on aluminum alloy surface is tested by immersion corrosion test. Contact angle is measured by immersion in 3.5% sodium chloride solution for different time (0~120 h).

3. RESULTS AND DISCUSSION

3.1 Surface morphology and composition of aluminum alloy and different anodic oxide films

The surface morphology of aluminum alloy, anodic oxide film, anodic oxide film after sealing, anodic oxide film after sealing and surface modification is shown in Fig.1. According to Fig.1(b), it can be seen that a porous anodic oxide film is formed on the surface of aluminum alloy. Many pores with a diameter of about 50 nm are distributed on the surface. The special morphology is caused by the process of hydrogen evolution during anodic oxidation and the dissolution of anodic oxide film by electrolyte. After sealing process, the number of pores on the anodic oxide film surface is significantly reduced, because in the process of sealing, ammonium fluorotitanate hydrolyzes and reacts with anodic oxide film to generate titanium hydroxide and metal fluoride. The reaction formula is shown in Formula (1) and Formula (2)[18]. The reaction products deposited in the pores gradually thickened the pore wall and reduced the pore size, so as to seal the pore and improve the density of anodic oxidation film. After sealing and surface modification, there are few pores on the surface of anodic oxide film. In addition to the irregular bumps of micron level, there are also many nano sized particles distributed between the bumps. The cross distribution of micron bumps and nano particles forms micro/nano rough structure, which plays an important role in superhydrophobicity of anodic oxide film.

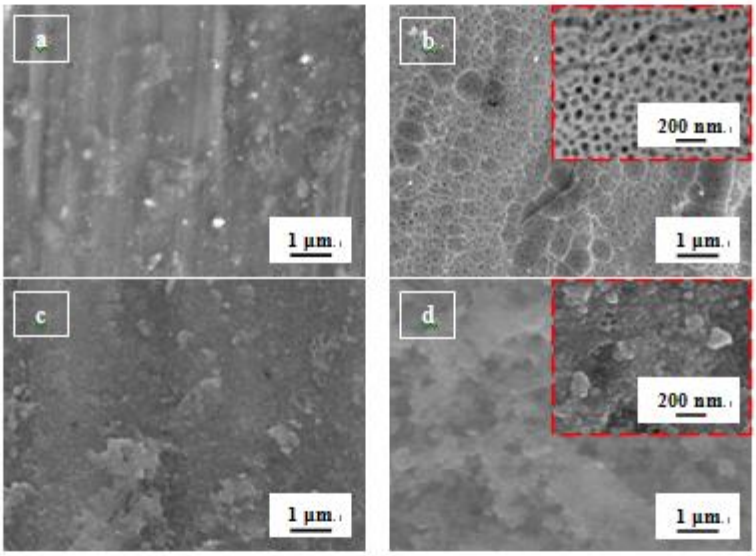


Figure 1. Surface morphology of aluminum alloy and different anodic oxide films; a-aluminum alloy, b-anodic oxide film, c-anodic oxide film after sealing, d-anodic oxide film after sealing and surface modification; (sample size 8 mm×8 mm×1 mm, magnification 30000 times, accelerating voltage 10 kV)

$$TiF_6^{2-} + 4H_2O \rightarrow Ti(OH)_4 + 6F^- + 4H^+ \quad (1)$$

$$2TiF_6^{2-} + 3Al_2O_3 + 9H_2O \rightarrow 2Al_3(OH)_3F_6 + 2Ti(OH)_4 + 4OH^- \quad (2)$$

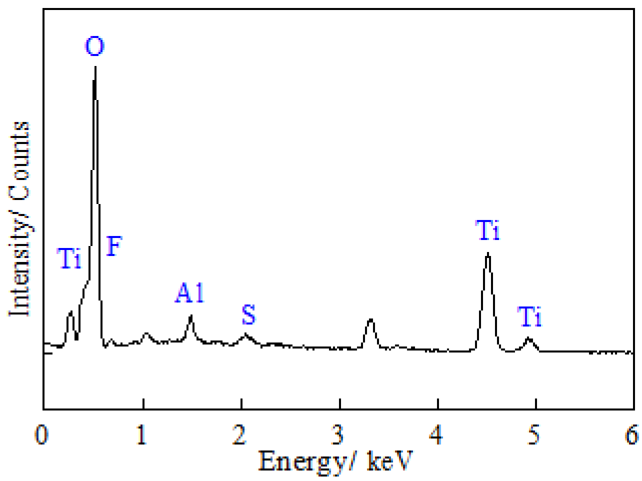
The surface composition of different anodic oxide films is shown in Table 1. It can be seen that the anodic oxide film mainly contains Al, O and S elements. The mass fraction of Al and O elements is high, because the anodic oxidation process is the oxidation reaction of aluminum alloy in the electrolyte. The mass fraction of S element is relatively low, and its existence is due to the involvement of sulfuric acid during anodic oxidation process. The reaction equation is shown in Formula (3)[19-20]. Besides Al, O and S elements, there are small amounts of Ti and F elements on the surface of anodic oxide film after sealing which originates from ammonium fluorotitanate. The surface composition of anodic oxide film after sealing and surface modification contains C element which is due to the perfluorooctanoic acid attached to the surface of anodic oxide film.

$$Al^{3+} + xH_2O + ySO_4^{2-} \rightarrow Al(OH)_x(SO4)_y + xH^+ \qquad (3)$$

Table 1. Composition of different anodic oxide films; b-anodic oxide film: the anodic oxide film is prepared on the surface of 2024 aluminum alloy from the electrolyte with 98% sulfuric acid mixed with tartaric acid; c-anodic oxide film after sealing: The anodic oxide film is immersed in the solution with ammonium fluorotitanate to seal; d-anodic oxide film after sealing and surface modification: After anodized and sealed, the anodic oxide film is immersed in 10% perfluorooctanoic acid alcohol solution to make surface modification.

Samples	Al	O	S	Ti	F	C
b	42.73%	48.77%	8.50%	-	-	-
c	16.72%	44.57%	3.78%	32.85%	2.08%	-
d	18.16%	42.88%	3.02%	28.85%	1.67%	5.42%

Fig.2 shows element distribution of anodic oxide film after sealing and surface modification. Characteristic diffraction peak of Al, O, S, Ti and F can be seen. Al and O elements distribution is dense. Ti, F and C elements distribution is sparse.



EDS spectra

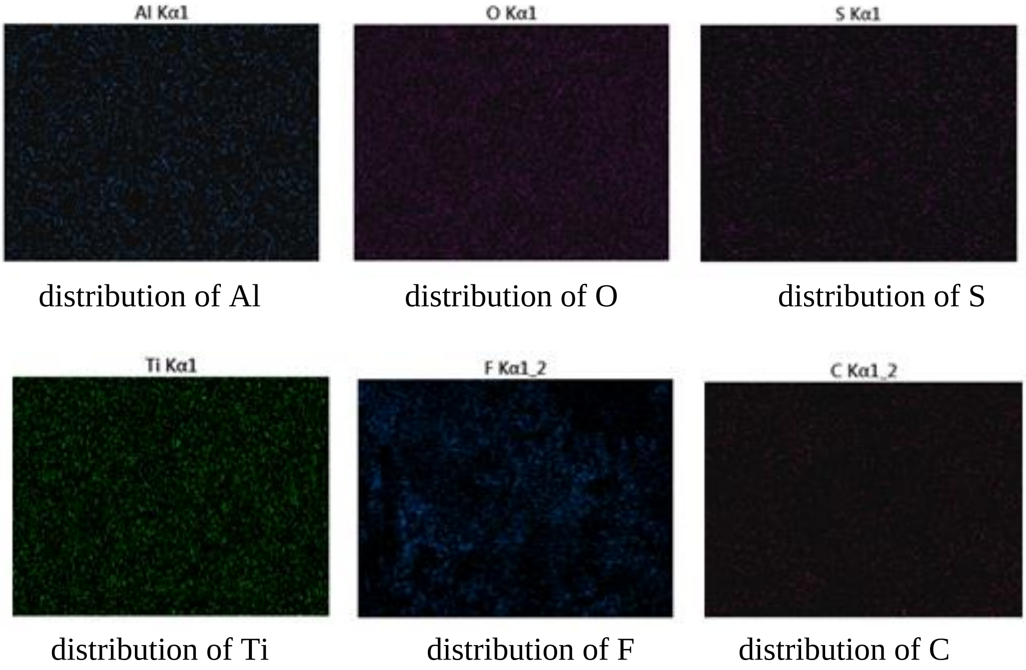


Figure 2. EDS spectrum and surface element distribution of anodic oxide film after sealing and surface modification (accelerating voltage 5 kV, surface sweep model, sampling depth 1 μm)

3.2 Surface wettability of aluminum alloy and different anodic oxide films

The droplet contact angles of aluminum alloy, anodic oxide film, anodic oxide film after sealing and anodic oxide film after sealing and surface modification are shown in Fig.3. It can be seen that the contact angle of water droplet on aluminum alloy surface is only 44.7°, and the surface is hydrophilic. The contact angle of water droplet on the surface of anodic oxide film is 62.5°, which is also hydrophilic and easy to be wetted. After sealing process, the contact angle of water droplet on anodic oxide film surface increases to 120.4°, showing good hydrophobicity. The droplet contact angles of aluminum alloy and anodic oxide films are reported by some scholars that are close to the results in the paper [21-23].

The sealing treatment makes the anodic oxide film surface irregular convex, reducing the contact area with water droplets. In addition, the following reactions may occur during the pore sealing process seen in Formula (4). A layer of TiO_2 film is generated and attached to the surface of anodic oxidation film, which reduces the surface energy and weakens the affinity for water droplets.

$$(TiF_6)^{2-} + (n+2)H_2O \rightarrow TiO_2 \cdot nH_2O + 4H^+ + 6F^- \quad (4)$$

After sealing and surface modification, the contact angle of water droplet on anodic oxide film reaches 155.6°, showing good superhydrophobicity. On the one hand, the surface of anodic oxide film forms micro and nano rough structure after surface modification treatment. This unique structure can capture air and form an air cushion to lift water droplet, reducing the contact area between water droplet and anodic oxide film surface. On the other hand, a layer of TiO_2 film generated could combine with perfluorooctanoic acid to further reduce the surface energy and weaken the affinity for water droplets. The mechanism of hydrophobicity after surface modification has also been reported [24-26].

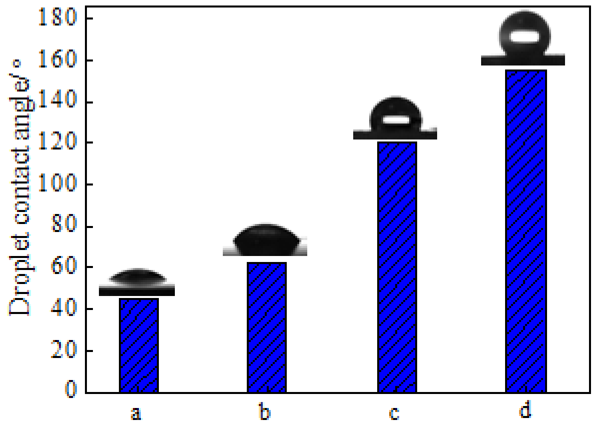


Figure 3. Droplet contact angle of aluminum alloy and different anodic oxide films, a-aluminum alloy, b-anodic oxide film, c-anodic oxide film after sealing, d-anodic oxide film after sealing and surface modification (water volume 4 μL, accuracy ±0.1°, sample size 15 mm×15 mm)

3.3 Corrosion resistance of aluminum alloy and different anodic oxide films

The polarization curves of aluminum alloy, anodic oxide film, anodic oxide film after sealing and anodic oxide film after sealing and surface modification are shown in Fig.4. The fitting results of polarization curves are shown in Tab.2, It can be seen that the corrosion potential of anodic oxide film after sealing moves more positive compared with aluminum alloy. Moreover, the corrosion current density decreases extremely after sealing treatment. In the process of sealing, the reaction products fill the pores which can effectively improve the density of anodic oxide film and increase the corrosion resistance resulting in the decrease of corrosion current. Many researchers also investigate the corrosion resistance of aluminum alloys and anodic oxide film which can provide valuable information for our experiment [27-30].

Compared with anodic oxide film and anodic oxide film after sealing, the anodic oxide film after sealing and surface modification possesses the most positive corrosion potential and the lowest corrosion current density, which is -0.510 V and 8.24×10^{-7} A/cm^2 respectively. The results show that the corrosion resistance of aluminum alloy is further improved after sealing and surface modification treatment. The surface density of anodic oxide film after sealing and surface modification is good, which effectively inhibits the corrosive medium from contacting the aluminum alloy. In addition, the surface of anodic oxide film is superhydrophobic makes it difficult for the corrosive medium to contact the anodic oxide film surface, so as to effectively prevent the corrosion process of aluminum alloy.

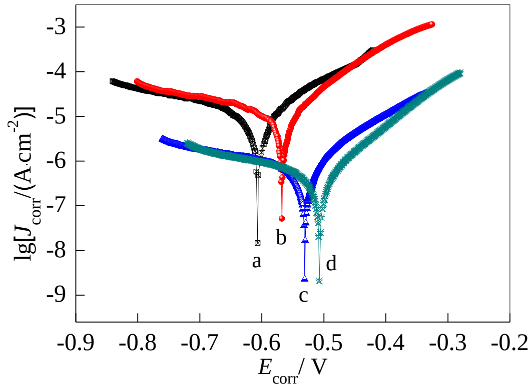


Figure 4. Polarization curves of aluminum alloy and different anodic oxide films, a-aluminum alloy, b-anodic oxide film, c-anodic oxide film after sealing, d-anodic oxide film after sealing and surface modification (scanning potential ranges from -250 mV~+250 mV with scanning rate 1 mV/s, saturated calomel electrode as the reference electrode, platinum plate as the auxiliary electrode and test plate as the working electrode, electrolyte is 3.5% sodium chloride solution)

Table 2. Corrosion potential and corrosion current density of aluminum alloy and different anodic oxide films; a-aluminum alloy, b-anodic oxide film, c-anodic oxide film after sealing, d- anodic oxide film after sealing and surface modification

Samples	E_{corr}/ V	J_{corr}/ A·cm^{-2}
a	-0.604	5.62×10^{-5}
b	-0.567	2.79×10^{-6}
c	-0.532	9.16×10^{-7}
d	-0.510	6.84×10^{-7}

Fig.5 shows the protective efficiency of anodic oxidation film, anodic oxidation film after sealing and anodic oxidation film after sealing and surface modification. It can be seen that the anodic oxide film has the lowest protection efficiency for aluminum alloy. However, the anodic oxide film after sealing and surface modification possesses the highest protection efficiency for aluminum alloy, up to 98.8%, which can better prevent corrosion medium from inhibiting corrosion development, thus playing a good protection effect on aluminum alloy.

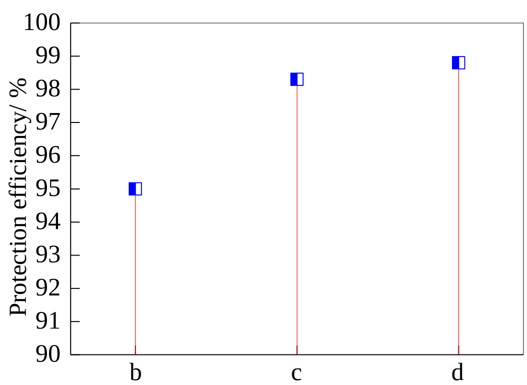


Figure 5. Protection efficiency of different anodic oxide films for aluminum alloy, b-anodic oxide film, c-anodic oxide film after sealing, d-anodic oxide film after sealing and surface modification

3.4 Stability of superhydrophobic film

Fig.6 shows the contact angle of water droplets of anodic oxide film after sealing and surface modification during immersion experiment. It can be seen that with the extension of immersion time, the droplet contact angle decreases gradually. At the initial immersion stage (0~48 h), the droplet contact angle basically remains unchanged. After immersion for more than 48 h, the contact angle of water droplets decreases obviously, but they are still superhydrophobic. The results indicate that the superhydrophobic state of the anodic oxide film surface after sealing and surface modification is stable, which can effectively prevent the corrosive medium, reduce the contact area, and maintain good corrosion resistance, thus providing stable corrosion protection for aluminum alloy.

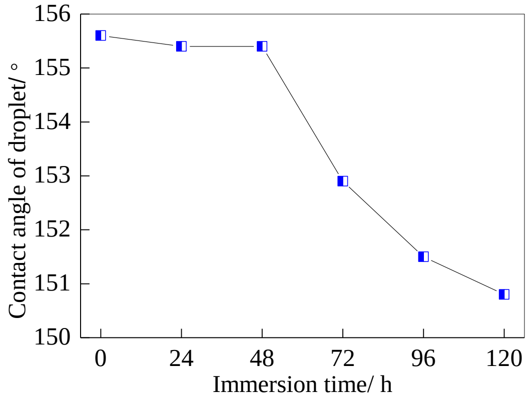


Figure 6. Contact angle of water droplets of anodic oxide film after sealing and surface modification during immersion experiment (corrosive medium is 3.5% sodium chloride solution, static immersion for 0~120 h, water volume 4 µL, accuracy ±0.1°)

4. CONCLUSIONS

Superhydrophobic film was prepared on the surface of aluminum alloy by anodic oxidation, ammonium fluorotitanate sealing and perfluorooctanoic acid modification sequentially. It is found out that the superhydrophobic film is dense and has special rough structure with Al, O, S, Ti, F and C elements resulting in optimal superhydrophobicity, better stability and good corrosion resistance. The superhydrophobic film possesses the most positive corrosion potential and the lowest corrosion current density, which is -0.510 V and 8.24×10^{-7} A/cm^2 respectively. The superhydrophobic surface makes it difficult for the corrosive medium to contact the anodic oxide film surface, so as to effectively prevent the corrosion process of aluminum alloy.

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