Adhesion and Corrosion Resistance of Micro-Arc Oxidation/Polyurethane Composite Coating on Aluminum Alloy Surface

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Abstract: The adhesion and bonding performance of waterborne polyurethane (PU) coating on aluminum alloy surface was improved in this study. To achieve this objective, the effects of different sodium silicate concentrations on the aluminum alloy micro-arc oxidation (MAO) layer and the adhesion strength and corrosion resistance of MAO-PU composite coating before and after modification by MAO treatment of the 7050 aluminum alloy were studied. The experimental results showed that the modification of the MAO membrane layer by a silane coupling agent could significantly improve the adhesion strength and corrosion resistance of the composite coating. Moreover, the maximum adhesion strength was obtained when the concentration of sodium silicate was 12 g L\(^{-1}\).

Keywords: micro-arc oxidation; polyurethane coating; silane coupling agent; adhesion strength; corrosion resistance

1. Introduction

Aluminum alloys are widely used in rail transit vehicles, aircraft, and other manufacturing industries because of their high strength and low density [1–4]. In the manufacturing of high-speed electric multiple units (EMU), the commonly used 7050 aluminum alloy has low electrode potential; indeed, when it is in contact with other metals, its corrosion as an anode gets easily accelerated. Unfortunately, its wear resistance is also poor. Therefore, one or more types of coatings are often sprayed on the surface of the aluminum alloy for protection against corrosion [5–7]. Polyurethane (PU) coating used as the topcoat has the advantages of high gloss, excellent weather resistance, and excellent wear resistance [8,9]. However, the adhesion of PU coating on light metals such as aluminum alloy is poor and their anti-corrosion performance is also not good. In general, an epoxy coating with excellent adhesion and good anti-corrosion performance is selected as the primer to form the epoxy–polyurethane (EP–PU) coating system [10]. However, the commonly used epoxy primer is a two-component coating; therefore, it needs a suitable pot life in order to maintain the chemical reaction speed to be moderate, thus the drying speed of the EP coating is slow, which eventually affects the manufacturing efficiency [11]. In conclusion, it is crucial to explore alternative technologies to improve the corrosion resistance and adhesion strength of PU on aluminum alloy substrates.

As a new surface treatment technology, micro-arc oxidation (MAO) can significantly improve the corrosion resistance of the substrate by direct in situ formation of ceramic coating with alumina as the main component on the surface of aluminum and its aluminum alloy materials [12–16]. After MAO treatment, two different layers are grown on the aluminum alloy: a dense layer with excellent corrosion resistance and a porous layer capable of improving the adhesion strength of organic coating on the surface of aluminum alloy [17,18]. Thus, it can be speculated that by comparing the aluminum
alloy substrates with and without MAO treatment, it can be verified whether spraying PU coating on the aluminum alloy after MAO treatment can improve the corrosion resistance and the adhesion strength between the PU coating and the aluminum alloy substrate. For example, Lu et al. [19] studied the effect of MAO pretreatment on the protection performance of epoxy magnesium (Mg)-rich primer on a AZ91D Mg alloy. They demonstrated that the adhesion strength of epoxy resin to the Mg substrate increased due to the surface morphology endowed by MAO. Rad et al. [15] showed that the adhesion strength of aluminum alloy samples after MAO treatment to epoxy coating was about twice that of samples without MAO treatment. Cui et al. [20] investigated the effect of baking coating on the corrosion resistance of the MAO layer. It was found that the corrosion current density of Mg alloy samples sprayed with baking coating after MAO decreased by two or three orders of magnitude compared to the samples treated only by MAO; furthermore, no corrosion phenomenon was observed during the long-term immersion test for about 500 h.

The molecular structure formula of the silane coupling agent 3-aminopropyltriethoxysilane (APTES) is NH\(_2\)(CH\(_2\))\(_3\)Si(OCH\(_2\)CH\(_3\))\(_3\). Silyloxy groups are not only reactive toward inorganic compounds, but also reactive or compatible with organic compounds. Therefore, when the APTES is present between the inorganic and the organic interface, the organic matrix/silane coupling agent/inorganic matrix bonding layer can be formed, which benefits the organic coating to effectively improve the adhesion on the inorganic substrate [21,22]. Da Ponte et al. [23] used APTES as an adhesive promotion layer in epoxy resin/stainless steel composites to increase the adhesion strength of epoxy resin to stainless steel by more than 20 MPa.

In this study, MAO layers with different thicknesses were prepared by MAO with varying concentrations of sodium silicate. The micromorphology of MAO layers was characterized by scanning electron microscopy (SEM) and the samples were analyzed by X-ray diffraction (XRD). The MAO layer was first modified by a silane coupling agent; then, the PU coating was sprayed. The adhesion strength was measured by the pull-out method, and the corrosion resistance was evaluated on an electrochemical workstation.

2. Experimental Section

2.1. Pretreatment of the Aluminum Alloy Substrate

In this study, 7050 aluminum alloy was used as the experimental material. The 7050 aluminum alloy contains nearly 90% aluminum and its elemental composition is listed in Table 1 [24]; its specification is 150 mm × 75 mm × 3 mm. The treatment method is as follows: The test panel was manually ground with 60, 300, 1000, and 2000 mesh sandpapers until the surface was smooth and free of scratches. Then, the samples were cleaned, degreased with acetone solvent, and dried for further use.

| Chemical Composition | Zn | Mg | Cu | Zr | Ti | Mn | Cr | Fe | Si | Al |
|----------------------|----|----|----|----|----|----|----|----|----|----|
| Mass fraction/%      | 6.42 | 2.25 | 2.02 | 0.13 | 0.03 | 0.10 | 0.04 | 0.11 | 0.07 | Bal. |

2.2. MAO Treatment

A series of samples was obtained by MAO in the experimental device, as shown in Figure 1. The experimental conditions were as follows: In DC pulse mode, the NaOH concentration was 4 g L\(^{-1}\), the NaF concentration was 6 g L\(^{-1}\), the duty cycle was 30%, the pulse frequency was 500 Hz, and the oxidation time was 10 min. Concentrations of Na\(_2\)SiO\(_3\) were 7.5, 10, 12.5, 15, and 17.5 g L\(^{-1}\), respectively. In order to remove the residual alkali solution on the surface of the MAO layer and prevent it from eroding the film, the finished samples were treated as follows: the prepared samples were added into deionized water, cleaned by ultrasonication for 10–15 min, dried, and finally classified and numbered.
were used to prepare EP–PU composite coating for a performance comparison test. Before use, the base was washed with water and then dried at 140 ± 5 °C for 2 h. Further, the samples were immersed in APTES glycol organic solution (mass fraction, 4.1%) and placed in a constant temperature bath to allow it to react for 2 h at 78 ± 2 °C. Finally, they were dried at 200 ± 5 °C for 2 h.

2.3. Spraying of Polyurethane Coatings

The two-component PU topcoat (Newmat company, Beijing, China), which meets the requirements of EMU protection, was used in the experiment to prepare MAO–PU composite coating. The two-component epoxy primer and two-component PU topcoat (Newmat Company, Beijing, China) were used to prepare EP–PU composite coating for a performance comparison test. Before use, the base and hardener of the two-component coating were thoroughly mixed. After air spraying, the coating was placed in a ventilated environment at 25 °C for seven days to carry out the follow-up test.

2.4. Testing and Analysis Instruments

The thickness of the MAO layer was measured using a TT260 eddy current coating thickness tester; however, the MAO layer roughness was measured using a TR200 handheld roughness tester. The micromorphology of the MAO layer was observed and tested by Merlin Compact Zeiss field-emission scanning electron microscopy (FESEM). The porosity of the MAO layer was analyzed and calculated by using Image J software. The “threshold” tool was used to calculate the pore area and the porosity factor was obtained by dividing the pore area by the total area. The results of the porosity factor, thickness, and roughness were measured by the average of three measurements. XRD was used to measure the structural characteristics of the MAO layer.

The adhesion strength was tested according to the ASTM D4541-17 standard test method for the pull-off strength of coats using portable adhesion testers and the test instrument was the Elcometer 510.

The action potential polarization curves of the 7050 aluminum alloy and its MAO layer were measured on a CHI760E electrochemical workstation. The corrosion solution was sodium chloride solution with a mass fraction of 3.5%.

3. Results and Discussion

3.1. Composition and Morphology of MAO Layer

Figure 2 exhibits the phase composition results of the coating. The 7050 aluminum alloy was treated by single-phase pulse and two-phase pulse mode MAO (NaOH concentration, 4 g L⁻¹; Na₂SiO₃ concentration, 12 g L⁻¹; NaF concentration, 6 g L⁻¹; current density of 8 A dm⁻²; and treatment time
of 10 min). Figure 2c exhibits that the phase composition of the 7050 coating after MAO treatment is mainly $\gamma$-$\text{Al}_2\text{O}_3$, as there is no obvious $\alpha$-$\text{Al}_2\text{O}_3$ peak in the spectrogram. This may be attributed to the fact that the MAO layer is too thin and the molten oxide cools too fast after discharge, which prevents the conversion of $\gamma$-$\text{Al}_2\text{O}_3$ into $\alpha$-$\text{Al}_2\text{O}_3$. The specific surface area of $\gamma$-$\text{Al}_2\text{O}_3$ is larger than that of $\alpha$-$\text{Al}_2\text{O}_3$; therefore, the interface area between MAO layer and subsequent PU coating is increased, which is beneficial to the improvement of adhesion strength [25].

![Figure 2](image_url)

**Figure 2.** Composition and micromorphology of the MAO layer. (a) the MAO layer surface zoom in 200x; (b) the MAO layer cross section zoomed in at 1000x; and (c) the XRD pattern of the layer under unidirectional pulse and bidirectional pulse conditions.

Figure 2a shows the SEM micrographs of the MAO layer surface, exhibiting that the surface is porous. Based on the cross-section morphology observation of the MAO ceramic layer by SEM images shown in Figure 2b, the MAO layer can be divided into a dense internal layer and an external porous layer. The porous layer has a porous structure that can form a wedge-shaped structure with PU coating to increase its adhesion; the dense internal layer is the main strengthening layer, and thus, can improve the corrosion resistance of the aluminum alloy substrate [26].

### 3.2. Effect of Different Concentrations of Sodium Silicate on Porosity, Thickness, and Roughness of Layers

Sodium silicate has the most significant influence on the growth rate and morphology of the layer. Therefore, the effects of different concentrations of sodium silicate on the thickness, porosity, roughness, adhesion strength, and corrosion resistance of the MAO–PU composite coating were studied.

SEM images with small magnification were selected to exclude the influence of uneven local distribution on the measurement results. Figure 3 displays the test results, indicating that with the increase of the sodium silicate concentration, the discharge channel of the MAO layer gets gradually blocked with the ejecta produced by the discharge. Moreover, the diameter of holes formed by the cooling of the discharge channel gradually increases and the porosity increases. At the same time, the increase of the layer thickness leads to the increase of stress and the appearance and increase of cracks in the MAO layer.
The MAO layer was prepared at 8, 10, 12, 14, and 16 g L\(^{-1}\) Na\(_2\)SiO\(_3\) concentrations. Figure 3 shows that when the concentration of sodium silicate is between 8 and 12 g L\(^{-1}\), the roughness of the film is ~1 µm; however, the thickness is ~10 µm. The porosity factor increases gradually with the increase of sodium silicate concentration from 0.3 to 1.8%. Under other similar conditions when the concentration of sodium silicate is higher than 12 g L\(^{-1}\), the growth rate of the film becomes extremely fast, resulting in the abrupt change of the film roughness and thickness. The thickness reaches 28 µm, while the roughness becomes 7 µm.

In order to find the abrupt change point of the relationship between the concentration of sodium silicate and the roughness and thickness of the MAO layer more accurately, MAO layers were prepared at 11, 12, 13, 14 and 15 g L\(^{-1}\) sodium silicate concentrations. It can be seen from Figure 4 that 12 to 14 g L\(^{-1}\) is the abrupt range of the effect of sodium silicate concentration on the roughness and thickness of the MAO layer.

These results showed that the addition of sodium silicate in the electrolyte is beneficial to the formation of a high-impedance film on the surface of aluminum alloy. Moreover, the increase of sodium silicate concentration can promote the arc discharge on the surface of aluminum alloy and reduce the energy consumption in the arcing process of MAO.

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3.3. Adhesion Strength of Composite Coatings

3.3.1. Effect of Silane Coupling Agent Modification on the Contact Angle of the MAO Layer

In order to further improve the adhesion strength of PU coating on the aluminum alloy, the surface of the MAO layer was modified by the silane coupling agent. The reaction of silicon dioxide on the surface of the MAO layer with the silane coupling agent can reduce the silicon hydroxyl group on the surface of silicon dioxide to form organic groups on the surface, which can then increase the affinity of organic resin. Furthermore, the silane coupling agent can also react with hydroxyl groups on alumina on the surface of the MAO layer with a reaction equation similar to that of the silicon hydroxyl group.

\[
3 \text{ Si} - \text{OH} + \text{NH}_2(\text{CH}_2)_2\text{Si(OCH}_2\text{CH}_3)_3 \rightarrow (\text{ Si} - \text{O})_3\text{Si(CH}_2)_3\text{NH}_2 + 3\text{C}_2\text{H}_5\text{OH} \quad (1)
\]

The contact-angle test results between distilled water and aluminum alloy samples treated with two different MAO process conditions before and after silane coupling agent modification are illustrated in Figure 5. The modification of the MAO layer by silane coupling agent improves the average contact angle, which can be used to judge the occurrence of surface modification reaction and makes the alkane carbon chain grow on the surface of the MAO layer.

Figure 4. Influence of sodium silicate concentration (11–15 g L\(^{-1}\)) on thickness and roughness of the MAO film.

Figure 5. Contact angle test before and after treatment with the silane coupling agent: (a,b) are the contact angle test results before and after treatment of the same sample with an initial contact angle of 20.9\(^\circ\).
Measurement results of the apparent contact angle clearly indicate that the contact angle increases to a value in the range of 50.2° from 20.9°, which is in accordance with the literature report [27]. At the same time, as shown in the reaction (Formula (1)), a large number of –NH₂ groups are introduced on the surface of aluminum alloy by APTES modification. When PU coating is applied in the subsequent process, the isocyanate group in PU coating reacts with it as shown in reaction Formula (2), which further enhances the adhesion strength of the coating.

\[
\text{O} \\
\text{\|}
\]

\[
R\text{–NCO + R}²\text{–NH}_2 \rightarrow R'\text{–NH} \rightarrow C\text{–NH–R}
\]  

(2)

### 3.3.2. Adhesion Strength of Composite Coatings

PU coating was sprayed on the MAO layer prepared under different sodium silicate concentration conditions; and further, the adhesion strength was tested. At the same time, the influence of silane coupling agent APTES on the adhesion strength of composite coating before and after modification of the MAO layer was tested (Figure 6). The change of the adhesion strength with the concentration of sodium silicate in the electrolyte indicates that the adhesion strength first increases and then decreases with the increase in the concentration of sodium silicate in the electrolyte, regardless of whether the surface modification has been carried out by the silane coupling agent. The red line in Figure 6 indicates that after the silane coupling agent has been used to modify the MAO surface, the adhesion strength between the composite coating and aluminum alloy improved significantly (more than twice that of the untreated blank sample as indicated by the black line in Figure 6), thus fulfilling the requirements of the rail transit vehicle industry requiring that the adhesion strength between the coating and the aluminum alloy substrate to be greater than 10 MPa [28].

The fracture parts of the composite coatings modified with silane are all loose layers of the MAO layer, while the fracture parts of composite coatings without silane modification contain the interface between MAO and PU coatings (as shown in the fracture images in Figure 6). This also shows the effectiveness of silane modification to improve the adhesion strength of MAO and PU coatings.

![Figure 6. Adhesion strength between modified and unmodified MAO samples.](image)

### 3.4. Corrosion Resistance of Composite Coatings

The samples of blank aluminum alloy, MAO treated aluminum alloy, MAO–PU composite coating, and EP–PU composite coating were immersed in 3.5% sodium chloride solution for 20 min. After the open-circuit voltage was stabilized and the polarization curve was measured, saturated calomel
electrode (SCE) was used as a reference electrode. Figure 7 illustrates the corresponding cathodic and anodic potentiodynamic polarization (PP) curves. Taking into consideration the cathodic branches of the PP curves, it is assumed that the sample MAO–PU (represented by the black curve) demonstrates lower cathodic current densities compared to the blank aluminum alloy (represented by the red curve), indicating that the treatment/application of MAO-PU to the aluminum alloy could possibly reduce the cathodic reactions. Furthermore, by studying the anodic branches of the polarization curves, it is mentioned that the sample MAO-PU exhibits lower anodic current densities compared to the blank aluminum alloy sample, meaning an effective inhibition of the anodic reactions. Regarding the corresponding Eoc (open circuit potential) values, it is observed that the sample MAO–PU demonstrates nobler Eoc values compared to the blank aluminum alloy sample denoting that they are less prone to corrosion after exposure to the corrosive environment. It is important to mention that the PP method was used only for qualitative estimations because the determination of Rp and corrosion current (icorr) values via the linear fitting of the polarization curves according to the Tafel method was impossible, due to the fact that the Tafel method only yields an average uniform corrosion rate and is not appropriate for localized corrosion, such as pitting corrosion; aluminum alloy 7050 is corroded via pitting corrosion [29–31].

![Electrochemical polarization curve test results.](image)

**Figure 7.** Electrochemical polarization curve test results.

4. Conclusions

The adhesion strength and corrosion resistance of the polyurethane (PU) coating on 7050 aluminum alloy were improved by MAO treatment and modification of the MAO layer with a silane coupling agent. The results demonstrated that the thickness, roughness, and porosity of the MAO layer increased with the increase of the concentration of sodium silicate solution. When the concentration of sodium silicate in MAO treatment was 12 g L⁻¹, the adhesion strength between PU coating and aluminum alloy reached the highest value. Therefore, it can be inferred that the adhesion strength of the MAO-PU composite coating can be significantly improved by modifying the MAO layer with a silane coupling agent, which led to an increase from 8.8 to 18.81 MP. Through the test of the electrochemical polarity curve, it was found that the corrosion resistance of MAO-PU composite coating was higher than that of the EP-PU coating system without MAO treatment.

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