Corrosion Behaviors of Microarc Oxidation Coating and Anodic Oxidation on 5083 Aluminum Alloy

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Abstract: The microarc oxidation (MAO) coating and anodic oxidation coating were prepared on 5083 aluminum alloy. The surface morphology, elemental composition, and electrochemical behavior of the two coatings were analyzed. The results proved that the corrosion resistance of the MAO coating is superior than that of the anodic oxidation coating. The protective ability of the coating deteriorated gradually with the increase in immersion time. The corrosion process is controlled by ion diffusion throughout the coatings.

1. Introduction

The air intake filter is generally equipped in front of the gas turbine to filter out the salt sprays contained in the intake airflow, and thus, the service life of the gas turbine could be effectively guaranteed and extended [1–5]. In order to meet the requirements of high efficiency and low resistance of the air intake filter, the cyclone filter usually serves as the first stage. The cyclone filter is generally exposed to the marine atmosphere and is susceptible to corrosion due to the salt spray particles of the marine environment [6–11]. In addition, to reduce the weight and the quality control cost of the cyclone filter and its components, the cyclone filter is generally made from aluminum alloy [6, 12]. The surface coating technology is an effective and economical way to enhance the anticorrosion resistance of the aluminum alloy substrate [13]. Therefore, the surface coating technology and the degradation behaviors of the cyclone separators in corrosive environment are the necessary guarantee for the safe operation of the cyclone separators. So the research and development of the surface coating technology for aluminum alloy has important significance.

Since the 1970s, a large amount of literatures concentrated on the cyclone separators have been published. Tabakoff and Grant [14] proposed a purely empirical formula to describe the collisional motion between the particles and the wall. Kim and Lee [15] developed a two-phase flow model to investigate the sedimentation and turbulent diffusion effects of solid particles in the boundary layer. Brouwers [16] used the numerical and experimental method to investigate the separation efficiency of the rotational axial-flow separator. Zhang et al. [17] conducted an experimental research on an axial-flow multitube cyclone separator. The results indicated that the axial-flow multitube cyclone has a higher separation efficiency and lower resistance than the tangential inlet cyclone. However, aluminum and aluminum alloys are reported to corrode mainly in the forms of pitting, intergranular corrosion (IGC), and stress corrosion cracking (SCC), when they are exposed to the solutions containing chloride ions [18–23]. Al coating, i.e., microarc oxidation (MAO) and anodic oxidation coating, can significantly improve the anticorrosion resistance of the aluminum alloys. Wang et al. [24] investigated a ceramic coating deposited on Al matrix composite by MAO and found that surface hardness wear resistance of the composite can be significantly improved. Chen et al. [25] investigated the corrosion performance of MAO coatings on different regions of the friction stirred 6061 aluminum alloy plate and found that the...
corrosion protection performance of the MAO coating can be improved by inducing the coarse and congregated Al-Fe-Si particles into fine and disperse distributed particles. Krishtal [26] found that the substantial improvement in corrosion resistance of the friction stir welds of 7075 aluminum alloy can be achieved by MAO treatment. Xin et al. [27] investigated the properties of alumina coatings prepared by the MAO process using direct current (DC) and unbalanced alternative current (AC) power supplies. The results showed that the coating deposited by AC possesses higher density, hardness, and corrosion resistance. Li et al. [28] investigated the microstructure for MAO coating on the 6061 aluminum alloy in the Na2SiO3-CH3COONa-Na5P3O10 electrolyte system. The results showed that the size of spark was exponentially related to thickness of coating, and the structure of the coating was in a three-dimensional network. Du et al. [29] developed a black MAO coating on 2A12 aluminum alloy and found that the coating has superior adhesion and corrosion resistance. This will provide further research direction for developing MAO black coating on aluminum and aluminum alloy. Nalivaiko et al. [30] investigated the preparation of aluminum hydroxide obtained by aluminum anodic oxidation. The coating formed on high purity alumina consists of 4 stages from Al(OH)3-NH4Cl-H2O to α-Al2O3.

In this paper, alumina coatings on 5083 aluminum alloy were prepared by MAO and anodic oxidation, respectively. The microstructure, elemental composition, and the corrosion behaviors of the two coatings were investigated. At the end, the corrosion mechanism of the two coatings was discussed in brief.

2. Experimental

The cyclone filter used in this work is made of commercial 5083 aluminum alloy. The chemical compositions of the commercial 5083 aluminum alloy are shown in Table 1. Prior to the experiments, the specimen was cut in pieces with dimensions of 60 × 55 × 3 mm. The geometrical schematic diagram of the cyclone filter is shown in Figure 1.

Microarc oxidation and anodic oxidation techniques were used to prepare the coatings surface on the experimental samples of the cyclone filter, and the surface sealing treatment of the microarc oxidation coating was performed with 5% saline solution. Samples of the cyclone filter with the microarc oxidation treatment and the anodic oxidation treatment are shown in Figure 2.

The electrochemical response of MAO coating, anodic oxidation coating, and 5083 aluminum alloy was obtained using IM6/IM6e electrochemical workstation (ZAHNER, Germany) in 3.5 wt.% NaCl solution. A classic three-electrode system is used, which composed of a saturated Ag/AgCl reference electrode, a platinum sheet with dimensions of 20 × 20 × 0.1 mm, and 5083 aluminum alloy and coatings as a working electrode [31]. The potentiodynamic polarization curves were conducted by sweeping the potential from −0.6 V/Ag/AgCl below open circuit potential (OCP) with a scanning rate of 0.333 mV/s. The electrochemical impedance spectroscopy (EIS) tests were performed at OCP with a sinusoidal potential perturbation of 10 mV in a frequency range from 10 kHz to 10 mHz. The tested solution was maintained at 25 ± 1°C in the air without stirring.

The salt spray test for MAO and anodic oxidation coating on 5083 aluminum alloy was conducted using machine DJS-EN61 according to the ISO 14993:2001 standard. The solution is 5 wt.% NaCl solution, pH of salt solution is 6.8, the temperature of the salt solution barrel is 35°C, and the sample place angle is 25°. The examination of the specimen was performed after 63 days of experiment. After the test, the samples were cleaned by flow water of temperature not higher than 35°C to remove the sample surface residual salt spray solution and then dried using hot air.

3. Result and Discussion

3.1. Surface Characterization of the Two Different Coatings

Figure 3 shows the surface morphologies of the MAO coating on 5083 aluminum alloy samples, revealing volcano-like morphologies with micropores of various sizes that can be observed on the surface. As is seen from Figure 3, the micropores are smaller in size with diameters of 2 μm and distributed uniformly. This is the characteristic of MAO coatings obtained by microsparks on the sample surface of alloys [25, 32]. Still some of the pores in the MAO are blocked. In Figure 3, the number of small white particles identified by EDS is Fe-rich particles. This is consistent with the finding of Chen [25]. In addition, no crack exists in Figure 3, which indicates that the MAO coating is very adhesive to 5083 aluminum alloy substrate [33].

The surface morphologies of anodic oxidation coating formed on 5083 aluminum alloy are shown in Figure 4. The anodic oxidation coating surface looks very dense, but there are a lot of cracks staggered on the surface. So, the corrosion properties would deteriorate due to these cracks.

Table 1: Chemical compositions of the 5083 aluminum alloy (wt.%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Si</th>
<th>Mg</th>
<th>Zn</th>
<th>Fe</th>
<th>Cr</th>
<th>Ti</th>
<th>Mn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity</td>
<td>0.09</td>
<td>0.31</td>
<td>4.1</td>
<td>0.21</td>
<td>0.35</td>
<td>0.05</td>
<td>0.05</td>
<td>0.47</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Figure 1: Test trial sample of cyclone separator.
3.2. Potentiodynamic Polarization Curves. The potentiodynamic polarization curves for MAO coating, anodic oxidation coating, and 5083 aluminum alloy in 3.5 wt.% NaCl solution are shown in Figure 5. The curves indicated that the MAO coating and anodic oxidation coatings lead to the changes in the anodic current, pitting potential ($E_{\text{pit}}$), and
corrosion rate. The potentiodynamic polarization curves indicated that the corrosion resistance of the MAO and anodic oxidation coatings can be significantly improved compared to the 5083 aluminum alloy matrix. It was obvious that MAO coating and anodic oxidation coating led to the positive shift in corrosion potential.

The corrosion potential \(E_{\text{corr}}\) of the 5083 aluminum alloy, anodic coating, and MAO coating is \(-694 \pm 8, -636 \pm 12,\) and \(-385 \pm 11\) mV/Ag/AgCl. Compared with the 5083 aluminum alloy, the corrosion potentials shifted nobly for the MAO and anodic oxidation coatings. The corrosion current density \(i_{\text{corr}}\) value of the 5083 aluminum alloy, anodic coating, and MAO coating is \(3.33 \pm 0.11 \times 10^{-6}, 7.33 \pm 0.24 \times 10^{-7},\) and \(1.07 \pm 0.18 \times 10^{-9}\) A/cm\(^2\), respectively. This suggests that the corrosion resistance for MAO coating is two orders higher than that for 5083 aluminum alloy. This indicates that both of the MAO and anodic oxidation coatings can reduce the corrosion rate of the 5083 aluminum alloy specimens in 3.5 wt.% NaCl solution [34–36].

### 3.3. Electrochemical Impedance Spectroscopy

#### 3.3.1. MAO Coating

The Bode (Figure 6(a)) and Nyquist (Figure 6(b)) plots for MAO coating on 5083 aluminum alloy after immersion in 3.5 wt.% NaCl solution for 1 day are presented in Figure 6. The Nyquist plots exhibit two capacitive semicircles, suggesting the inductive behavior [34, 37]. Figure 7 presents the equivalent circuit used to simulate the EIS data, in which \(R_s\) is the resistance of the 3.5 wt.% NaCl solution and \(C_{dl}\) and \(R_{dl}\) are the capacitance and resistance of the adsorption layer, respectively. CPE and \(R_p\) are the capacitance and polarization resistance of the MAO coating, respectively. The use of a constant phase element (CPE) was used in place of capacitance because of the distribution of relaxation times resulting from heterogeneities at the electrode surface [31, 33, 38, 39]. The fitted parameters in the equivalent circuit in Figure 7 are given in Table 2.

The Bode (Figure 8(a)) and Nyquist (Figure 8(b)) plots for MAO coating on 5083 aluminum alloy after immersion in 3.5 wt.% NaCl solution for 12 days are presented in Figure 8. The Nyquist plots exhibit a capacitive semicircle in high-frequency region and an inductive loop in low-frequency region [19]. The capacitive reactance arc corresponds to the process of ions passing through the MAO coating, and the inductive arc corresponds to the desorption process of the adsorbed intermediate products [40–42]. Figure 9 presents the equivalent circuit used to simulate the EIS data, in which CPE\(_f\) is the capacitance of the MAO coating, \(R_{pore}\) is the resistance of defects, \(C_{dl}\) is the double layer capacitance, \(R_p\) is the polarization resistance, \(L\) is the inductive resistance, and \(R_L\) is the inductive resistance, which is related to the active dissolution of MAO coating [43]. The fitted parameters in the equivalent circuit in Figure 9 are given in Table 3.

The Bode (a) and Nyquist (b) plots for MAO or 32 and 63 days are presented in Figure 10. The Nyquist plots exhibit a capacitive semicircle and a bias line at low-frequency region. The capacitive reactance arc corresponds to the process of ions passing through the MAO coating [43]. The bias line at low frequency corresponds to the diffusion process of Cl⁻.
through the MAO coating [44]. Figure 11 presents the equivalent circuit used to simulate the EIS data, in which $W$ is the Warburg impedance. $W$ was used to fit the data of MAO coatings suggesting the responses induced by diffusion in paths of semi-infinite length [43, 44]. The fitted parameters in the equivalent circuit in Figure 11 are given in Table 4.

From the EIS response, it can be inferred that three stages for MAO coating during the immersion time can be identified. In the first stage, the equivalent circuit in Figure 7...
Figure 9: Equivalent circuit used to evaluate the EIS data presented in Figure 10 (Figure 9 is reproduced from [42] under the Creative Commons Attribution License/public domain).

Table 3: Fitting results of the equivalent circuit obtained by fitting the EIS data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ (Ω·cm$^{-2}$)</td>
<td>7.42</td>
</tr>
<tr>
<td>$Y_0$ (Ω$^{-1}$·s$^0$·cm$^{-2}$)</td>
<td>$5.19 \times 10^{-4}$</td>
</tr>
<tr>
<td>$n$</td>
<td>0.89</td>
</tr>
<tr>
<td>$R_{pore}$ (Ω·cm$^{-2}$)</td>
<td>$5.18 \times 10^2$</td>
</tr>
<tr>
<td>$C_{dl}$ (F·cm$^{-2}$)</td>
<td>$4.57 \times 10^{-5}$</td>
</tr>
<tr>
<td>$R_p$ (Ω·cm$^{-2}$)</td>
<td>$7.21 \times 10^5$</td>
</tr>
<tr>
<td>$L$ (H·cm$^{-2}$)</td>
<td>$3.21 \times 10^2$</td>
</tr>
<tr>
<td>$R_L$ (Ω·cm$^{-2}$)</td>
<td>$4.50 \times 10^4$</td>
</tr>
</tbody>
</table>

Figure 10: (a) Bode and (b) Nyquist curves of MAO coating after being immersed in 3.5 wt.% NaCl solution for 32 and 63 days.
Table 4: Fitting results of the equivalent circuit obtained by fitting the EIS data.

<table>
<thead>
<tr>
<th>$R_s$ ($\Omega \cdot \text{cm}^{-2}$)</th>
<th>$Y_0$ ($\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2}$)</th>
<th>$N$</th>
<th>$R_{\text{pore}}$ ($\Omega \cdot \text{cm}^{-2}$)</th>
<th>$C_{\text{dl}}$ ($\text{F} \cdot \text{cm}^{-2}$)</th>
<th>$R_p$ ($\Omega \cdot \text{cm}^{-2}$)</th>
<th>$W$ ($s^{-0.5} \Omega \cdot \text{cm}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.13</td>
<td>$2.16 \times 10^{-5}$</td>
<td>0.85</td>
<td>$1.78 \times 10^5$</td>
<td>$1.57 \times 10^{-5}$</td>
<td>$7.16 \times 10^5$</td>
<td>$3.21 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Figure 11: Equivalent circuit used to evaluate the EIS data presented in Figure 10.

Figure 12: Continued.
indicates that the MAO has superior corrosion protection ability. In the second stage, identifying at increasing immersion time, the EIS presents desorption characteristics at low frequencies connecting to a capacitive semicircle at high frequencies (Figure 9). In this stage, local pitting corrosion in the MAO coating takes place stimulating Al matrix dissolution through corrosion pits [45]. After long immersion time, the chloride effectively induces local breakdown of the MAO coating, which is in agreement with the reported findings in the literature. The chloride ion may penetrate through the MAO coating and reach matrix/coating interface. As a result, an additional Warburg impedance at low frequency is employed.

3.3.2. Anodic Oxidation Coating. The EIS plots for anodic oxidation coating on 5083 aluminum alloy after immersion in 3.5 wt.% NaCl solution for 1, 12, 32, and 63 days are presented in Figure 12. The Warburg impedance in Figure 11 is due to the existence of cracks (Figure 3(b)), which can act as the diffusion path for the corrosive ions. The equivalent circuit used to interpret the EIS data is shown in Figure 12. The fitted parameters obtained are given in Table 5. As is seen from Table 5, the value of $R_p$ decreased with the increase in immersion time. It indicated that the protective performance of the anodic oxidation coating on 5083 aluminum alloy surface deteriorated and the risk of corrosion increased [45, 46].

3.4. Salt Spray Test. Figure 13 shows the surface morphologies of the two different coatings on 5083 aluminum alloy after the salt spray test for 63 days. The breakdown of the both coatings is not visible observed. As is seen from Figure 13, there are almost no signs of corrosion on the surface of MAO coating. However, there was slight corrosion on
anodic oxidation coating. This is in good agreement with the electrochemical measurement.

4. Conclusions

The protective performance of the MAO is superior than that of the anodic oxidation coating. The 5083 aluminum alloy with MAO coating showed a good corrosion resistance at the initial stage. With the increase in immersion time, the pitting corrosion occurs in the MAO coating, and the protective ability of the coating deteriorated gradually. In contrast, the existence of the cracks in anodic oxidation coating can act as the diffusion path for the corrosive ions. The corrosion process is controlled by ion diffusion throughout the coatings.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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