Study on Corrosion Resistance of Anodized 6463 Aluminum Alloy as Construction Material in 3.5% Sodium Chloride Solution

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6463 aluminum alloys used for construction materials were anodized from the solution mixed with sulfuric acid and boric acid to improve mechanical and anticorrosion properties. The influences of current densities on hardness, roughness, thickness, corrosion resistance and surface morphology of anodized aluminum were investigated. It is found out that the oxidation process of aluminum alloy is accompanied by the formation and dissolution of alumina. The outer layer of anodized aluminum is porous and the inner layer is a barrier layer with high impedance. Higher current density will get anodized aluminum with larger surface roughness. With the increase of current density, the thickness and hardness of anodized aluminum increase gradually and then decrease. Anodized aluminum obtained at the condition of 2 A/dm² shows even and porous structure resulting in higher hardness and optimal corrosion resistance performance with minimum corrosion current density equal to 4.365 μA/cm².

Keywords: 6463 aluminum alloys; construction materials; anodizing; Corrosion resistance;

1. INTRODUCTION

Although pure aluminum possesses good ductility, its low strength makes it not suitable for a kind of excellent construction materials. However, by adding a small amount of magnesium, copper, silicon, chromium and other elements, aluminum alloys can be obtained. Aluminum alloys has the advantages of good plasticity, excellent electrical conductivity and high strength which are widely used in construction manufacturing, aerospace and chemistry industries [1-5]. According to a recent survey, the use of aluminum alloy in the construction industry is increasing year by year. One reason is that aluminum alloys are only one-third as dense as steel, but their strength can exceed that of structural steel. Moreover, aluminum alloys are easy to be made into various complex joints for construction
industry. Using aluminum alloys as construction materials could greatly reduce the weight of buildings, save materials and reduce cost, which have significant economic benefits [6-8]. Therefore, more than thirty percent of the world's aluminum alloys are used for construction industry.

Aluminum alloys can be divided into deformation aluminum alloys, ordinary aluminum alloys, heat resistant aluminum alloys and so on. Meanwhile, deformation aluminum alloys not only have good strength, but also possess good plasticity, which are widely used in construction industry. Common deformed aluminum alloys include 2000 series, 5000 series, 6000 series and so on. Among them, 6000 series aluminum alloys possess optimal strength widely used in construction materials with high strength requirement. However, 6000 series aluminum alloys contain a small amount of copper and magnesium resulting in poor corrosion resistance. Therefore, anodizing technology is needed to improve corrosion resistance of aluminum alloys to meet the requirement of construction materials. For example, Zhang investigated electrochemical behavior and corrosion mechanism of anodized 7B04 aluminum alloys.[9] Zineb used anodizing treatment technology to improve corrosion resistance of 5005 aluminum alloys.[10] Corrosion resistance of 6063 aluminum alloys was improved by anodizing reported by Maryam.[11] Peter reported a kind of multistep anodization to improve corrosion resistance of 7075 aluminum alloys.[12] There are many anodic oxidation methods for aluminum alloys, such as sulfuric acid anodic oxidation, oxalic acid anodic oxidation, chromic acid oxidation and so on.[13-15] Each anodic oxidation method possesses its advantage and disadvantage. For example, sulfuric acid oxidation is cheap and simple, but the wear resistance and bonding force of the oxide layer is poor. The energy consumption and cost of oxalic acid oxidation are much higher. Chromic acid anodized film has good corrosion resistance, but chromic acid is poisonous and harmful to the environment. Compare to anodizing with only one kind acid, mixed acid oxidation technology has many advantages, such as more even surface morphology, lower cost and so on. Therefore, sulfuric acid mixed with boric acid were used to anodize 6463 aluminum alloys used for construction to greatly improve mechanical and anticorrosion properties. The effects of current densities on hardness, roughness, thickness, corrosion resistance and surface morphology of 6463 aluminum oxide films were studied.

2. EXPERIMENTAL

2.1 Anodizing solution and parameters

In the paper, 98% concentrated sulfuric acid (50 g/L) mixed with boric acid (100 g/L) were used to anodize 6463 aluminum alloys for construction to greatly improve mechanical and anticorrosion properties. The anodizing process keeps at 35 °C for one hour. The current density ranges from 1 A/dm² to 3 A/dm² to study the effect on properties of anodizing aluminum.

2.2 Experimental process

6463 aluminum alloy plate with 3 cm × 3 cm size was chosen as the anode while pure titanium
plate with 5 cm × 5 cm size was used as the cathode. Before the experiment, the 6463 aluminum alloy plate must be pretreated. Firstly, the substrate was polished with a polishing machine and put into 10% sodium hydroxide solution at 60 °C for 15 minutes. And then, the substrate was pickled with 50% hydrofluoric acid for 3 minutes. After the pretreatment, the substrate was cleaned with deionized water and anodized.

2.3 Testing methods

Vickers hardness tester (HVS-1000A) was used to test the surface hardness of oxide films. Surface Profiler (KLA Tencor P6) was chosen to test the surface roughness of samples. The thickness of samples was calculated by thickness meter (CT800). The electrochemistry station (CHI660E) was used to evaluate the corrosion resistance of samples based on polarization curves at the condition of 1 mV/s scanning rate from -0.8 V to -0.5 V in 3.5% sodium chloride solution. Platinum plate with 2 cm×2 cm was used as anode while the oxide film with 1 cm×1 cm was used as cathode. The reference electrode was saturated calomel electrode. Scanning electron microscope (Hitachi S4700) was used to observe the surface morphology of samples.

3. RESULTS AND DISCUSSION

3.1 Thickness and hardness of anodized 6463 aluminum alloys

![Figure 1. Effect of current density from 1 A/dm² to 3 A/dm² on thickness and hardness of anodized aluminum](image)
The relationship among current densities, thickness and hardness is shown in Fig.1. According to Fig.1, with the increase of current density, the thickness of oxide film first increases and then decreases. The maximum thickness around 18 μm could be obtained at the condition of 2 A/dm².

Aluminum alloys used as the anode placed in acid solution, under the action of electric current to form oxide film on the surface of aluminum alloys, known as the anodic oxidation treatment. The chemical reactions that occur during aluminum oxidation are as followings:[16-17]

\[ 2Al + 3H_2O - 6e^- \rightarrow Al_2O_3 + 6H^+ \]  \hspace{1cm} (1)

\[ Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O \]  \hspace{1cm} (2)

\[ 2H^+ + 2e \rightarrow H_2 \uparrow \]  \hspace{1cm} (3)

In the process of aluminum alloy oxidation, hydrogen reaction mainly takes place at the cathode while aluminum atoms lose electrons and are oxidized to alumina at the anode. During the anodic oxidation process, the formation and dissolution of the oxide film is simultaneous. When the formation rate is greater than dissolution rate, the oxide film can be grown and thickened. Therefore, it is generally believed that the anodic oxidation of aluminum alloy is the electrolytic process of water, accompanied by the formation and dissolution of aluminum oxide film. Aluminum oxide film is composed of porous layer and barrier layer. At the initial stage of anodic oxidation, a continuous nonporous film layer is formed, which has a great resistance and is called barrier layer. With the increase of oxidation current, the surface of barrier layer is chemically dissolved to form porous layer. The structure model of anodized aluminum is reported in detail by many researchers.[18-19]

Regarding to Fig.1, with the increase of the current density from 1 A/dm² to 2 A/dm², the growth rate of the oxide film accelerates. At this time, the growth rate of the oxide film is greater than the dissolution rate, so the thickness increases. Because the oxidation process is exothermic reaction, when the current density is greater than 2 A/dm², the larger heat accumulation in the film accelerates the dissolution of alumina, so the thickness decreases. The relationship between oxide current density and growth rate of the oxide film is researched in many literatures which are basically consistent with the results of the paper.[20-21]

When the current density increases from 1 A/dm² to 3 A/dm², the hardness of oxide film ranges from about 100 HV to 350 HV. The oxidation treatment significantly increases the hardness of the aluminum alloy. The oxide film of aluminum alloy is mainly composed of α-Al₂O₃ and γ-Al₂O₃ which is reported in many papers.[22-23] Meanwhile, α-Al₂O₃ belongs to corundum structure with higher hardness. γ-Al₂O₃ is equiaxed crystal system and is metastable phase. The hardness of the oxide film is greatly increased by the combination of α-Al₂O₃ and γ-Al₂O₃.

However, when the oxidation current density is greater than 2 A/dm², higher oxidation heat will accelerate the dissolution process of oxide film and form loose surface structure resulting in the decrease of surface hardness.

3.2 Roughness and surface morphology of anodized 6463 aluminum alloys

Surface roughness refers to the unevenness between tiny peaks and valleys on the samples
Surface roughness is an important parameter for oxide film of aluminum alloys which can be used to roughly judge the porosity and uniformity. In this section, the contour arithmetic mean deviation $Ra$ in the length of 4 mm is used to characterize the roughness value of oxide film shown in Fig.2. It is obvious that oxide films of 6463 aluminum alloys prepared by different current densities show various surface roughness. With the current density increases from 1 A/dm$^2$ to 3 A/dm$^2$, the surface roughness increases from 0.1677 $\mu$m to 0.9545 $\mu$m.

![Figure 2](image1.png)

**Figure 2.** Effect of current density on roughness of anodized aluminum, (a) 1 A/dm$^2$; (b) 1.5 A/dm$^2$; (c) 2 A/dm$^2$; (d) 2.5 A/dm$^2$; (e) 3 A/dm$^2$; Scanning rate is 50 $\mu$m/s with 4 mm scanning length.

![Figure 3](image2.png)

**Figure 3.** Effect of current density on surface morphology of anodized aluminum, (a) 1 A/dm$^2$; (b) 1.5 A/dm$^2$; (c) 2 A/dm$^2$; (d) 3 A/dm$^2$; 100 nm scale with 50000 magnification.
Higher current density will get oxide films with larger surface roughness. At the condition of lower current density, the growth rate of the oxide film is slower, resulting in less porous alumina on the surface of aluminum alloys. Along with the current density increases, oxide films with more porous alumina obtained will increase the surface roughness. However, the excessive current density will produce higher oxidation heat that contributes directly to dissolution of oxide films resulting in loose and uneven surface with larger roughness.

Regarding to Fig. 3, the oxide film is composed of many porous alumina. The oxidation process of aluminum alloy is accompanied by the formation and dissolution of alumina. When the current density keeps at 1 A/dm², the formation rate of alumina is slow resulting in less and thinner alumina. With the current density increases, the formation rate of alumina increases gradually that leads to more porous alumina. However, the oxide film prepared by the current density of 3 A/dm² possesses rougher and uneven surface morphology due to larger amount of joule heat generated by high current density. Moreover, the pore diameter of oxide film increases with the increase of current density. The pore diameter of oxide film prepared at 2 A/dm² is around 20 nm.

3.3 Corrosion resistance of anodized 6463 aluminum alloys

Effect of current density on polarization curve of anodized aluminum in 3.5% sodium chloride solution is shown in Fig. 4. Tafel extrapolation is used to calculate corrosion current density and self-corrosion potential based on polarization curves to evaluate the corrosion resistance of oxide films listed in Tab. 1. According to the results of Fig. 4 and Tab. 1, with the increase of current density, the corrosion current density of oxide film decreases gradually and then increases. Oxide film obtained at the condition of 2 A/dm² possesses optimal corrosion resistance with minimum corrosion current density equal to 4.365 μA/cm². Similar corrosion resistance of aluminum alloy oxide film has also been reported.[24-25] From the discussion above, it knows that the oxide film prepared at 2 A/dm² has even porous structure and thicker oxide layer resulting in optimal corrosion resistance.

![Figure 4. Effect of current density on polarization curve of anodized aluminum in 3.5% Sodium Chloride Solution. (a) 1 A/dm²; (b) 1.5 A/dm²; (c) 2 A/dm²; (d) 2.5 A/dm²; (e) 3 A/dm²; Scanning from -0.8 V to -0.5 V in the rate of 1 mV/s.](image-url)
Table 1. Corrosion current density and self corrosion potential of anodized aluminum calculated by Tafel extrapolation method based on polarization curves

<table>
<thead>
<tr>
<th>Current density/ A/dm²</th>
<th>J/ μA/cm²</th>
<th>E/ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.118</td>
<td>-0.648</td>
</tr>
<tr>
<td>1.5</td>
<td>18.663</td>
<td>-0.629</td>
</tr>
<tr>
<td>2</td>
<td>4.365</td>
<td>-0.625</td>
</tr>
<tr>
<td>2.5</td>
<td>15.848</td>
<td>-0.723</td>
</tr>
<tr>
<td>3</td>
<td>31.622</td>
<td>-0.731</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

Sulfuric acid mixed with boric acid were used to anodize 6463 aluminum alloys used for construction materials to greatly improve mechanical and anticorrosion properties. The effects of current densities on hardness, roughness, thickness, corrosion resistance and surface morphology of oxide films were studied. With the increase of current density, the thickness and hardness of oxide film increases gradually and then decreases. Higher current density will get oxide films with larger surface roughness. Oxide film obtained at 2 A/dm² shows even and porous structure resulting in optimal corrosion resistance with minimum corrosion current density equal to 4.365 μA/cm².

References


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