Preparation of Trivalent Chromium and Rare Earth Composite Conversion Coating on Aluminum Alloy Surface

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Abstract. In this paper, the surface conversion film on 6063 aluminum alloy was prepared by chemical plating process with chromium sulfate, lanthanum sulfate and sodium phosphate as film forming agent. The corrosion resistance and surface morphology of the conversion film were analyzed by pitting corrosion test of copper sulfate and SEM. The results show that when Cr_2(SO_4)_3 is 10 g/L, La_2(SO_4)_3 is 2 g/L, Na_3PO_4 is 8 g/L, pH value is 3, temperature is 40 °C, reaction time is 10 min, the corrosion resistance of the surface conversion film is the best. The conversion coating is light green, composed of Cr, La, P, Al, O and other elements.

1. Introduction

Aluminum alloy has been widely used in automobile, building, aerospace, mechanical industry and other fields because of its excellent physical and chemical properties, light weight, high strength and easy processing. In order to enhance Aluminum Alloy corrosion resistance, prolong the service life of Aluminum Alloy, Aluminum Alloy has to be conducted surface treatment; surface treatment process include anodic oxidation, surface chemical conversion, electroplating. Because of its simple operation, strong applicability, low cost etc, the surface chemical conversion has become one of the surface treatment process the most commonly used [1-4].

At present, the common chemical conversion coatings are phosphate conversion film, titanium zirconium salt conversion film, silicate conversion film, molybdate conversion film, tungstate conversion film and so on. Chromate conversion film has been used for more than 100 years since it was successfully developed by Bauer and Vogel in 1915 because of its good corrosion resistance and high performance price ratio. However, hexavalent chromium is a primary carcinogen, and the ecological environment pollution is serious, so chromate conversion film has been banned by European and American developed countries for electronic and electrical equipment. In recent years, scholars have begun to trivalent chromium conversion coating, anti corrosion properties and mechanism were studied, and some progress has been made; the literature results show that, compared with the six properties of hexavalent chromium, trivalent chromium conversion coating or not satisfactory; but by optimizing the trivalent chromium conversion film preparation process, performance of transformation the film makes the trivalent chromium improved [5-10].

In this paper, chromium sulfate, lanthanum sulfate and sodium phosphate as film-forming agent to prepare lanthanum chromium composite film on surface of Aluminum Alloy, chromium sulfate concentration, lanthanum sulfate concentration and pH value on coating corrosion resistance influence, and surface morphology by scanning electron microscopy of lanthanum chromium composite conversion coating were characterized.
2. Experiment

6063 aluminum alloy was used in this experiment, and its chemical composition was shown in table 1.

Table 1. Chemical composition of aluminum alloy

| Element | Mg  | Si  | Zn  | Fe  | Cu  | Mn  | Cr  | Ti  | Al   |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|------|
| W/%     | 0.55| 0.39| 0.23| 0.02| 0.03| 0.02| 0.01| 0.01| Balance |

The aluminum alloy surface chemical conversion treatment process using 600# and 1000# sandpaper polishing, alkali washing (50 g/L NaOH, 2 min, room temperature, water washing, pickling (20%) nitrate, 1 min, room temperature), water washing, chemical conversion (10 min), the experimental reagents were analytically pure, the experiment water was deionized water. The typical aluminum alloy surface conversion solution composition is as follows: Cr$_2$(SO$_4$)$_3$ is 10 g/L, La$_2$(SO$_4$)$_3$ is 2 g/L, Na$_3$PO$_4$ is 8 g/L, pH value is 3, temperature is 40 °C, reaction time is 10 min.

Corrosion resistance of the coating with (3gCuSO$_4$+1mLHCl+75mLH$_2$O) copper sulfate test; surface conversion film was analyzed by SEM; Aluminum Alloy converted to surface dissolved by aqua regia, using ICP-OES to analyze the composition; the conversion film density calculated by the following formula: $P = (W_2 - W_1) / S$, $W_1$ is the transformation of aluminum the weight of the alloy, the quality of transformed $W_2$ Aluminum Alloy, $S$ is Aluminum Alloy surface area.

3. Results and Discussion

3.1. Effect of Chromium Sulfate Concentration

When lanthanum sulfate is 2 g/L, pH value is 3, temperature is 40 °C, reaction time is 10 min, the influence of chromium sulfate concentration on the corrosion resistance and density of the conversion film is shown in figure 1. According to the diagram, with the increase of chromium sulfate concentration, the density of the conversion film is increased. The density of the conversion film 230 Mg/m$^2$ increased to 385 Mg/m$^2$, but its corrosion resistance has an optimum value. When the concentration of chromic sulfate is less than 10 g/L, the CuSO$_4$ dropping time increase with the chromic sulfate concentration. When the concentration of chromium sulfate was greater than 10 g/L, the CuSO$_4$ dropping time decrease with the chromic sulfate concentration. This is mainly because of low concentration, the reaction rate is smaller, conversion of liquid ingredients are enough time surface evenly deposited on Aluminum Alloy, thus forming a conversion film uniform; but the concentration is too high, because of the chemical reaction rate is too large, resulting in some active sites of deposition is too thick, and some place. Thin, thus have a negative impact on the corrosion resistance of the conversion film.

![Figure 1. Effect of chromium sulfate concentration](image-url)
3.2. Effect of Lanthanum Sulfate Concentration
Lanthanum sulfate is not only a film-forming agent in the process of conversion, but also a film-forming accelerator. When chromium sulfate is 10 g/L, pH value is 3, temperature is 40 °C, reaction time is 10 min, the influence of lanthanum sulfate concentration on the corrosion resistance and density of the conversion film is shown in figure 2. When the concentration of lanthanum sulfate is 2 g/L, the density of the conversion film was the highest (When the concentration is 1, 1.5, 2, 2.5 g/L, the density of film is 283, 303, 343, 333 g/m²). When the concentration of lanthanum sulfate is 2 g/L, the time of drip test was the longest (When the concentration is 1, 1.5, 2, 2.5 g/L, the time of drip test was 100, 120, 138, 130 s). The concentration of lanthanum sulfate is less than 2 g/L or greater than 2 g/L, the performance of the conversion film is poor. In the process of chemical conversion, lanthanum sulfate will react with chromium sulfate on the surface of aluminum alloy to form protective film.

![Figure 2. Effect of lanthanum sulfate concentration](image)

3.3. Effect of pH Value
When the chromium sulfate is 10 g/L, lanthanum sulfate is 2 g/L, the temperature is 40 °C, the reaction time is 10 min, the influence of pH value on the corrosion resistance and density of the conversion film is shown in figure 3. When the pH value of the conversion solution is between 3, the corrosion resistance of the conversion film is the best, and the density is the maximum; when the pH value is less than 3 or greater than 4, the corrosion resistance of the conversion film is poor. The pH value in the conversion solution is the best point control conversion film deposition, it can produce corrosion activation effect on Aluminum Alloy, on the other hand, the rate can be controlled by adjusting the pH value of chemical conversion reaction; the interaction of these two aspects can affect the quality of the conversion film.

![Figure 3. Effect of pH value](image)
3.4. Surface Morphology and Composition

Figure 4 is simple aluminum alloy and under optimized conditions (chromium sulfate is 10 g/L, lanthanum sulfate is 2 g/L, pH value is 3, temperature is 40 °C, and reaction time is 10 min) after transformation treatment of aluminum alloy SEM diagram. Conversion film is composed of a scattered distribution, the particle size of 3~4 nm ultrafine spherical particles, through the analysis of ICP-OES, Cr, La, conversion film containing Mg, Al, O and other elements, the mass fraction as shown in table 2.

![Figure 4. SEM image of aluminum alloy after surface treatment](image)

| Element | Si   | Al  | P   | Cr  | La  |
|---------|------|-----|-----|-----|-----|
| w/%     | 0.3  | 91.24 | 0.45 | 0.64 | 0.33 |

4. Conclusion

(1) The optimum technological conditions for the preparation of trivalent chromium conversion coating on the surface of aluminum alloy were as follows: chromium sulfate was 10 g/L, lanthanum sulfate was 2 g/L, pH value was 3, temperature was 40 °C, and reaction time was 10 min.

(2) Chromium lanthanum conversion coating is composed of particle size of 3~4 nm ultrafine spherical particles, which contain Cr, La, Al, O and other elements.

(3) The performance of trivalent chromium conversion coating has been enhanced by the composite transformation of chromium and lanthanum.

5. References

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