

Preparation and Corrosion Resistance of Trivalent Chromium-Zirconium Composite Coating

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Abstract. Aluminum alloy are widely used in the industries because of its superior advantages. However there will be a thin oxide layer on the surface of the pure aluminum to inhibit corrosion, when adding some other elements, the obtained aluminum alloy is easy to be corroded. Surface protection is an important means to improve the corrosion resistance of aluminum alloy. The formal research had already confirmed that the trivalent chromium conversion coating can significantly improve the corrosion resistance, and the usage of the zirconium solution can also protect the aluminum alloy from corrosion. In this study, we constructed the binary conversion coating with the $\text{Cr}_2(\text{SO}_4)_3$ and the K_2ZrF_6 . The optimum reaction conditions are as follows: 10g/L H_3PO_4 , 2g/L K_2ZrF_6 , 28g/L $\text{Cr}_2(\text{SO}_4)_3$, pH=2.5~3.5, temperature 40°C, and reaction time 10 min. Copper sulfate titration experiment confirmed that the corrosion resistance was significantly improved.

1. Introduction

However there is a thin surface oxide layer on the pure aluminum, which makes it stable in the external environment, the lacking of the high specific modulus of elasticity, specific strength and hardness limits the wide range of applications. When adding some other elements, such mechanical and physical properties will be significantly improved. But the new formed aluminum alloy will be easily corroded. there will be hundreds of millions economic loss each year because of the metal corrosion, so it is necessary to development a new simple and efficient method to improve the corrosion resistance of the alloy. The using of the chromate conversion coatings to protect the alloy from corroding has been confirmed to be a most effective method. Apart from the the excellent corrosion resistance ability, hexavalent chromium conversion coating also has brilliant wear resistance and self-repair ability, which makes it widely used in many industries. However, because of the toxicity of



the hexavalent chromate, it can lead to the digestive tract, respiratory tract, skin and mucosal damage, more serious even cancer. Thus it is prohibited in electrical and electronic products according to the the Restriction of Hazardous Substances (RoHS) [1-3].

The researchers have developed new hexavalent chromium conversion coating alternatives to improve the corrosion resistance of aluminum alloys, while avoiding the toxicity. Among them trivalent chromium has been considered as most promising substitutes of the hexavalent chromium coating, because of the similar characteristic and low toxicity. Yu et al. used the $\text{KCr}(\text{SO}_4)_2$ to make the green trivalent chromium coating on the surface of the 6063 aluminum alloy, they adjusted the coating temperature, deposition time, the concentrations of the $\text{KCr}(\text{SO}_4)_2$ and H_3PO_4 and the pH to formed the trivalent chromium conversion coating, which showed excellent corrosion resistance ability, also they found that the quality and formation of the coating were most sensitive to the pH.[2,3] Although the researchers have devoted their effort to explore the optimum reaction conditions, the additives [4,5] and the mechanism of the formation of the coating [6,7], the anti-corrosion mechanism is still not clear. Apart from this, the Zr-based conversion coating has also been widely studied and has showed good application prospects [8-10]. Treatment of aluminum alloy with zirconium solution can increase the adhesion of the coating to the substrate and improve the corrosion resistance. However, the treated metal can not be used directly, it is necessary to paint the paint, and the widely use is limited. So in this study, the $\text{Cr}_2(\text{SO}_4)_3$ and the K_2ZrF_6 were used to constructed the binary conversion coating. We designed the experiment to confirmed the optimum reaction conditions, such as the concentration of the $\text{Cr}_2(\text{SO}_4)_3$, the K_2ZrF_6 and the H_3PO_4 , pH, temperature and the reaction time. Copper sulfate titration experiment was used to evaluate the corrosion resistance of the conversion coating and the morphology and electrochemical properties were studied with SEM.

2. Experimental

2.1. Materials

The 6063 aluminum alloy was utilized to obtained the binary conversion coating in this study. The major elements of aluminum alloy are listed in Table 1. All chemicals of this work were AR grade. And deionized water was used to prepare all solutions.

Table 1. Chemical composition of 6063 aluminum alloy

Element	Mg	Si	Fe	Cu	Zn	Mn	Cr	Ti	Al
W/%	0.54	0.38	0.22	0.02	0.03	0.03	0.01	0.02	Balance

2.2. Preparation of trivalent chromium conversion coating

The 6063 aluminum was polished with 400#, 600#, 800#, 1000#, 1200# abrasive paper. Then the aluminum was washed with acetone and deionized water. After that the aluminum was reacted with 50g/L NaOH at 60 °C for two minutes and 20% HNO_3 at room temperature for two minutes. After the surface oxide film is removed, the aluminum was washed with deionized water.

After the water evaporates completely, the aluminum was immersed in the solution. And the reaction conditions for each experiments were described in Table 2.

Table 2. The reaction conditions for each experiments

	T/°C	pH	Cr ₂ (SO ₄) ₃ /(g/L)	H ₃ PO ₄ /(g/L)	t/min
Fig. 1.	40	2.5	4,10,16,22,28,34	20	10
Fig. 2.	40	2.5	10,28	5, 10, 20, 30	10
Fig. 3.	40	2, 2.5, 3, 3.5	28	10	10
Fig. 4.	30, 40, 50	2.5	28	10	10

2.3. Preparation of binary conversion coating

When the reaction conditions conditions were determined in the one-component conversion coating, the K₂ZrF₆ was added in to the solution. The reaction conditions for the experiment were described in Table3.

Table 3. The reaction conditions for binary conversion coating

	T/°C	pH	Cr ₂ (SO ₄) ₃ /(g/L)	H ₃ PO ₄ /(g/L)	t/min	K ₂ ZrF ₆ /(g/L)
Fig. 5.	40	2.5	10	20	10	1,2,3,4

After that five-factor four-level orthogonal test were designed to find the best conditions and the influence of each factor in the preparation of binary conversion coating. The reaction conditions for the orthogonal test were described in Table4.

Table 4. The reaction conditions for the orthogonal test

	T/°C	pH	Cr ₂ (SO ₄) ₃ /(g/L)	H ₃ PO ₄ /(g/L)	K ₂ ZrF ₆ /(g/L)
1	20	2	2	5	1
2	30	2.5	6	10	2
3	40	3	10	20	3
4	50	3.5	14	30	4

2.4. Copper sulfate titration experiment

6.2g CuSO₄·5H₂O and 2mL Concentrated hydrochloric acid were dissolved into 150mL Deionized water. The obtained solution was dropped on the surface of the aluminum. the time from which the color changed from blue to red was recorded.

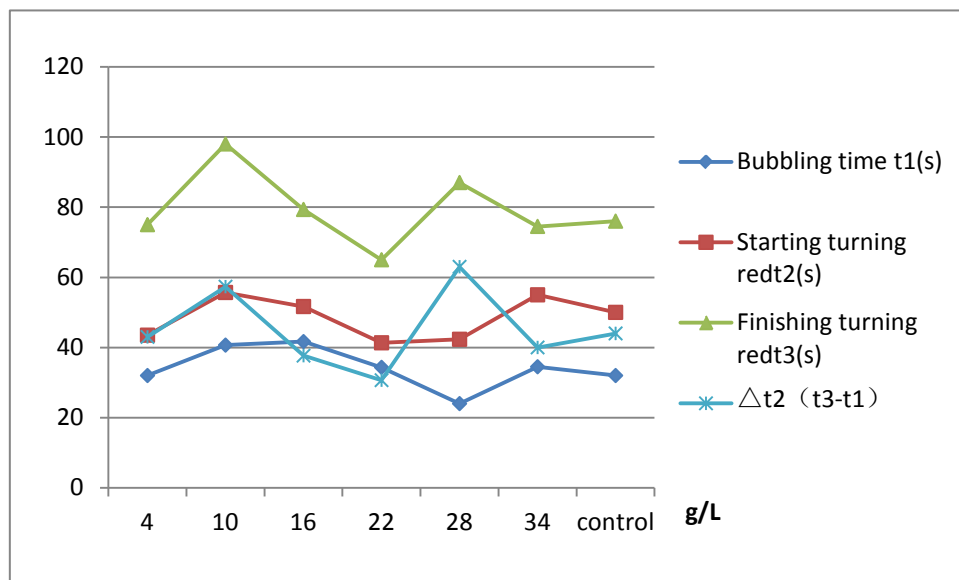
3. Results and discussion

3.1. Effect of Cr₂(SO₄)₃ concentration

Chromium ion is the main element of the film-forming reaction. According to the literature, we set six equal gradient parameters. 6063 was subjected to pretreatment for 10 min at a solution of different Cr₂(SO₄)₃ containing 20 g / L H₃PO₄ at pH 2.5, 40 ° C. From the results, 10g / L and 28g / L group of film effect and anti-corrosion effect is very prominent, anti-corrosion effect compared to other groups and control group are better, can reach 60 seconds. At the same time, the bubbling time of the 10 g / L group and the time of starting the replacement of copper were significantly later, so that 10 g / L and 28 g / L of the two preferred groups were considered to be Under these conditions the best reaction of Cr₂(SO₄)₃ concentration.

Table 5. The concentration gradient of $\text{Cr}_2(\text{SO}_4)_3$ and the corrosion resistance of conversion coating

ph2.5, 40°C, 10min, 20g/L H_3PO_4	Bubbling time t1 (s)	Starting turning red t2(s)	Finishing turning red t3(s)	$\Delta t1$ (t3-t2)	$\Delta t2$ (t3-t1)
4	32	43.5	75	31.5	43
10	40.67	55.67	98	42.33	57.33
16	41.67	51.67	79.33	27.66	37.66
22	34.33	41.33	65	23.67	30.67
28	24	42.33	87	44.67	63
34	34.5	55	74.5	19.5	40
control	32	50	76	26	44

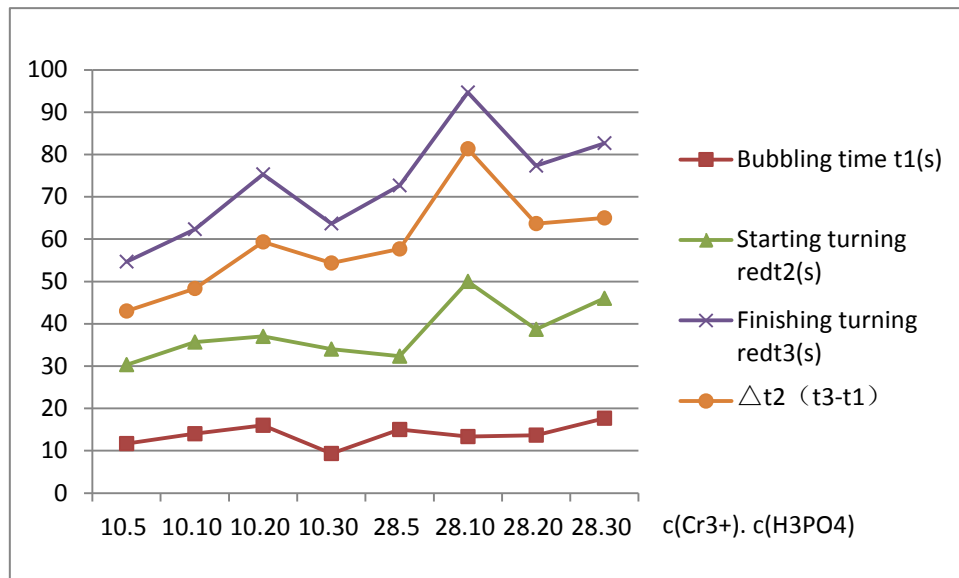
**Figure 1.** Effect of $\text{Cr}_2(\text{SO}_4)_3$ concentration on the corrosion resistance of conversion coating

3.2. Effect of H_3PO_4 concentration

Considering the phosphoric acid in the formation of the conversion film also has a great role, due to the presence of non-metallic non-conductive isolation layer, hindering the formation of micro-cell surface of the metal process, so the concentration of phosphoric acid will also affect the film quality. The concentration of $\text{Cr}_2(\text{SO}_4)_3$ in the two groups was 10g / L and 28g / L, respectively. Therefore, the gradient of 5-30g / L was set up in the literature. It can be seen from the experimental results that the optimum concentration of $\text{Cr}_2(\text{SO}_4)_3$ is 10g / L when the phosphoric acid concentration is 20g / L. However, when the concentration of phosphoric acid is 10g / L, the optimum concentration of $\text{Cr}_2(\text{SO}_4)_3$ 28g / L. The foaming time of the 10 g / L group and the time of starting copper replacement were significantly later, but the anti-corrosion effect was better in the 28 g / L group than in the 10 g / L group for less than 70 seconds , 28g / L of the overall red time up to 81 seconds. Therefore, a combination of a number of conditions, the concentration of phosphoric acid 10g / L, $\text{Cr}_2(\text{SO}_4)_3$ concentration 28g / L can be considered the reaction of the best phosphoric acid and chromium sulfate concentration.

Table 6. The concentration gradient of H_3PO_4 and the corrosion resistance of conversion coating

$c(\text{Cr}^{3+})$ 、 $c(\text{H}_3\text{PO}_4)$	Bubbling time t_1 (s)	Starting turning red $t_2(\text{s})$	Finishing turning red $t_3(\text{s})$	Δt_1 (t_3-t_2)	Δt_2 (t_3-t_1)
10.5	11.67	30.33	54.67	24.34	43
10.10	14	35.67	62.33	26.66	48.33
10.20	16	37	51.33	38.33	67.33
10.30	9.33	34	63.67	29.67	54.34
28.5	15	32.33	72.67	40.34	57.67
28.10	13.33	50	94.67	44.67	81.34
28.20	13.67	38.67	77.33	38.66	63.66
28.30	17.67	46	82.67	36.67	65
Control	15.5	30.75	66.33	35.58	50.83

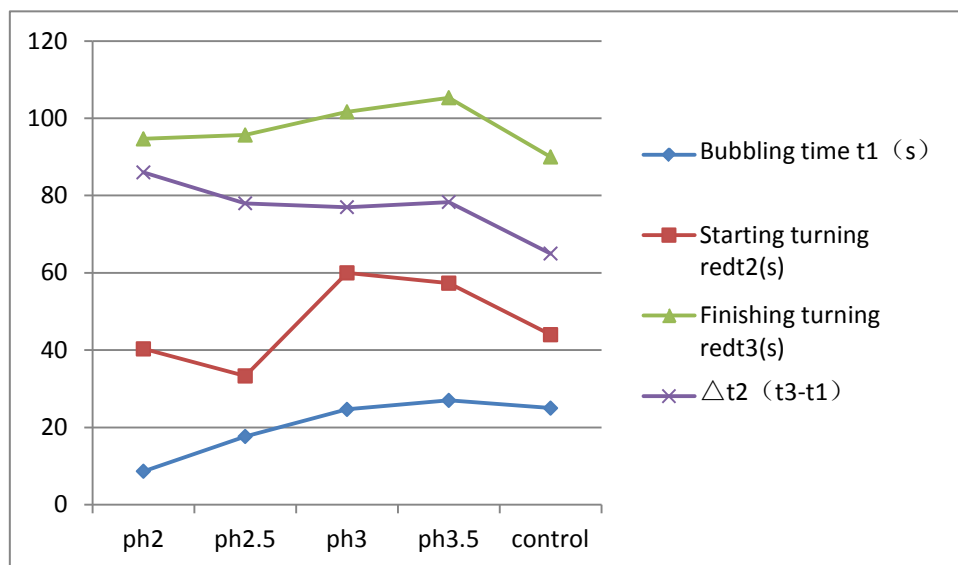
**Figure 2.** Effect of H_3PO_4 concentration on the corrosion resistance of conversion coating

3.3. Effect of pH

The pH of the reaction has an important effect on the formation of the conversion film. For 10 g / L phosphoric acid and 28 g / L $\text{Cr}_2(\text{SO}_4)_3$ solution at different pH values, the coating reaction was carried out at the same temperature. The time of bubbling was delayed with increasing pH, while the aluminum plate was replaced with copper at pH 3-3.5, and the corrosion resistance was better between pH 2.5-3.5. From this result, the best pH is between 2.5 and 3.5.

Table 7. The concentration gradient of pH and the corrosion resistance of conversion coating

28g/L, 40°C, 10min, 10g/L H ₃ PO ₄	Bubbling time t1 (s)	Starting turning red t2(s)	Finishing turning red t3(s)	$\Delta t1$ (t3-t2)	$\Delta t2$ (t3-t1)
ph2	8.67	40.33	94.67	54.34	86
ph2.5	17.67	33.33	95.67	62.34	78
ph3	24.67	60	101.67	41.67	77
ph3.5	27	57.33	105.33	48	78.33
ph4	80	133.33	∞		
control	25	44	90	46	65

**Figure 3.** Effect of pH on the corrosion resistance of conversion coating

3.4. Effect of temperature

According to the basis of literature research, in the case of other conditions of unity, we tried 30, 40 and 50 °C three temperatures. As can be seen from the data, 50 °C although the corrosion time is very long, but because the beginning of the replacement reaction time earlier. 30 and 40 °C of the three time parameters are very different, three temperatures in the results of the red time is almost the same. So a comprehensive analysis of view, 30-40 °C are reasonable temperature.

Table 8. The gradient of temperature and the corrosion resistance of conversion coating

28g/L, pH 2.0, 10min, 10g/L H ₃ PO ₄	Starting turning red (s)	Finishing turning red (s)	Δt
30°C	28	58	30
40°C	29	60	31
50°C	16.33	60	43.67
Average	23.22	75.38	52.16
control			

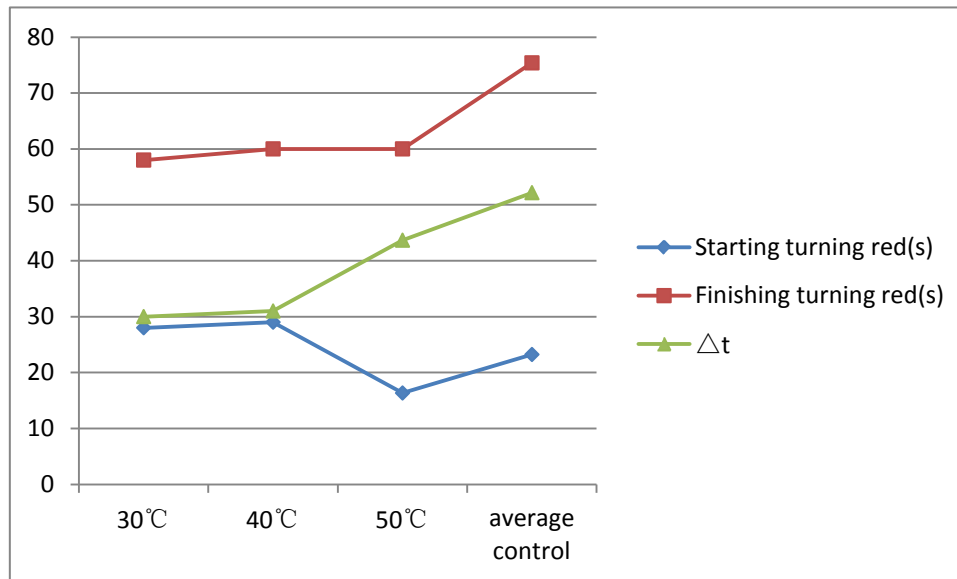


Figure 4. Effect of temperature on the corrosion resistance of conversion coating

3.5. Effect of K_2ZrF_6 concentration

The zirconium titanate oxide film formed by zirconium titanium has good protective properties and self-healing ability, but the concentration of zirconium and titanium in the conversion film is too high or too low to affect the quality of film formation. After the reaction conditions in the reference literature, we selected the process parameters of 20 g / l H_3PO_4 , 10 g / l chromium sulphate solution at 40 ° C and pH 2.5 for 10 minutes, and the concentration of K_2ZrF_6 was 1, 2, 3 and 4 g / L of the parallel test. It can be seen that the replacement time of the 3g / L group is the shortest and the corrosion time is the shortest, indicating that the conversion efficiency of the conversion film is the lowest. In contrast, the replacement reaction at 1 g / L group began to be the longest and the conversion time was the highest. In summary, the binary system of K_2ZrF_6 concentration should be 1g / L.

Table 9. The concentration gradient of K_2ZrF_6 and the corrosion resistance of conversion

ph2.5, 40°C, 10min, 20g/l H_3PO_4 , 10g/l $Cr_2(SO_4)_3$	Starting turning red t1(s)	Finishing turning red t2(s)	Δt (t2-t1)
1	22.67	47	24.33
2	17.33	39.33	22
3	13	30.33	17.33
4	22	43	21

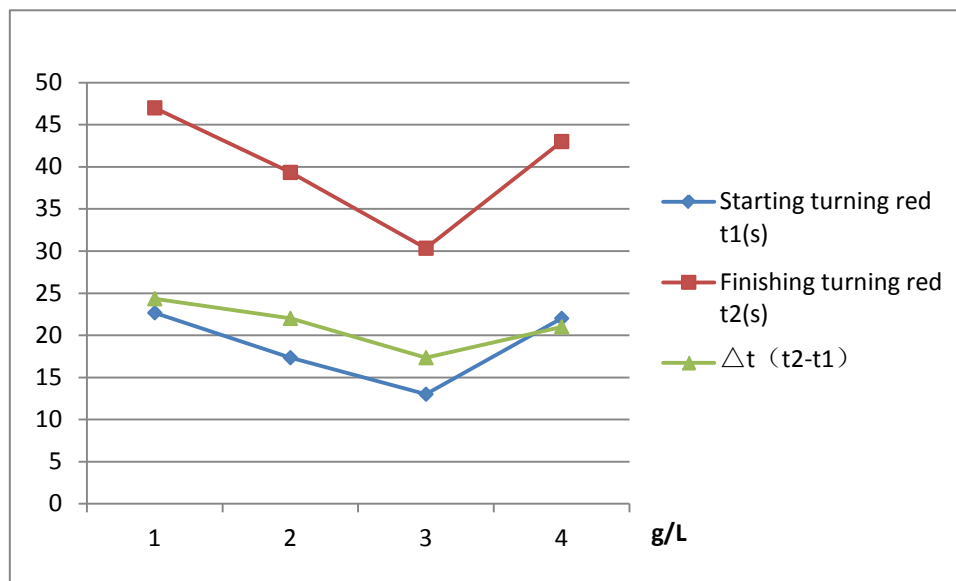


Figure 5. Effect of K_2ZrF_6 concentration on the corrosion resistance of conversion coating

3.6. Optimum reaction conditions

On the basis of above discussion, the optimum reaction conditions were obtained as follows: the concentration of chromium sulfate was 10 g / L, the concentration of phosphoric acid was 5 g / L, the reaction pH was 3.5, the reaction temperature was 40°C, and the concentration of potassium fluorozirconate was 1 g / L. At the same time, it can be seen from the very poor size that the effect of pH on the film formation is the largest, followed by $Cr_2(SO_4)_3$ concentration and phosphoric acid concentration.

4. Conclusion

(1) The optimized process condition for unitary conversion treatment are as follow: $Cr_2(SO_4)_3$ concentration 28g / L, phosphoric acid concentration 10g / L, reaction pH 2.5, reaction temperature 40 °C.

(2) The optimized process condition for binary conversion treatment are as follow: $Cr_2(SO_4)_3$ concentration 28g / L, phosphoric acid concentration 10g / L, K_2ZrF_6 concentration 1g/L, reaction pH 2.5, reaction temperature 40 °C.

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