

Short Communication

## The Effect of Sealing and Trivalent Chromium Passivating on Anodized Aluminum

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The green trivalent chromium coating on the surface of anodization film was successfully made. The anodized film was dealt with nickel and cobalt salt sealing and combination of the passivating and sealing process. Corrosion resistance of anodized films after passivation were evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy. Scanning electron microscopy (SEM) were used to investigate the morphologies of the coatings. According to the polarization curves, corrosion potentials of the passivating and sealing-anodized film were more positive than that of the anodized film. However, the corrosion potential of the combination of the passivating and sealing process were more negative than the separate process. It was found that the pore size decreased obviously after the sealing and passivating treatment from the SEM results. The chromium(III) chemical conversion coating with the thickness of 1  $\mu\text{m}$  was observed from the cross-morphologies results.

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**Keywords:** Al alloy; anodization; passivation; sealed; morphologies; potentiodynamic polarization

### 1. INTRODUCTION

Aluminum has been used in many fields, such as aerospace systems, aviation systems, auxiliary parts of locomotive and so on. However, aluminum alloys possess many disadvantages, such as poor corrosion resistance and lower strength. It is essential to improve the corrosion properties of aluminum alloys through anodization technology or passivation directly [1]. Anodization technology is very efficiency and effective to enhance the performance of aluminum alloys associated with corrosion resistance, wear resistance and tensile strength. The structure of anodized aluminum consists of an inner thin barrier layer and an outer thick porous layer. Porous layers could be the defects reducing corrosion resistance of anodized aluminum. Pitting corrosion could be easily developed in porous

layers due to electrochemical activities between intermetallics and grain boundaries [2]. Hence, it is necessary to find a kind of methods to seal the pores of porous layers and improve corrosion resistance. Sealing and passivation technologies are two approaches to seal pores of porous layers which could help improve mechanical and chemical properties [3-5]. The two methods possess totally different chemical mechanisms. Conversion coatings would form at the surface of porous layers by passivation technology [6]. However, the sealing technology would tend to deposit hydrate in the pores to improve corrosion resistance [7]. Regarding to the results reported by others, passivation and sealing technology with Cr(VI) solutions may extensively improve corrosion resistance due to the self-healing ability of chromium. [8] Nevertheless, Cr(VI) is very dangerous to the environment and human beings which is forbidden to use in many areas. Many industries have been asked to choose other chemistry to replace Cr(VI) [9]. Some researchers have reported using benchmarked hydrothermal, sodium silicate and nickel to replace sodium dichromate for sealing technology [10]. With the above methods, the surface of anodized aluminum films would be sealed with aluminium hydroxide, aluminosilicates or nickel hydroxides respectively to improve corrosion resistance. Sealing and passivation technology with Cr(III) have been applied in the industry extensively [11,12]. It was found that conversion coating with Cr(III) may improve anti-corrosion performance of 6061 aluminum alloys against  $\text{Cl}^-$  or  $\text{O}_2$  attack. The effect of the combination of sealing and passivating process for the anodized aluminum has been seldom reported.

The aim of our present work was to study the characteristic and performance of the anodized aluminum alloys treated with special sealing and passivation technology. Potentiodynamic polarization, electrochemical impedance spectroscopy, surface morphology and cross-morphology of samples were investigated.

## 2. MATERIALS AND METHODS

### 2.1 Material

The material used is 6061 aluminum alloy. The major alloying elements are given in Table 1. The specimens, 6cm×2cm×5mm in dimensions, were used as a substrate.

**Table 1.** Alloying elements

Alloying elements	Mg	Si	Fe	Mn	Cu	Cr	Zn	Ti
wt%	0.8~1.2	0.4~0.8	≤0.70	≤0.15	0.15~0.40	0.04~0.35	≤0.25	≤0.15

### 2.2 Surface modification process

The aluminum alloy was polished with abrasive paper, ultrasonic degreasing treatment in acetone. Activation was conducted in 0.5 mol/L nitric acid for 1 min after etching in a 2.5 mol/L

NaOH solution at 80°C for 30 s. Anodizing solution was composed of citric acid (153.6 g/L) and 8 ml/L sulfuric acid (98%) with voltage of 16 V, temperature of 37°C and the anodizing time of 40 min.

The trivalent chromium compounds (Cr(III)) solution with pH 3.9 were chosen to do the passivation process. The electrical parameters were fixed as follows: Experiment temperature and duration were controlled at 35°C and 2 min, respectively. The sealing solution is 4 g/L NiSO<sub>4</sub>·7H<sub>2</sub>O, 0.8 g/L CoSO<sub>4</sub>·7H<sub>2</sub>O and 3 g/L H<sub>3</sub>BO<sub>3</sub>. Reacting temperature and time are 50°C and 30 min, respectively.

### 2.3 Electrochemical tests

Potentiodynamic polarization and EIS measurements were carried out in a 3.5 wt. % NaCl solution, which is used as the corrosive media. All these electrochemical measurements were carried out in a conventional three-electrode electrolyte cell with a sample as the working electrode, a platinum plate as the auxiliary electrode and a saturated calomel electrode(SCE) as the reference. Scanning rate of potentiodynamic polarization measurements is 1mv/s. EIS measurements were performed in a range of 0.01 Hz and 100 kHz [13].

### 2.4 Morphologies tests

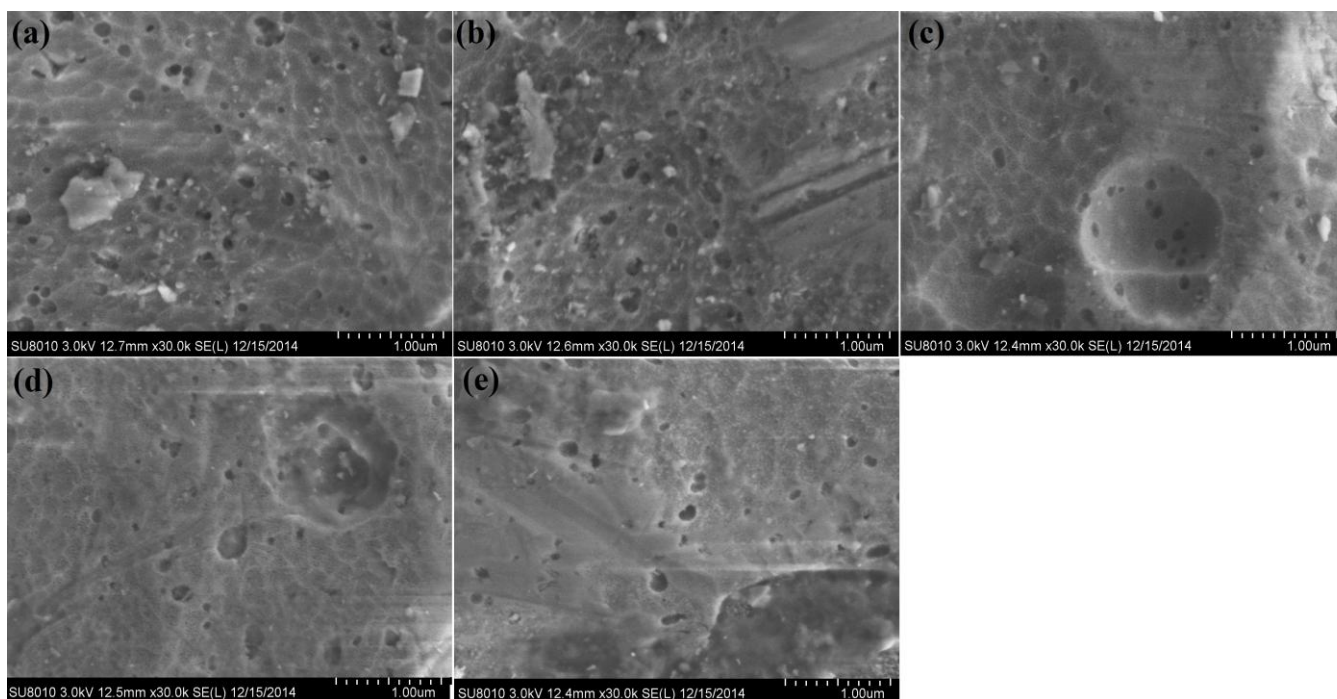
Surface morphologies of the coating were examined with field-emission scanning electron microscope(FESEM, JEOL JSM-6700F, Japan) at an accelerating voltage of 20 kV.

## 3. RESULTS AND DISCUSSION

### 3.1 Surface morphology of anodized aluminum

The microstructure of anodized aluminum before- and after- passivating and sealing treatment was observed using FE-SEM. The results were shown in Fig. 1. The porous structure of anodic aluminum oxide nanostructure appeared on the anodized film (Fig.1(a)). After passivating and sealing treatment, diameter of center pore had decreased obviously.

Figure.1(b) shows the SEM image of chromium(III) coatings formed at the anodized aluminum after 5 min exposure to the Cr(III) bath. After the treatment, it was assumed that passivation films with chromium could be formed at the surface of anodized aluminum. Moreover, according to Fig.1 (c), the surface was entirely covered with round particles, which merged together to form a compact surface. It was assumed that anodized film was filled with nickel hydroxide and cobalt hydroxide after sealing treatment(Fig.1 (c)). The Fig.1 (d,e) shows SEM images of anodized aluminum after the combination of passivation and sealed treatment. After the combination process, the anodized films seemed to be more compact and less porous.

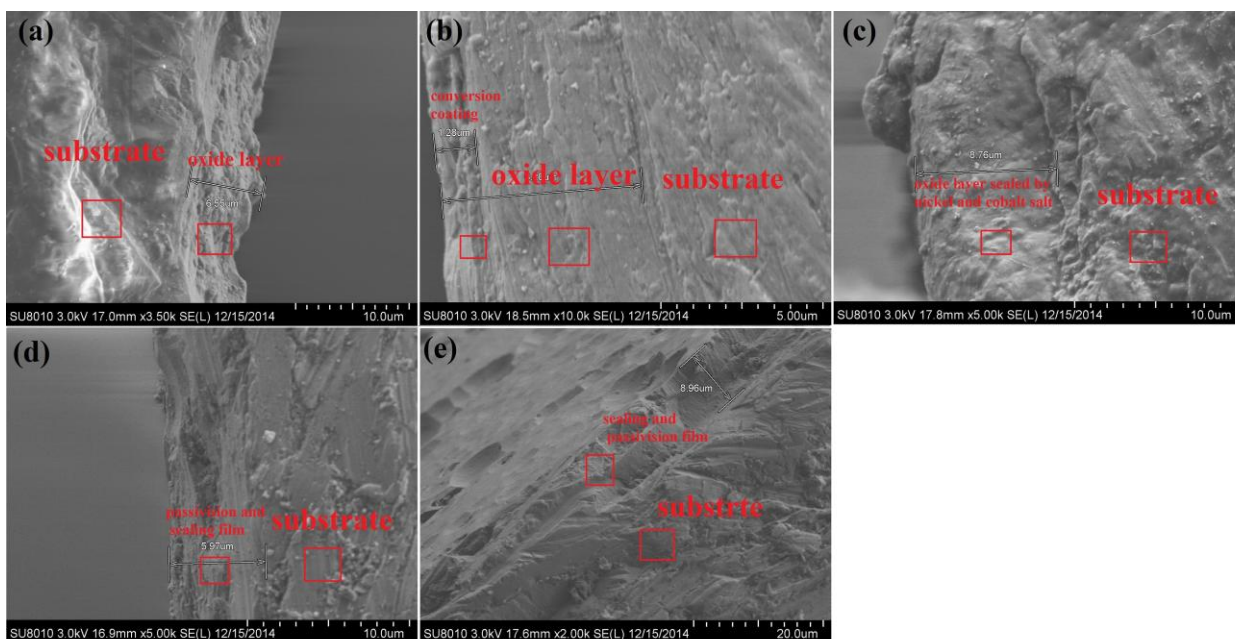


**Figure 1.** Surface morphologies of anodization film: (a) anodization film without passivation or sealing. (b) passivation by trivalent chromium solution. (c) sealing by nickel and cobalt salt solution for 5 min. (d) passivating film after sealing for anodized alloy. (e) sealing film after passivating for anodized alloy.

### 3.2 Cross-section characterization of the anodized aluminum treated by passivating and sealing

Cross section of anodized aluminum after sealing or passivating treatment was observed using FE-SEM. Fig.2 (a) shows anodization film without passivation or sealing. Fig.2 (b) shows the passivating coating thicker than the anodized alloy. Fig.2 (c) shows there was no noticeable change in thickness before and after sealing. The reason is that sealing process form hydrate deposited in the hole[14-15]. There was passivating film formed on the sealed coating from Fig.2 (d). However, from Fig.2 (e) we can see the cross-section morphology of the sealing of the passivation film. It is similar to the anodized alloy, which is assumed that the passivation film was dissolved and destroyed after sealing with heat treatment.

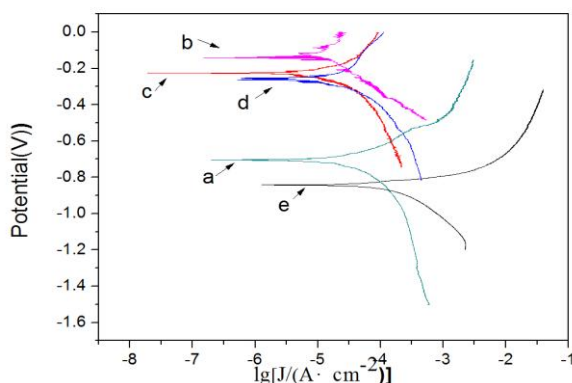
Influences of different sealing and passivating process on film thickness are described in Figure 2. Fig.2 (a), (c) and (e) show the total thickness after sealing and passivating are about 13  $\mu\text{m}$ . It can be found that there is no difference on the thickness of the anodization films, which are filled by nickel hydroxide and cobalt hydroxide after sealing treatment. The thickness of the Fig.2 (b), (d) is 14  $\mu\text{m}$ , it can be explained that there is a chemical conversion coating with the thickness about 1  $\mu\text{m}$  formed on the substrate of anodized alloy.



**Figure 2.** Cross section morphologies of anodized alloy: (a) anodization film without passivation or sealing. (b) passivation by trivalent chromium solution. (c) sealing by nickel and cobalt salt solution for 5 min. (d) passivating film after sealing for anodized alloy. (e) sealing film after passivating for anodized alloy.

### 3.3 Electrochemical behavior

Figure 3 shows polarization curves of bare anodization film and four conversion films, The corrosion potential ( $E_{\text{corr}}$ ), and corrosion current density ( $i_{\text{corr}}$ ) of the testing specimens are summarized in Table 2. The corrosion potential of the anodized alloy after passivating by trivalent chromium solution and sealing by nickel and cobalt salt for 5 min are significantly positive than that of anodized films, anodized alloy after passivation, and anodized alloy after sealing treatment. Corrosion potential of anodized film is  $-0.72$  V vs. Ag/AgCl (curve 1 in Fig. 3); corrosion potential of anodized film sealed by nickel and cobalt salt solution is  $-0.21$  V vs. Ag/AgCl (curve 3 in Fig.3). It is assumed that the decreased current was attributed to a disturbance of corrosion media penetrating through the pores by sealing; Corrosion potential of passivation by trivalent chromium solution is  $-0.12$  V vs. Ag/AgCl (curve 2 in Fig.3). But the corrosion potential of the combination of the passivation and sealed process were lower than the separate passivating or sealing process, especially the sealing process after the passivation film. The sequence of corrosion was: anodized alloy after passivating > anodized alloy after sealing > passivating film after sealing for anodized alloy > anodization film > sealing film after passivating for anodized alloy. The  $i_{\text{corr}}$  initially declines sharply, attains a steady value, and finally rises the drop in the current is attributed to the passivation film which favors the formation of a greater amount of Cr(III) coatings on the surface. The current density  $i_{\text{corr}}$  of the passivation film and sealing coatings is much lower than the anodization film[16].



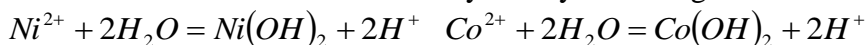
**Figure 3.** Polarization curves of (a) anodization film without passivation or sealing. (b) passivation by trivalent chromium solution. (c) sealing by nickel and cobalt salt solution for 5 min. (d) passivating film after sealing for anodized alloy. (e) sealing film after passivating for anodized alloy after 20min of immersion in a 3.5wt.% NaCl solution. Temperature: 298K. Scan rate: 1mv/s.

**Table 2.** Electrochemical parameters obtained from the polarization curves in Fig.3.

Specimen	$E_{corr}$ (V vs. Ag/AgCl)	$i_{corr}$ (A/cm <sup>2</sup> )	$\beta_a$ (mV/Dec.)	$\beta_c$ (mV/Dec.)
a	-0.72	1.58E-5	44.5	36.4
b	-0.12	6.31E-6	50.6	34.4
c	-0.21	5.62E-6	34.4	30.6
d	-0.30	5.24E-6	36.4	32.3
e	-0.88	1.26E-5	57.7	14.1

It was expected that the corrosion resistance would be improved considerably after passivating and sealing treatment, because the pores were covered by chromium(III) chemical compound. Although trivalent chromium coating showed good corrosion potential, the sealing process after passivating-anodized film showed the most negative corrosion potential. The reason was supposed to be attributed to the presence of cracks on the chromium(III) coating during sealing process by heating treatment. Therefore, the temperature of the sealing process should not be too high. Combing the two process does not seem to be an effective method to improve the corrosion resistance [17].

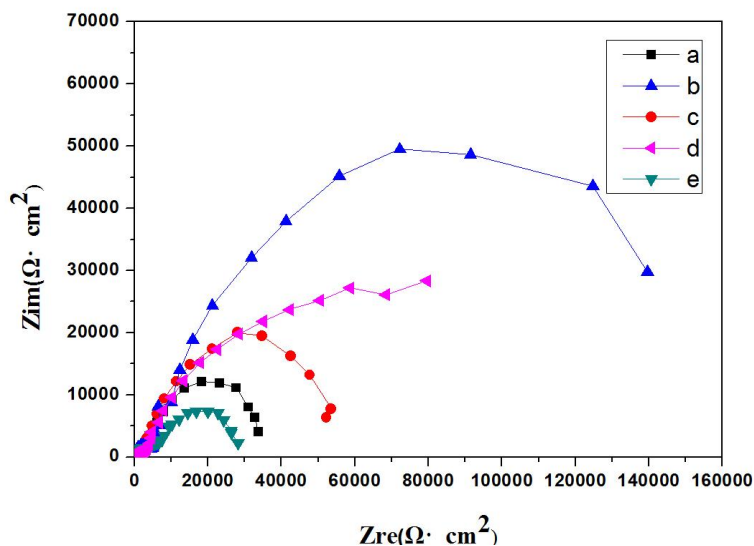
The reaction mechanism was discussed to study the potentiodynamic polarization process. The sealing behavior of anodization film was analyzed by following chemical reaction:



Transfer process of aggressive ions would be blocked by porous layer. During the sealing process, most porous are fully sealed. Moreover, moving speed and amounts of chloride ions would decrease which contribute directly to the increase of corrosion resistance [18].

Fig.4 (a) shows the size of the first capacitive loop is about 3843  $\Omega\text{cm}^2$ . The corrosion resistance is relatively small. However, the first capacitive loop of passivating sample (Fig.4 (b) open circle)

presents a larger one. The electrochemical reactions can not easily occur at the surface of the anodized film. The diameter of this semicircle reaches about  $4820 \Omega\text{cm}^2$ .



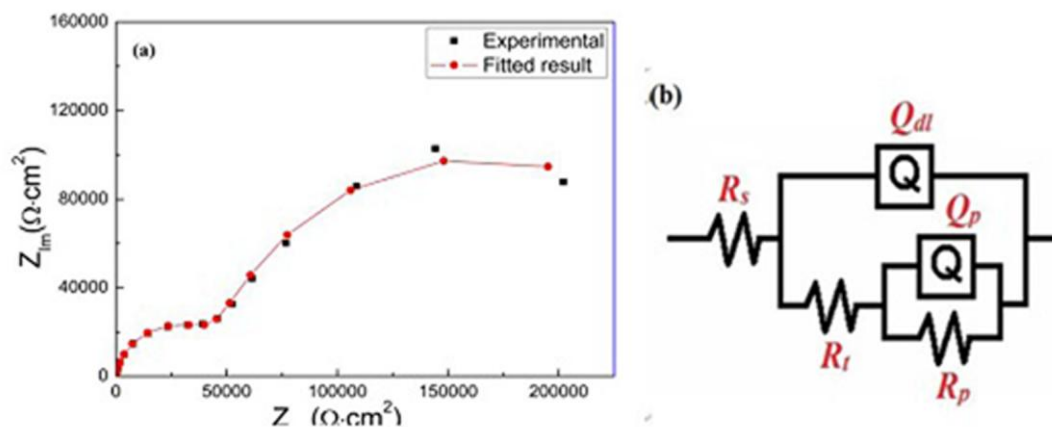
**Figure 4.** Bode phase of anodic oxidation film with different treatment : (a) anodization film without passivation or sealing. (b) passivation by trivalent chromium solution. (c) sealing by nickel and cobalt salt solution for 5 min. (d) passivating film after sealing for anodized alloy. (e) sealing film after passivating for anodic oxidation film immersed in 3.5wt. % NaCl solution (20min)

**Table 3.** EIS data simulations for aluminum anodic film with different passivating and sealing treatment in a 3.5% NaCl solution.

Different treatment methods	R <sub>s</sub> (Ωcm <sup>2</sup> )	Q <sub>dl</sub> (cm <sup>2</sup> s <sup>n</sup> Ω)	n	R <sub>t</sub> (Ωcm <sup>2</sup> )	Q <sub>p</sub> (cm <sup>2</sup> s <sup>n</sup> Ω)	n	R <sub>p</sub> (Ωcm <sup>2</sup> )
a	0.01	$3.082 \times 10^{-6}$	0.8	3842	$4.377 \times 10^{-6}$	0.8	$1.230 \times 10^4$
b	0.01	$9.107 \times 10^{-6}$	0.8	4820	$7.85 \times 10^{-6}$	0.71	$5.121 \times 10^4$
c	0.01	$7.287 \times 10^{-6}$	0.8	4193	$5.33 \times 10^{-6}$	0.68	$4.809 \times 10^4$
d	0.01	$4.302 \times 10^{-6}$	0.8	3523	$4.23 \times 10^{-6}$	0.8	$4.582 \times 10^4$
e	0.01	$6.619 \times 10^{-6}$	0.8	4365	$4.32 \times 10^{-6}$	0.8	$4.652 \times 10^4$

The capacitance is  $3.082 \times 10^{-6} \text{cm}^2 \text{s}^n \Omega$  calculated by equivalent circuit (table 3) of the anodized film. The capacitance then gradually increased when the anodized film after sealing-passivating treatment. Capacitance becomes  $9.107 \times 10^{-6} \text{cm}^2 \text{s}^n \Omega$  of the trivalent chromium conversion coating (table 3), and capacitance of the anodized film sealed by nickel and cobalt salt becomes  $7.287 \times 10^{-6} \text{cm}^2 \text{s}^n \Omega$  (table 3). The EIS result further supports the testing conclusion based on the polarization curve[19].

Detail information about impedance results were shown in Figure 5. Regarding to Fig.5(a), the experimental data were well matched. It was found out that the equivalent circuit fully fits model EIS results of anodized films. [20-21]



**Figure 5.** (a) Example of a fitted result for a selected EIS diagram (20min); (b) Equivalent circuit of 6061 alloy immersed in 3.5wt. % NaCl solution (20min)

#### 4. CONCLUSIONS

Aluminum anodized films were sealed and passivated by different methods. Effects of different methods on corrosion properties and surface morphology were investigated.

(1) According to polarization curves, corrosion potential of anodized film sealed by nickel and cobalt salt solution and passivated by trivalent chromium solution was more positive than that of anodized film. However, the corrosion potential of the combination of the passivating and sealing process were negative than the separate passivating or sealing process due to the presence of cracks on the trivalent chromium coating during sealing treatment under high temperature.

(2) Anodized films prepared with different methods showed various impedance patterns. It was found out that impedance almost maintained the same with higher frequency condition, which meant that double layer capacitor and transfer resistance did not change significantly. The passivating process forming conversion coatings on the anodized alloy can improve the corrosion resistance.

(3) There was no noticeable change in thickness before and after sealing. The reason is that hydrate during sealing process deposited in the porous hole. There was passivating film formed over the sealed film. However, the cross-section of the sealing-passivating film is similar to the anodized film. It is assumed that the passivating film was dissolved and destroyed after sealing through heat treatment.

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#### Reference

1. X.F. Meng, G.Y. Wei, H.L. Ge, Y.D. Yu, *Int. J. Electrochem. Sci.*, 8(2013) 10660-10671.
2. Y. Guo, G.S. Frankel, *Surf. Coat. Techno.*, 206 (2012) 3895–3902.



3. K.Z. Chong, T.S. Shih, *Mater. Chem. Phys.*, 80 (2003) 191
4. C. Quan, Y.D. He, *Surf. Coat. Technol.*, 269 (2015) 319–323.
5. X.K. Yang, Q. Li, S.Y. Zhang, F. Liu, S.Y. Wang, H.X. Zhang, *J. Alloys Compd.*, 495 (2010) 189–195.
6. H.C. Yu, X.Y. Huang, F.H. Lei, X.C. Tan, Y.Y. Han, *Surf. Coat. Technol.*, 218 (2013) 137–141.
7. S. S. Golru, M.M. Attar, B. Ramezanzadeh, *Prog. Org. Coat.*, 87 (2015) 52–60.
8. P. S.Coloma, U. Izagirre, Y. Belaustegi, J. B. Jorcin, F. J. Cano, N. Lapena, *Appl. Surf. Sci.*, 345(2015) 24-25.
9. S. Mahdavi, S. R. Allahkaram, Composition, *J. Alloys Compd.*, 635(2015) 150-157.
10. V. Dehnavi, X.Y. Liu, B.L. Luan, D.W. Shoesmith, S. Rohani, *Surf. Coat. Technol.*, 251 (2014) 106–114.
11. M. Whelan , K. Barton , J. Cassidy, J. Colreavy , B. Duffy, *Surf. Coat. Technol.*, 227 (2013) 75–83.
12. D.J. Kong, J.C. Wang, *J. Alloys Compd.*, 632 (2015) 286–290.
13. J.H. Lee, Y.H. Kim, H. Jang, W. Chung, *Surf. Coat. Technol.*, 243 (2014) 34–38.
14. U. Donatus, G.E. Thompson, D. Elabar, T. Hashimoto, S. Morsch, *Surf. Coat. Technol.*, 277 (2015) 91–98.
15. Z. Wu, Y. F. Cheng, L. Liu, W.J. Lv, W.B Hu, *Corros. Sci.*, 98(2015) 260–270.
16. W.K. Chen, C.Y. Bai, C.M. Liu, C.S. Lin, M.D. Ger, *Appl. Surf. Sci.*, 256 (2010) 4924–4929
17. S. Mathieu, C. Rapin, J. Steinmetz, P. Steinmetz, *Corros. Sci.*, 45 (2003) 2741
18. N.P. Hu, X.H. Dong, X.Y. He, J.F. Browning, D. W. Schaefer, *Corros. Sci.*, 97 (2015) 17–24.
19. C.J. Wang, S.M. Chen, *Surf. Coat. Technol.*, 200 (2006) 6601–6605.
20. K.H. Dong, Y.W. Song, D.Y. Shan, E. Han, *Surf. Coat. Technol.*, 266 (2015) 188–196.
21. L.Y. Niu, S.H. Chang, Y.C. Su, G.Y Li, *J. Alloys Compd.*, 635 (2015) 11–15.