Effect of Gelatin On The Corrosion Resistance Of Cr-ZrO₂ Coatings In 3% NaCl Solution

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Abstract. In this work, Cr-ZrO₂ composite coating were prepared by electrodeposition method on aluminium substrate from chromic acid based electrolytes containing gelatin. The effect of gelatin on the corrosion resistance of Cr-ZrO₂ coatings were studied in 3 wt.% sodium chloride solutions. Potentiodynamic polarization studies were performed using a Versastat 3 (Princeton Applied Research) electrochemical system with a three-electrode cell. Results shows that the corrosion resistance of Cr-ZrO₂ coating on Al substrate was improved by the addition of gelatin to the coating solution. The addition of gelatin shifted the potentiodynamic polarization curved in the noble direction. The corrosion potential changed positively from -778 mV to -259 mV. The corrosion rate of Cr-ZrO₂ coating decreased from 4.44±0.93 mpy to 0.13±0.01 mpy with the addition of 3g/L gelatin.

Keywords: electrodeposition, corrosion, gelatin, corrosion rate.

1. Introduction

Aluminum and its alloys are characterized by their high strength-to-weight ratio, good corrosion resistance, high thermal and electrical conductivity, good appearance and good fabrication characteristics. These properties make aluminum a very important material for applications in the aircraft and automotive industries [1]. However, the surface properties of aluminum need to be improved because it has a relatively low hardness and poor wear resistance [2-5]. Hard chromium coatings were often used to improve the surface performance of aluminum, thanks to its low frictional coefficients, high hardness, good corrosion resistance and good aesthetic appearance [6-11].

Recently, significant interest has been growing in the fabrication of Cr composite coatings, where ceramic particles are incorporated into a Cr layer. Jasim et al. [12] showed that the hardness of the Cr-ZrO₂ composite coating can increases with increasing zirconia concentration
in the coating. The addition of 4g/L zirconia into Cr layer improves the hardness up to 1017 HV0.2. Similar works by Hashimoto et al [7] showed that the addition of zirconia particles, ZrO₂, as much as 2g/L in Cr solution succeeded in increasing the hardness of the chromium layer on a steel substrate up to 1200 HV. However, the authors could not find any work related on the deposition of Cr directly on the aluminum substrate. Based on these fact, recently, Luthfiani [13] have been trying to deposit Cr-ZrO₂ particles on the aluminium substrate and evaluate its mechanical properties. Gelatin additive agent was used to improve the dispersion ability of ZrO₂ in the Cr plating solution. The addition of 1-wt% gelatin on the electrolyte suspension was found to improve the hardness of Cr-ZrO₂ layer up to 1220 VHN. In this work, the effect of gelatin on the corrosion resistance of Cr-ZrO₂ coatings will be studied in 3 wt.% sodium chloride solutions.

2. Materials and Methods

Aluminum series 1100 were selected as a substrate. The Al specimens were cut into coupon (20 x 10 x 1 mm) and mechanically polished with various size of abrasive paper up to 2000 grit. The area of specimens exposed to the plating solution was limited to the size of 10 x 10 mm. Afterwards the coupons were degreased with 50% HNO₃ for 1 minute at room temperature, followed by rinsing, and immersion in zincate solution (525 g/L NaOH and 98 g/L ZnO) for 2 minutes. Finally, the specimens were rinsed, and ready for electrodeposition process. Electrodeposition experiments were carried out at 45-50 °C in chromic acid electrolytes, under a constant current density of 0.8 A/cm² and deposition time of 120 minutes. The content of nano ZrO₂ in the solution was fixed at 3 g/L to improve the hardness of Cr layer. The gelatin content was varied from 0 to 3 g/L to improve the uniformity/homogeneity of the coating. The details of bath composition and plating parameters are shown in Table 1.

| Table 1. The composition of the experimental electrolytes |
|----------------------------------------------------------|
| Electrolyte composition                                | Chrome coatings | composite coatings |
| CrO₃                                                    | 250 g/L         | 250 g/L           |
| H₂SO₄                                                  | 2.5 g/L         | 2.5 g/L           |
| ZrO₂ particles                                         | 3 g/L           |                   |
| Gelatin                                                | 0, 1, 3 g/L     |                   |

Microstructure observation and thickness of Cr-ZrO₂ coating was evaluated from its cross-section, using optical microscope (OM). Potentiodynamic corrosion test was carried out in a 3 wt% NaCl solution at room temperature with a Verstatat 3 electrochemical system using a three-electrode cell configuration. The schematic experimental setup can be observed in Figure 1. Cr-ZrO₂ composite coating was set as the working electrode (WE). Graphite rod was set as the counter electrode (CE), and saturated calomel electrode (SCE) was set as the reference electrode (RE). The measurement was conducted in the range of -0.3V (initial potential) to +0.2V (final potential). The corrosion potential (Ecorr) and corrosion current density (Icorr) of the produced coatings were determined from the intersection of the cathodic and anodic curves by using tafel extrapolation method. After the test, the corrosion rate of specimen was calculated according to the following equation:

\[ CR_{mpy} = \frac{[0.131]}{I_{corr} \times EW/\rho} \]  \[1\]
Where CR, Icorr, EW and ρ are the corrosion rate in mpy (mils/year), corrosion current density (µA/cm²), equivalent weight and density in g/cm³.

![Diagram](image)

Figure 1. (a) schematics three electrode connection method and (b) actual experimental setup for corrosion test.

3. Results and Discussion

3.1 Coating thickness

The coating thickness of pure Cr, Cr-ZrO₂ with or without gelatin addition in the bath are shown in Figure 2.

![Images](image)

Figure 2. Cross section of (a) Cr coating, (b)Cr-ZrO2 coating and (c) Cr-ZrO2 coating with gelatin

In general, the cross-section micrograph shows a homogeneous and compact Cr and Cr-ZrO₂ coating without microcracks. The addition of nano ZrO₂ particles in the electrolytes slightly increase the thickness of Cr coating from 67 μm to 76 μm. The addition of gelatin in the electrolytes increases the thickness of Cr-nano ZrO₂ coating from 76 μm to 88 μm. Several researchers [14-15] have been reported that the addition of additive agent into electrolytes may improve the deposition rate and adherence of the coating into the substrate. Gelatin is a hydrolyzed form of collagen, which is sometimes added to electroplating baths to control the deposition rate, crystallization, leveling and brightness of the deposit [16]. During electrodeposition, gelatin were found to modify the characteristics and enhance the electrodeposition efficiency and/or corrosion resistance of Zn–Ni deposits [17-19]. In this work, it seems that gelatin affected the Cr-ZrO₂ deposition process through preferential adsorption on
the surface of the cathode. As a result, the deposition rate of Cr-ZrO₂ is higher with the presence of gelatin in the electrolyte, resulted in thicker coating.

3.2 Corrosion resistance

Tafel polarization curves of Cr-ZrO₂ electrodeposited coating at different gelatin concentration in the plating bath are shown in Fig. 3. According to these figures, the corrosion potential and corrosion current density of as deposited Cr-ZrO₂ coating (3 wt%) is about -778 mV and 4.66 μA/cm², respectively. It can be observed that by increasing the concentration of gelatin in the plating bath, the corrosion potential of Cr-ZrO₂ coating shifts to the noble direction, from -778 mV to about -259 mV. In this condition, the corrosion current density decreases from 4.66 μA/cm² to 0.11 μA/cm².

![Figure 3. Potentiodynamic polarization curves of The Cr-ZrO₂ coating with or without gelatin](image)

The change of corrosion potential, corrosion current density, and corrosion rates of Cr-ZrO₂ coating vs. gelatin concentration in the plating bath are also presented in Table 2. It can be concluded that the produced Cr-ZrO₂ coating at higher gelatin concentration in the plating bath exhibit better corrosion resistance on 3 % NaCl solution. The corrosion rate of Cr-ZrO₂ coating decreases from 4.44±0.93 mpy to 0.13±0.01 mpy with the addition of 3g/L gelatin in the plating bath.

| Coating System | Corrosion Rate (mpy) | 𝐸_{corr} (mV) | 𝐼_{corr} (µA) |
|----------------|----------------------|--------------|---------------|
| Cr + 3g/L ZrO₂| 4.44 ± 0.93          | -778         | 4.66          |
| Cr + 3g/L ZrO₂ + 1g/L Gelatin | 0.15 ± 0.02 | -428 | 0.22 |
| Cr + 3g/L ZrO₂ + 3g/L Gelatin | 0.13 ± 0.01 | -259 | 0.11 |

The higher corrosion resistance of Cr-ZrO₂ coating with the increase of gelatin concentration in the plating bath can be attributed to the:
1. Increase of ZrO$_2$ content in the Cr matrix. The addition of gelatin to the plating bath may also promote the formation of a relatively stable suspension of ZrO$_2$ particles. The adsorbed gelatin layer on the surface of ZrO$_2$ particles provides electrostatic stabilization for the suspension, preventing particle agglomeration [20]. As a result, the addition of gelatin improve the co-deposition of ZrO$_2$ particles in chrome matrix.

2. Formation of a uniform and highly protective passive film at the surface of Cr-ZrO$_2$ coating. Adsorption of gelatin into the Cr-ZrO$_2$ layer promotes the formation of passive films [21-22].

3. Lack of defect, such as grain boundaries or porosity in the coating. The presence of gelatin in the bath may covering the microcrack/porosities available at the Cr-ZrO$_2$ coating surface [13].

4. Conclusions
Based on our investigation about fabrication of Cr-ZrO$_2$ coating by means of electrodeposition, we summarize the primary results as follows. Cr-ZrO$_2$ coating were successfully formed during electrodeposition process. The addition of gelatin in the plating bath improves the deposition rates and corrosion resistance of Cr-ZrO$_2$ coatings. The corrosion rate of Cr-ZrO$_2$ coating decreases from 4.44±0.93 mpy to 0.13±0.01 mpy with the addition of 3g/L gelatin in the plating bath.

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6. References
[1] Dong, H 2010. Surface engineering of light alloys Aluminium, magnesium and titanium alloys. (Washington DC: Woodhead Publishing Limited)
[2] G.E. Totten 2003 Handbook of Aluminium: Physical Metallurgy and Processes (CRC Press)
[3] ASM Handbook Vol. 5 Surface Engineering. p797
[4] Deqing W, Ziyuan S and Tangshan K 2005 Sur. Coat. Technol. 191(2) 324
[5] Wan S, Li D, Zhang G, Tieu AK and Zhang B 2017 Tribol Int 106 10
[6] Zhenkun Yang. 2011 Alternatives to hard chromium plating on piston rods (Karlstads Universitet:Sweden)
[7] Hashimoto K, Sugio K, Sasaki G, Setiawan AR and Ramelan A 2016 Mech. Eng. J 3(2) 15
[8] Barbato RS, Ponce FJ, Jara VM, Cuevas SJ and Egaña AR 2008 J. Chilean Chem. Soc. 53 1429
[9] Svenson, E 2006 Dura Chrome Hard Chromium Plating. (USA: Plating Resources, Inc. Cocoa).
[10] Wu C, Hong Y, Chen W, Chen J, Yuan M and Liao XA 2016 298 83
[11] Biberger J, Füßer H-J, Klaus M, Genzel C. 2017 Wear 376 1502
[12] Jasim, T. 2015. J. Sci. Eng. Res. 6, 7
[13] Luthfiani, F 2018 Study the Effect of Gelatin on Corrosion Rate on deposition of Cr-Nano ZrO2 Coatings, (Thesis, Bandung Institute of Technology).
[14] Schrieber, R 2007 Gelatine Handbook Theory and Industrial Practice. (Germany: WILEY-VCH Verlag GmbH & Co.)
[15] Basics of Metal Matrix Composites 2006 Metal Matrix Composites: Custom-Made Materials for Automotive and Aerospace Engineering, ed K.U Kainer (Wiley-VCH Verlag GmbH & Co) pp 1–54
[16] American Society for Metals 1984 Aluminum: Properties and Physical Metallurgy, ed J.E. Hatch (ASM) pp. 30–35
[17] Torralba J., da Costa C and Velasco F 2003 J. Mat. Proc. Techno. 133(1) 203
[18] Lurie S, Volkov-Bogorodskiy D, Solyaev Y, Rizahanov R and Agureev L 2016 Comp. Mat. Sci. 116 62
[19] U. Pramod, K 2015 Int. J. Thin. Fil. Sci. Tec. 4(2) 147
[20] Afifi SE, Ebaid AR, Hegazy MM and Barakat AK 1992 JOM 44(1) 32
[21] Soares ME, Souza CAC and Kuri SE 2006 Sur. Coat. Technol. 201(6) 2953
[22] Pedroza GAG, de Souza CAC, Carlos IA and de Andrade Lima LRP 2012 Sur. Coat. Technol. 206(11) 2927