



Preparation and electrochemical properties of Cr(III)–Ti-based coatings on 6063 Al alloy

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ARTICLE INFO

Article history:

Received 6 September 2012

Accepted in revised form 28 December 2012

Available online 6 January 2013

Keywords:

Coating

Aluminum alloy

Polarization

EIS

Trivalent chromium

Corrosion resistance

ABSTRACT

Trivalent chromium–titanium (Cr(III)–Ti-based) coatings were prepared on a 6063 Al alloy by using chromic potassium sulfate and titanium(IV) oxysulfate to improve corrosion resistance. Polarization curves and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical characteristics of the Cr(III)–Ti-based coatings formed with different titanium oxysulfate concentrations. The polarization curves show that the coatings formed in $2.5 \text{ g} \cdot \text{L}^{-1}$ to $4.5 \text{ g} \cdot \text{L}^{-1}$ titanium(IV) oxysulfate solution have a lower corrosion current density (i_{corr}) than the coatings without titanium and the bare aluminum alloy. EIS found that the Cr(III)–Ti-based coatings have a better protective effect. The morphology, composition, and valence state of the coatings were examined by using a scanning electron microscope, energy dispersive X-ray, and X-ray photoelectron spectroscopy (XPS), respectively. The morphology of the Cr–Ti-based coatings remains almost unchanged, and the coatings consist mainly of Cr, Ti, P, and O after the addition of titanium(IV) oxysulfate. The SEM results are consistent with electrochemical phenomena. XPS analysis reveals that the Cr is in a Cr^{3+} state and Ti is in a Ti^{4+} state in the coatings.

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1. Introduction

Chromate (Cr(VI)) conversion coatings are extensively used to improve the corrosion resistance of metals such as aluminum, zinc, magnesium alloys, and galvanized steel. However, hexavalent chromium is highly toxic and carcinogenic, and the European Union has prohibited its use in the electrical and electronic industries [1]. Therefore, various environmentally friendly corrosion protection methods have been actively developed in the past decade [2,3]. However, no suitable replacement for chromate has been developed for use in the most demanding applications [4]. Recent research focuses on a wide variety of new chemical conversion coatings including Ti, Mo, Co, and Zn compounds, and rare earth metal salts. These elements have low toxicity levels and are relatively abundant in nature [5–7], although their anticorrosive performance still needs to be improved.

Cr(III) coatings offer highly effective protection for most active metals and are less toxic than Cr(VI) [8]. Scientists have been studying the attributes of these coatings and have reported valuable findings and processes. Chen et al. found that the corrosion resistance of Cr(III) coatings declines with increasing immersion time [9]. Wen et al. reported that to a large extent, the protection properties of the Cr(III) conversion coatings depend on the surface preparation prior to cerium pretreatment [10]. Lee et al. discovered that the hardness, wear resistance, and corrosion resistance of an Al alloy surface improved after

Cr_2O_3 sealing [11]. Mu et al. produced a transparent passive film on an electroless nickel phosphorus coating in a Cr(III) bath [12].

Ti-based conversion coatings can also provide good protection for most metals and are potential replacements for traditional Cr(VI) coatings. Saarimaa et al. confirmed that the Ti-based pretreatment layer could provide protection mainly via its barrier mechanism for hot dip-galvanized steel [13]. Wu et al. found that this Ti-based coating/substrate system could effectively improve the corrosion resistance of AZ31 magnesium alloy, as well as provide the alloy with excellent mechanical strength and surface hardness [14]. Several researchers have shown that Ti-based conversion coatings can improve the corrosion resistance of metal substrates. However, Nordlien et al. found that the formation of a uniform Ti-based conversion layer is impaired by Al(Fe,Mn)Si intermetallics in the microstructure of the Al alloy [15]. The intermetallics are preferential sites for the nucleation of the conversion layer because of their cathodic behavior, which indicates that a completely protective coverage could not be obtained on Al alloys with Ti element alone because of the presence of Al(Fe,Mn)Si particles. After investigating the corrosion resistance of trivalent chromium, titanium, and hexavalent chromium conversion coatings on AA 7075 alloys, Chen et al. found that Cr(III)–Zr-based coatings have the best corrosion resistance, the corrosion resistance of Cr(VI)-based coatings is poorer, and that of Ti-based coatings is the worst [16]. Distinguishing the treated and untreated ones in the production line is difficult because of the colorlessness of the Ti-based coating, which limits its applications to a large extent. Therefore, Ti-based or Cr(III)-based coatings do not have sufficiently strong corrosion protection properties for Al–Si alloys. To explore

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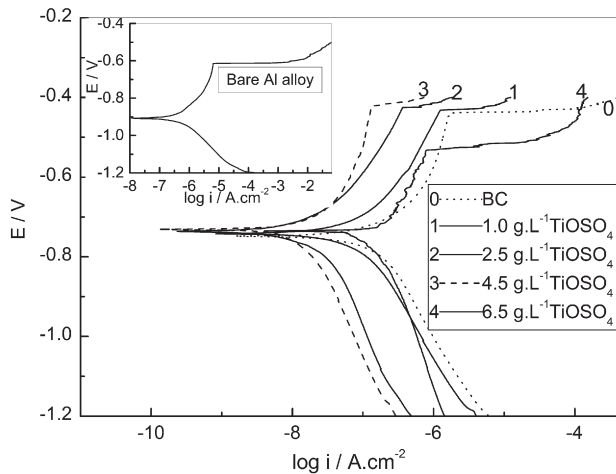


Fig. 1. Polarization curves measured from the 6063 Al alloy samples coated with Cr(III) conversion solutions that contain different amounts of titanium(IV) oxysulfate, including the BC-only and the bare (uncoated) samples [BC= basic composition, containing $25 \text{ g} \cdot \text{L}^{-1} \text{ KCr}(\text{SO}_4)_2$, $20 \text{ g} \cdot \text{L}^{-1} \text{ H}_3\text{PO}_4$, and pH $2.8 (\pm 0.1)$].

the combined advantages of both materials, this study investigated the effects of Cr(III)–Ti-based coatings. Furthermore, 6063 Al alloys reinforced with SiC particles have many applications in the aerospace, transportation, and industrial sectors because of their high wear resistance, low thermal expansion coefficient, and high mechanical strength/density ratio [17]. Therefore, a 6063 Al alloy was used as the experimental substrate.

This study aims to describe the effect of titanium(IV) oxysulfate concentration on the corrosion resistance of Cr(III) conversion coatings. The corrosion resistance of the coatings was investigated by using linear polarization curves and electrochemical impedance spectroscopy. The morphology, composition, and valence state of the coatings were examined by employing scanning electron microscope (SEM), energy dispersive X-ray (EDX), and X-ray photoelectron spectroscopy (XPS), respectively. The effects of Cr(III)–Ti-based and Cr(III)-based coatings on an Al alloy were compared.

2. Experimental procedure

2.1. Materials

A 6063 Al alloy was investigated in this study. The nominal composition of this alloy is as follows (wt.%): <0.3 Cu; 0.635Mg; 0.19 Fe; 0.443 Si; 0.04 Mn; <0.002 Cr; <0.002 Zn; <0.002 Ti; remainder Al. All solutions were made by using reagent grade chemicals and distilled water.

2.2. Surface modification process

Surface modification processes are based on our previous work [18]. The basic composition (BC) of the bath for the Cr(III) coating was $25 \text{ g} \cdot \text{L}^{-1} \text{ KCr}(\text{SO}_4)_2$ and $20 \text{ g} \cdot \text{L}^{-1} \text{ H}_3\text{PO}_4$. The pH of the deposition bath was fixed at $2.8 (\pm 0.1)$, and the temperature was maintained

Table 1
Corrosion resistance parameters obtained from the polarization curves in Fig. 1.

Condition	$E_{\text{corr}}/\text{mV}$	$i_{\text{corr}}/\mu\text{A}/\text{cm}^2$	E_{pit}/mV	$(E_{\text{pit}} - E_{\text{corr}})/\text{mV}$
Uncoated	−907	6.28	−615	292
BC	−748	0.14	−439	309
BC + $1.0 \text{ g} \cdot \text{L}^{-1} \text{ T}$	−742	0.12	−432	310
BC + $2.5 \text{ g} \cdot \text{L}^{-1} \text{ T}$	−736	0.04	−425	311
BC + $4.5 \text{ g} \cdot \text{L}^{-1} \text{ T}$	−731	0.03	−422	309
BC + $6.5 \text{ g} \cdot \text{L}^{-1} \text{ T}$	−735	0.13	−532	203

Note: T—TiOSO₄.

at $35 (\pm 0.5)^\circ\text{C}$. Different quantities of titanium(IV) oxysulfate were added to the deposition bath. The Cr(III) conversion coating process involved the following steps: polishing by using 600#, 800#, 1000#, and 1200# abrasive paper → degreasing (5 min) → rinsing with distilled water (2 min) → activation by immersion in 5% NaOH aqueous solution for 2 min → rinsing with distilled water (2 min) → immersion in a Cr(III) conversion solution (9 min) → rinsing with distilled water (2 min) → drying in air (1 h) → testing (electrochemical, SEM, or XPS measurement).

2.3. Electrochemical measurements

Cylindrical rod samples were sealed in glass tubes by using an epoxy resin. The diameter of the cylindrical rod and the area of the surface exposed to the bath are 1 cm and 0.785 cm^2 , respectively. All electrochemical experiments were examined by using a CHI 660B electrochemical workstation (Cordova, USA).

Polarization curves and AC impedance spectra were obtained in 3.5% NaCl aqueous solution with pH 6.2 at room temperature. A three-electrode cell was employed, and the test materials were used as the working electrodes. A large platinum foil and saturated calomel electrodes were used as the counter and the reference electrodes, respectively. The measurements of polarization curves were performed at a scan rate of 0.5 mV/s (from -1200 mV to -400 mV) with respect to the corrosion potential (E_{corr}). AC impedance spectra were recorded in the frequency range of 100 kHz to 0.01 Hz with an AC amplitude of 5 mV at the open circuit potential. AC impedance spectra were collected at constant potential conditions.

2.4. Surface analysis

Surface morphologies of the coatings were obtained by using a JEOL JSM-6360 scanning electron microscope at an accelerating voltage of 20 kV. Their compositions were analyzed by using EDX-Genesis 60S (Edax, USA). XPS of the samples was conducted by using a Kratos Axis Ultra DLD spectrometer. The spectra were recorded by using monochromated Al K α X-rays ($h\nu = 1486.6 \text{ electron volts [eV]}$) which operated at 15 kV and 10 mA. The base pressure in the spectrometer chamber was less than $5 \times 10^{-9} \text{ Torr}$. The binding energies were calibrated with respect to the C 1s electron peak at 284.6 eV before the test.

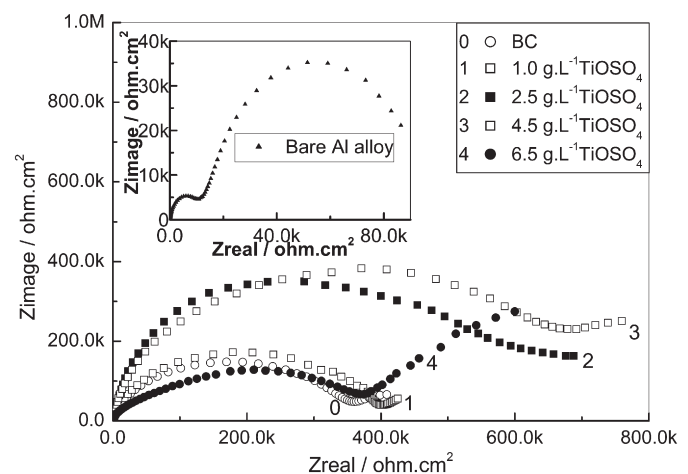


Fig. 2. Nyquist plots measured for 6063 Al alloy samples coated with Cr(III) conversion solutions that contain different amounts of titanium(IV) oxysulfate, including the BC-only and the bare (uncoated) samples [BC= basic composition, containing $25 \text{ g} \cdot \text{L}^{-1} \text{ KCr}(\text{SO}_4)_2$, $20 \text{ g} \cdot \text{L}^{-1} \text{ H}_3\text{PO}_4$, and pH $2.8 (\pm 0.1)$].

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