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Self-repairing vanadium–zirconium composite conversion coating for aluminum alloys

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ABSTRACT

In this paper, new self-repairing vanadium–zirconium composite conversion coating was prepared and investigated by Electrochemical impedance spectra (EIS), Scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. EIS results showed that V–Zr conversion coating with hydrogen peroxide modified (VZO) revealed an increasing corrosion resistance in corrosive media which meant a certain self-repairing effect. SEM comparison photos also disclosed that VZO treated with scratches was gradually ameliorated from the initial cracked configuration to fewer cracks and more fillers through an immersion of 3.5% NaCl solution. XPS results demonstrated that the content of vanadium on VZO increased and zirconium declined when immersed in the corrosive solution. This explained further that the self-repairing ability could be related to vanadium. From the above results, we inferred possible structures of VZO and proposed that self-repairing effect was achieved through a hydrolysis condensation polymerization process of vanadate in the localized corrosion area.

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1. Introduction

Aluminum alloy is widely used in various industries due to the combination of good mechanical properties and light weight. However, Al alloy is susceptible to localized corrosion because of the distribution of intermetallic compounds (IMCs). Chromate treatments had played an important role for corrosion protection on Al alloys owe to their self-repairing ability, simple application and high efficiency/cost ratio. Moreover, they provided the best corrosion resistance and facilitated the application of further treatment [1]. But, Cr (VI) has been identified as a carcinogen. Cr (VI)-based treatments are being phased out. Due to above reasons, new alternative and more eco-friendly surface treatments need to be studied.

To replace the toxic Cr (VI), a lot of studies have been invested for eco-friendly conversion treatments. Rare-earth element such as cerium seems to be a feasible replacement for chromates [2–5], which acts as a cathodic inhibitor by forming a cerium-riched layer [6]. Phosphate is another alternative of chromates [7–9]. It is usually used in conversion solution to form an insoluble phosphate layer [10]. Also, some organic compounds which contain nitrogen, sulfur and ring system have been used as corrosion inhibitors [11]. Titanium and zirconium conversion coatings are studied actively because of their excellent corrosion resistance [12,13]. In these non-chromate conversion coatings, however, only titanium and zirconium conversion coatings are used to substitute chromate-based conversion coatings occasionally at low demands.

In this paper, we prepared a vanadium–zirconium composite conversion coating as a new alternative for Cr (VI) conversion coating on Al alloy. As an anode corrosion inhibitor, vanadium is usually used on zinc and steel substrates. But it is rarely studied in the conversion coating field. Hamdy has identified that vanadium conversion coatings have a certain self-repairing functionality but a relative poor corrosion resistance [14–16]. This paper tried to endow a self-repairing ability to the zirconium-based conversion coating and explored whether V–Zr composite conversion coating worked for the corrosion protection on Al alloys or not. Using EIS, SEM and XPS, we discussed the properties and mechanism of V–Zr composite conversion coating and the possibility as an alternative for chromate coatings.

2. Experimental

2.1. Sample preparation

Al alloy (6063, wt%: Al 98.2, Zn 0.10, Mn 0.1, Fe 0.35, Si 0.40, Cu 0.10, Mg 0.55, Cr 0.10, Ti 0.10) was used as received. It was cut into 10 mm × 10 mm squares. One side of these specimens embedded in an epoxy resin holder was used as working electrode for electrochemical measurements.

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2.2. Preparation of conversion coating on Al alloy

The surface of Al alloy was abraded with emery papers of 600–1200 grit, ultrasonically degreased in acetone for 3–5 min and then rinsed with deionized water.

The V–Zr composite conversion coating was formed by immersing Al alloy specimens into the conversion baths for 5 min at 30 °C. HNO_3 was used to adjust the pH value to 3.

Table 1 shows the information of V–Zr composite conversion coating on Al alloy. Sodium metavanadate, sodium nitrate, borax, sodium fluoride and hydrogen peroxide were purchased from Tianjin Kermel Chemical Reagent Corporation. Hexafluorozirconic acid was purchased from Nantong Jinxing Fluorides Chemical Corporation and used as received. Sodium chloride of analytical grade and deionized water were used to prepare 3.5 %wt NaCl solution.

3. Testing

3.1. Electrochemical impedance spectroscopy (EIS)

Electrochemical measurements were performed by the CHI604D electrochemical workstation supplied by Shanghai Chenhua Instruments Inc. in a standard three-electrode cell at 25 °C. A naked or V–Zr coated Al alloy electrode was used as a working electrode. The exposed specimen surface area was 1 cm^2. Electrochemical impedance spectra were obtained at the open circuit potential (OCP) in the frequency range from 10 kHz to 0.01 Hz.

3.2. Surface morphology characterization

SEM was used to observe the surface morphology of coated specimens before and after immersed into 3.5% NaCl solution. SEM photos were obtained by a scanning electron microscope (SEM, Philips XL30, Japan).

3.3. Surface composition analysis

The chemical composition of conversion coatings was analyzed by XPS experiments. XPS experiments were performed on PHI 5000 C ESCA system (PE Company, America) using Al Kα radiation (1486.6 eV) at power of 250 W. The pass energy was set 93.9 eV and the binding energies were calibrated by using contaminant carbon at B.E. = 284.6 eV. The data analysis was carried out by using the RBD Auger Scan 3.21 software connected with XPS instrument.

4. Result and discussion

4.1. Electrochemical analysis

EIS shows information on interfaces and reveals the properties of the conversion coating layer on the surface of Al alloy. EIS can give important information on kinetics of the coating degradation and the corrosion activity during immersion in the corrosive media. The low frequency impedance is one of parameters which can be used to compare corrosion protection performances under different conditions. Higher impedance indicates a better protection [17]. So, EIS is used to evaluate the level of corrosion protection

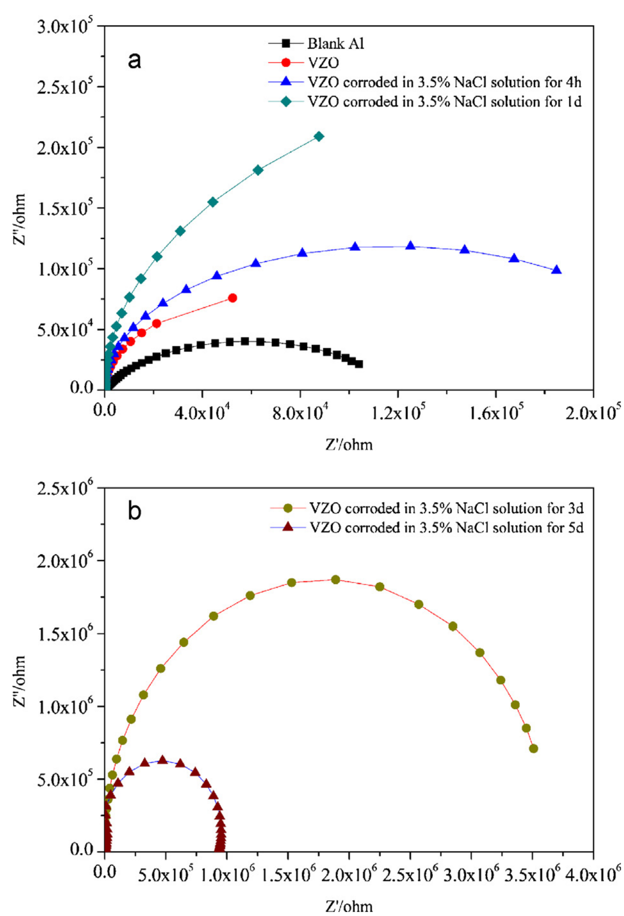

Fig. 1. Nyquist plots (a and b) of aluminum alloy eroded in neutral 3.5% NaCl solution for different time.

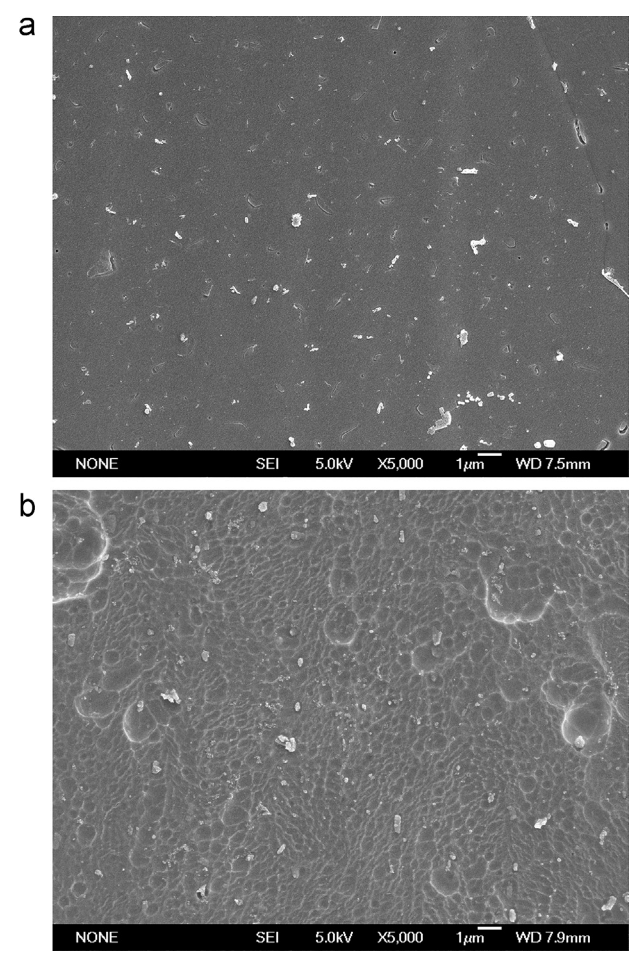

Fig. 2. SEM (5K×) for Al alloy specimens: (a) uncoated and (b) VZO.

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