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Using ToF-SIMS and EIS to evaluate green pretreatment reagent: Corrosion protection of aluminum alloy by silica/zirconium/cerium hybrid coating

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ABSTRACT

Increasing environmental concern has led to the restrictive use of chromate conversion coatings to protect Al-alloys from corrosion. Our research is under way to find environmentally compliant substitute coating such as Si/Zr/Ce hybrid coating. The corrosion protection effect of green pretreatment reagent consisted of Si-containing base solution, Ce- and Zr-containing sealing solutions on the corrosion protection of Al-alloys was studied with a 3.5% NaCl aqueous testing solution. The correlation between the corrosion resistance measured by electrochemical impedance spectroscopy (EIS) and surface chemical composition of the hybrid coating measured by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was studied. The proposed green pretreatment reagent was found improve the corrosion protection of Al-alloys, presumably due to the formation of protective oxide film acting as an oxygen barrier.

1. Introduction

Chromate conversion coatings are currently used to pretreat Al-alloys. It provides excellent corrosion protection and good adhesion properties [1]. However, the hexavalent chromium Cr(VI) ingredient is highly carcinogenic and is on the way of being abandoned. Current environmental regulations require the use of environmentally safe pretreatments. Process to prepare manganese [2], molybdenum [3], vanadium [4] and cerium [5] coatings are alternatives to chromate conversion coatings. Among these processes, sol–gel process, initially developed for depositing inorganic oxides, has recently being used to prepare hybrid coatings and were found to possess advantageous corrosion protection properties [6]. Our research is under way to find environmentally compliant substitute coating. A Si/Zr/Ce hybrid coating based on sol–gel process was proposed.

The corrosion protection effect of green pretreatment reagent consisted of Si-containing base solution, Ce- and Zr-containing sealing solutions on the corrosion protection of Al-alloys was studied with a 3.5% NaCl aqueous testing solution. We used electrochemical impedance spectroscopy (EIS) to measure the electrical resistance, which is a general indicator of its corrosion protection performance, of the coating. The surface chemical composition and elemental depth profile was measured using time-of-flight secondary ion mass spectrometry (ToF-SIMS). The correlations between the corrosion protection and the chemical composition were discussed. In addition, the morphology was examined with a scanning electron microscope (SEM).

2. Experimental

2.1. Materials

Sodium silicate, zirconium tetrachloride, and cerium sulfate hydrate were obtained from Sigma–Aldrich and used without purification. Reagent-grade sodium hydroxide, nitric acid and oxalic acid were purchased from Merck. DI water (resistivity of $1.8 \times 10^7\ \Omega\,\mathrm{cm}$) purified using a Milli-Q water ion-exchange system (Millipore) was used.

The Al-alloy (AA6061, Mg 1%, Cu 0.3%, Si 0.6%, Cr 0.2%, Fe 0.7%, Ti 0.15%, Mn 0.15%) specimens were cut into pieces with an area of 10 mm × 10 mm, mechanically polished with a 1200 finish SiC grit paper to a mirror polish (1 μm surface roughness), degreased in 1 M NaOH solution, cleaned in 0.1 M oxalic acid solution, and finally dried in acetone.

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The green pretreatment reagent contains different concentrations of sodium silicate (4, 8, and 16 g/L), zirconium tetrachloride (0.25, 0.5, and 1.0 g/L), and cerium sulfate hydrate (0.5, 1.0, and 2.0 g/L), respectively, were studied. The solution pH was adjusted to 2 and 9 with HNO_3 and NaOH solution, respectively. The cleaned Al-alloys were sequentially immersed in each of the aforementioned solutions agitated for 10 min and dried. The chemical conversion films that formed on the Al-alloy were dried shortly afterwards at 423 K for 5 min. The resultant testing specimen was designated as Si/Zr/Ce unless otherwise specified.

2.2. EIS measurement

EIS was used to assess the corrosion protective properties of the hybrid sol–gel pretreatments in a 3.5 mass% NaCl aqueous solution which was open to the air during each test and unstirred. EIS data were obtained using EG&G Princeton Applied Research Corp., model 378 electrochemical impedance system which consists of a complete hardware and software package that measures the response of an electrochemical system to AC excitation. A three-electrode arrangement was used, consisting of a saturated calomel reference electrode, a platinum foil as counter electrode and the exposed sample as working electrode. The working area was 1.0 cm × 1.0 cm. All the measurements were carried out at room temperature in a Faraday cage. The measurement conditions were an amplitude voltage of 10 mV, a frequency range of 0–50 Hz and a solution temperature of 303 K.

2.3. Surface analysis

Scanning electron microscope (Hitachi S-4700 Type II) operated in backscattered electron mode at an accelerating voltage of 15 kV was used to inspect the surface morphology. A ToF-SIMS (ION-TOF; Munich, Germany) operated in positive ion and dual beam mode was used to determine the depth profiles [7]. The first ion beam (1 keV O^+ ion source, current 200 nA) was used to sputter a crater with an area of 225 μm × 2252 μm; whereas the second ion beam (25 keV pulsed $^{69}Ga^+$ source, pulsed current 2.0 pA) was used to progressively analyze the crater bottom with an area of 100 μm × 100 μm. Charge compensation by applying low-energy electrons (ca. 30 eV) from a pulsed flood gun was used during the measurements.

3. Results and discussion

The corrosion protection performance of the coating was generally affected by factors such as the film structure, pH value of solution, and concentrations of sodium silicate, zirconium tetrachloride and cerium sulfate hydrate.

Corrosion is considered a sequential process with initial breakdown at either the Si/Zr or Si/Ce interface by chloride or hydroxide released from the silicate layer. The experiment to compare the performance between Si/Zr and Si/Ce film structure was conducted first. Fig. 1 shows that preparation of Si/Zr/Ce at pH 9 yields better corrosion resistance performance, i.e. with larger impedance. The specimens with Si/Zr/Ce coating prepared at pH 9 was subsequently used in later experiments.

The effect of base and sealing concentrations was examined next. Fig. 2 shows that the best corrosion resistance was obtained using an 8-g/L Si-containing base solution, 0.25-g/L Zr-containing and 1-g/L Ce-containing sealing concentrations. Too high Si-containing, i.e. 16-g/L, degrades the corrosion resistance, presumably due to the formation of a rigid glassy-like layer of silicates, which favors the propagation of cracks and leads to localized corrosion.

The surface morphology inspected with SEM (not shown) shows that the surface appears covered by protective layers with grains ranging from 50 nm and up to sub-micron size. Preliminary ToF-SIMS analysis revealed that the surface chemical composition of the protective coatings consisted of Al, Si, Zr, and Ce species. Detailed information was therefore sought from depth profiles (Fig. 3). The Al^+ profile starts to decline at ~150 nm, indirectly indicating that the thickness of the Si/Zr/Ce coating was ~150 nm thick. The Ce^+ profile maintains a constant plateau from 40 to 110 nm, indicating that the Ce-containing layer was ~70 nm thick.

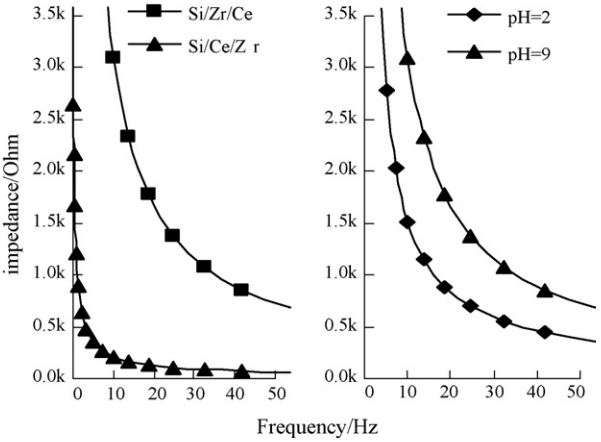

Fig. 1. Film structure and pH effects.

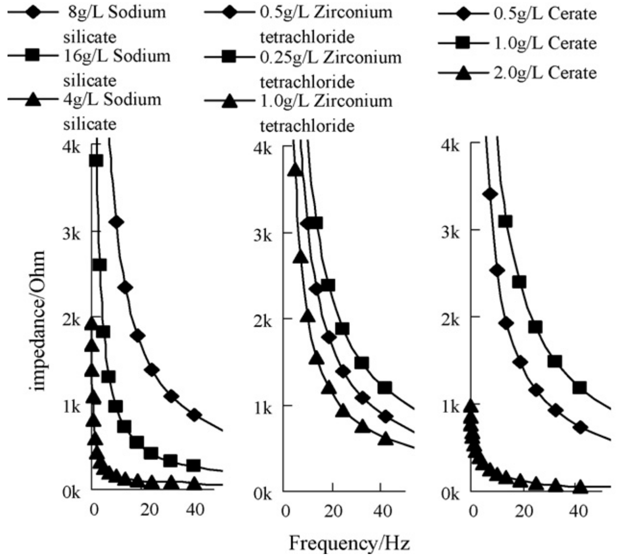

Fig. 2. Effects of base and sealing solution concentration.

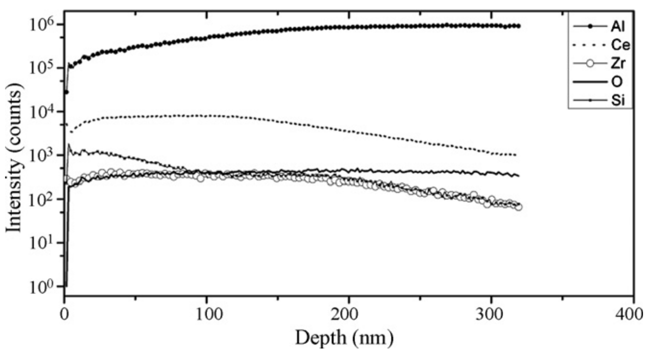

Fig. 3. ToF-SIMS depth profiles of a typical Si/Zr/Ce/Al-alloy specimen.

The Si^+ profile started to decline from the surface, indicating that the Si-containing layer was the top-most ~40 nm. The Zr^+ profile did not explicitly reveal its layer structure. The layer below the Ce layer was designated as Zr layer and was ~40 nm thick. The uniform O^+ profile was mostly due to the implantation from the O^+ sputtering ions. Nevertheless, ToF-SIMS profiles confirmed the chemical composition of the coating was Si/Zr/Ce. The presence of oxides indicates that the formation of protective oxide film acting as an oxygen barrier might be responsible for improving corrosion protection of Al-alloys. The Si/Zr/Ce hybrid coatings prepared by sol–gel process using the green pretreatment reagent showed improved corrosion protection. They are environmentally compliant substitute coating for chromate coatings used on Al-alloys.

The corrosion protection property of the hybrid coating strongly depends on the preparation process and conditions. The incorporation of Zr and Ce into the pores of silicate oxide film forms a high corrosion resistant layer.

4. Conclusions

The present work proposed a green pretreatment reagent forming a Si/Zr/Ce coating on Al-alloy for corrosion protection. The best corrosion resistance and chemical composition of the coating was correlated using EIS and ToF-SIMS, respectively. ToF-SIMS results reflect the contributions of depth profile to provide accurate coating chemical information for samples with inter-diffusion between adjoining layers.

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