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Sealing of anodized aluminum with phytic acid solution

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ABSTRACT

Sealing effect of phytic acid (PA) on the sulfuric acid anodized aluminum was studied by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning Kelvin probe (SKP), SEM and EDS. Unsealed anodized aluminum displayed a porous structure and had poor corrosion resistance. The pores were not only filled, but also a PA conversion film with 3–4 μm was formed when anodized aluminum was immersed in 2.5 wt.% PA solution with pH of 1.5 for 15 min at 90 °C. Anodized aluminum with PA sealing exhibited better corrosion resistance, compared to the anodized aluminums sealed by boiling water and dilute CrO_3 solution.

1. Introduction

Aluminum alloy 2024-T3 is used extensively in the aerospace industry, manufacturing industry and other applications due to its light weight and reliable high mechanical properties [1–2]. The high strength of this alloy is achieved through the reinforcement provided by Cu and Mg in intermetallic phases. However, the corrosion resistance of the alloy is significantly reduced due to the intermetallic phase particles. The alloy is susceptible to localized attack, resulting in pitting, intergranular corrosion and stress corrosion cracking [3–4]. So far, sulfuric acid anodizing is an attractive surface treatment for aluminum alloys to provide enhanced corrosion resistance, wear resistance, and adhesion of polymer coatings [5–7]. However, anodized aluminum has an unusual porous structure [6,8],and is composed of a thin barrier layer and a thick porous layer. The porous structure is reported to be an ordered hexagonal array of cells with cylindrical pores of diameter from 25 nm to 0.3 μm and depths exceeding 100 μm [8]. Unfortunately, these pores can adsorb the corrosive media and contaminants in the atmosphere, which in turn reduces the corrosion resistance of anodized oxide layer. Therefore, sealing after anodizing is needed to seal the pores on purposes of improving the corrosion and wear resistance.

The most conventional sealing methods used in industrial field are boiling water, dichromate, nickel acetate and cold nickel fluoride sealing [9–12]. In general, sealing methods based on various combinations of temperature and sealing bath can improve the corrosion resistance to some extent. Zuo et al. reported that boiling water and dichromate sealed films exhibit relatively higher corrosion resistance in acidic solutions, whereas, nickel fluoride sealed film is better in basic solution [9]. However, hot water sealing requires high energy consumption. Cr(VI) used for dichromate sealing is recognized as toxic, and nickel fluoride sealing is expensive. Recently, a number of green sealing methods have been proposed, including cerium nitrate and yttrium sulfate sealing [13–15], sol–gel sealing [16–17], and organic acid sealing [10,18]. In spite of these efforts to improve the performance, more convenient and effective processes are still needed.

Phytic acid (PA) ($C_6H_6(H_2PO_4)_6$), known as inositol hexakisphosphate, a naturally derived and nontoxic source, is an organic macromolecule consisting of 24 oxygen atoms, 12 hydroxyl groups, and 6 phosphate carboxyl groups [19]. The active groups of PA can strongly chelate with metal ions, and thereby form stable chelate complex compounds on the surface of a metal substrate. The interaction of PA leads to improved adhesion with subsequent paint systems via bonding with the phosphate and hydroxyl groups. In recent years, PA has been used to develop environmental-friendly conversion coatings on magnesium alloys and galvanized steel [20–23]. However, there is little work that reported the usage of PA for protection of aluminum alloys [24]. Moreover, the use of PA for sealing anodized aluminum remains unexplored.

A PA conversion coating that leads to excellent corrosion resistance, is formed on aluminum alloys by deposition of the reaction products formed between Al^{3+} and the phosphate groups in phytic acid molecules [24]. PA may also provide protection for anodized aluminum alloys. Therefore, in this work, the sealing effect of a PA solution on the anodized aluminum alloy was determined. The morphology and chemical composition of anodized aluminum treated by PA were analyzed by SEM and EDS. In addition, scanning Kelvin probe (SKP) technique, which is extremely sensitive to small changes in the surface state of a material [25–26] was used in this study. Our previous work

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[27] has confirmed that the surface morphology and corrosion resistance of anodized aluminum alloys can be characterized through measurements of the SKP potential. As such, the corrosion resistance of anodized aluminum sealed via various methods was determined by using the EIS and SKP technique. Moreover, the sealing mechanism of PA solution on anodized aluminum was discussed.

2. Experimental

2.1. Materials

Aluminum alloy 2024-T3 was used in this work. The chemical composition (wt.%) of AA 2024-T3 is 4.87 Cu, 1.56 Mg, 0.71 Mn, 0.17 Fe, 0.06 Si, balanced with Al. The material was cut into 10 × 10 × 2 mm samples. These samples were successively abraded to 2000 grade emery paper, washed with distilled water for 2 min, ultrasonicated in acetone for 10 min, and dried in an air flow.

2.2. Anodizing

Prior to anodizing, the samples were subjected to the following pre-treatments: alkaline etching in 60 g/L NaOH solution at 60 °C for 2–3 min, desmutting in 30–50 vol% HNO_3 at room temperature for 1 min, and then rinsing thoroughly in deionized water. The samples were anodized using a 15 wt.% sulfuric acid electrolyte for 30 min under a current density of 1.5 A dm^{-2}. The temperature of the electrolyte was maintained at 25 ± 2 °C and air was bubbled during the process for agitation.

2.3. Sealing

The anodized aluminum alloy was sealed by a phytic acid (PA) solution. The effects of the PA concentration, pH, temperature and time on the corrosion resistance of the anodized aluminum were investigated, and an optimized PA sealing technique was realized. Chemical purity grade phytic acid (PA, 70 wt.% in water) and deionized water were used to prepare the solution. Furthermore, small amounts of triethylamine were added to the solution in order to obtain phytic acid solutions with pH values of 1.5, 2.0, 3.0, and 4.0.

For the comparative studies with conventional sealing methods, boiling water and dilute CrO_3 sealing [15] were applied to anodized aluminum. The corresponding conditions are shown in Table 1.

2.4. Corrosion resistance

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements of the anodized aluminum in a 3.5 wt.% NaCl were conducted by using an Autolab PGSTAT 302 N. The tests were performed by using a three-electrode electrochemical cell. A saturated calomel electrode (SCE) and a platinum sheet were used as the reference and counter electrodes, respectively. The anodized aluminum specimens were coated with epoxy resin, and an area of 1 cm^2 was left exposed for electrochemical testing. Prior to testing, the specimens were immersed for ~1 h in a NaCl solution in order to stabilize the open circuit potential (OCP). The corresponding polarization curves were measured potentiodynamically at potentials ranging from −1.25 V–1.5 V (vs. SCE), at a scan rate of 1 mV/s. EIS were acquired at the OCP over the frequency range of $10^5 - 10^{-2}$ Hz using an AC signal amplitude of 10 mV. The equivalent circuits were fitted using the Zsimpwin software. All tests were performed at 25 ± 2 °C. Besides, all experiments were repeated by three duplicate specimens to confirm reproducibility of the results, and the typical result or the average of the three measurements was reported in this paper.

Neutral salt-spray tests were carried out according to ASTM B117, in which 125 × 75 × 2 mm^3 panels treated by different anodized processes were exposed to 5% NaCl solution in a salt-spray cabinet (CCT 10, SINGLETON), operated at 35 °C. Panels were mounted at an incline of 15° from vertical. Three parallel samples were used in each technique. The corrosion morphology of samples after salt-spray tests were obtained using KH-7700 three-dimensional microscope.

2.5. Surface characterization

The morphologies of anodized aluminum were analyzed by scanning electron microscopy (SEM) and field emission gun SEM (FEG-SEM), using QUANTA-200 and Nova Nano-SEM 450 instruments, respectively. The cross sections were prepared by bending the aluminum sample over 180° after cooling in liquid nitrogen for 2–3 min. Besides, samples were sputter gold coated prior to analysis. The chemical compositions were examined by energy dispersive X-ray spectroscopy (EDS, INCA 250).

In addition, the surface potential of the anodized aluminum was measured by a SKP system (KP technology Ltd., UK) at room temperature in air. The scanning microprobe was made by gold. The distance between the probe tip and the specimen was maintained at 100 μm ± 10 μm throughout the tests, thereby avoiding potential fluctuation stemming from the change in distance. A scanning step of 250 μm, was used for scans performed over a 2 mm × 2 mm region.

3. Results

3.1. PA sealing technique

In general, the corrosion resistance of anodized aluminum in 3.5 wt.% NaCl solution is reflected by its corrosion current density (i_{corr}). Another factor, the pitting breakdown potential (E_b), reflects the integrity of the anodizing film, as anodized aluminum is prone to pitting [9,13]. Therefore, the i_{corr} and the E_b of anodized aluminum sealed under various conditions were determined via polarization curves. The effects of PA concentration, pH value, temperature and time on the corrosion resistance of anodized aluminum were studied by i_{corr} and E_b.

Fig. 1 shows the polarization curves of anodized aluminum sealed by PA solution with various parameters. The corresponding fitting values of i_{corr} and E_b are shown in Fig. 2. It was found that the i_{corr} and E_b of unsealed anodized aluminum were 0.126 μA cm^{-2} and −0.567 V, respectively. For all anodized aluminums with PA sealing, the i_{corr} decreased and E_b raised greatly, which indicated PA sealing improved the corrosion resistance of anodized aluminum. As Fig. 2a shows, the i_{corr} decreased significantly at first, and increased slightly thereafter, with increasing PA concentrations. The E_b exhibited the opposite trend. The changes in i_{corr} and E_b showed that the corrosion resistance of anodized aluminum improved with increasing PA concentration ranging from 1.0 wt.% to 2.5 wt.%, but decreased slightly with higher concentrations. However, the i_{corr} increased whereas the E_b decreased continuously with increasing pH value of 1.5–4.0; in other words, the

Table 1
The conditions of boiling water and dilute CrO_3 sealing.

Sealing method	Composition	pH (at 25 °C)	Temperature	Immersion time
Boiling water sealing	Distilled water	6.0	100 °C	30 min
Dilute CrO_3 sealing	70 mg/L CrO_3 48 mg/L Na_2CrO_4	3.5	85–90 °C	20 min