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Property of anodic coatings obtained in an organic, environmental friendly electrolyte on aluminum alloy 2024-T3

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ABSTRACT

Anodic coatings were obtained by micro arc oxidation on aluminum alloy 2024-T3 in a solution containing only 10 g/L sodium phytate. The morphology, composition, structure and corrosion resistance of anodic coatings were systematically investigated. The results show that the working voltage continually increases during 3 min and bright sparks appear after 25 s. Anodic coatings are evenly formed on the substrate and about 2 μm thick. XPS and XRD analyses reveal that the obtained coatings are mainly composed of α-Al_2O_3 and γ-Al_2O_3. Compared with the substrate, the corrosion resistance of the anodized aluminum alloys is improved.

1. Introduction

Aluminum alloys are commonly used in the aircraft industry due to their high strength and low density [1]. Due to the presence of alloying elements, pitting attack by forming galvanic couples occurs, rendering an inferior corrosion resistance in comparison with relatively pure aluminum [2]. Micro arc oxidation (MAO), developed under the traditional anodization, can effectively improve the corrosion and wear resistance of aluminum alloys [3–6]. The compositions and concentrations of the used electrolytes play a main role in determining the coating properties [4,6–8]. At present, some environmentally friendly processes have been developed in weak alkaline solutions containing inorganic electrolytes such as silicate [3,7,8], aluminate [4], phosphate [5–7], tetraborate [6], etc. Compared with inorganic electrolytes, organic electrolytes are seldom used in MAO on aluminum alloys [6].

Phytic acid (*myo*-inositol hexakisphosphate, abbreviated in this work as $PhyH_{12}$) is a common constituent of most mature cereal grains, some vegetables and fruits and oilseeds and it often occurs as phytin (a mixed calcium-magnesium salt of phytic acid) [9]. As an organic macromolecule compound, phytic acid consists of 24 oxygen atoms, 12 hydroxyl groups and 6 phosphate carboxyl groups and its structure is shown in Fig. 1a. Phytic acid or phytate has a variety of benefits on human health including anti-cancer agent, inhibitor for renal stone development and anti-oxidation agent [10,11]. Sodium phytate ($Na_{12}Phy$) is the sodium salt of phytic acid and its structure is shown in Fig. 1b [12]. Compared with liquid $PhyH_{12}$, solid $Na_{12}Phy$ has some advantages, such as convenient to transportation and storage. In addition, $PhyH_{12}$ was not given the status of "generally recognized as safe (GRAS) by the Food and Drug Administration of the United States in their 1995 list [10], while $Na_{12}Phy$ was listed a GRAS substance by 1997 and has been used as a preservative for baked goods in the U.S. [10]. $Na_{12}Phy$ has been used as an environmentally friendly corrosion inhibitor of copper [12,13] and recently was used as a main electrolyte in MAO on Mg-1.0Ca alloys by the authors [14]. The results show that $Na_{12}Phy$ can improve the coating corrosion resistance by developing thick coating with stable composition. However, to the best of the authors' knowledge, there is no report about the property of anodic coatings formed in a solution containing $PhyH_{12}$ or $Na_{12}Phy$ on aluminum alloys. In the paper, the coating property obtained in a solution containing $Na_{12}Phy$ on 2024-T3 was investigated by using field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy and potentiodynamic polarization tests.

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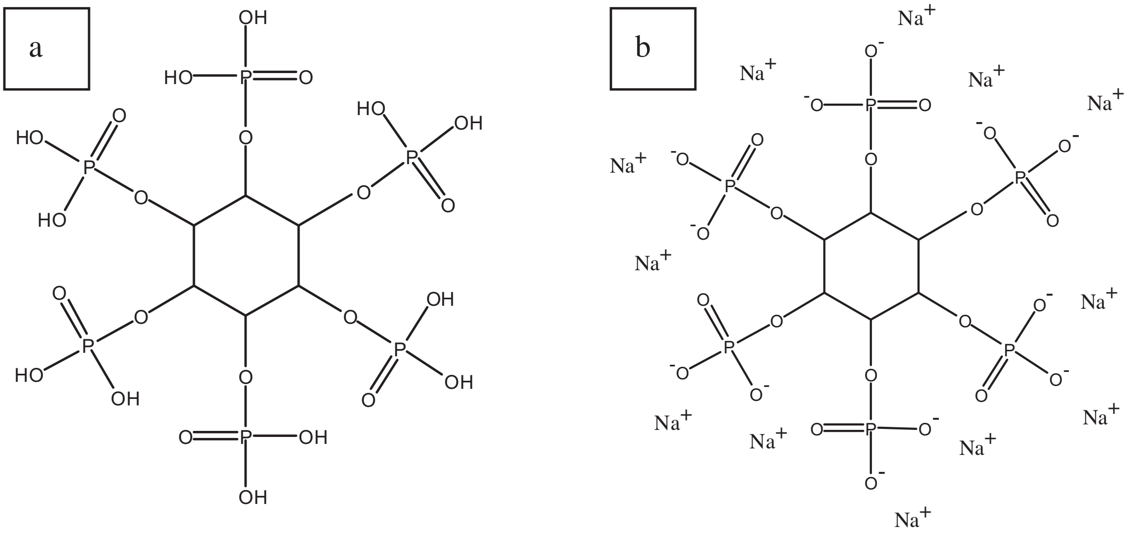

Fig. 1. Chemical structures of $PhyH_{12}$ (a) and $Na_{12}Phy$ (b).

2. Experimental

Aluminum alloy 2024-T3 was used as the substrate, which was separately cut into 50 mm × 70 mm × 10 mm and 10 mm × 10 mm × 10 mm and masked with sealant. High quality sodium phytate (purity ≥98%) was used in the experiment. The solution contains only 10 g/L $Na_{12}Phy$ and its pH value is 11.95, which was measured by PHS-3C pH Meter (Yoke Instrument CO.LTD, Shanghai). The solution conductivity, measured by a DDS-307W Microprocessor Conductivity Meter, is 7.20 mS/cm at 20 °C.

Samples were anodized after they were ground successively with SiC paper up to 1200 grit, degreased by acetone, washed with distilled water and dried in a cool air stream. The equipment for MAO consisted of a MAOI-50C power supply, a stainless steel barrel and a stirring and cooling system that controlled the solution temperature below 30 °C In the experiment, the treatment was performed under a constant current control mode. The used electric parameters were current density 50 mA/cm^2, frequency 2000 Hz, duty cycle 20% and treating time 3 min.

Surface and cross-sectional morphologies of the anodized samples were observed using a ΣIGMA FE-SEM after they were rinsed with distilled water, dried in a cool air stream and coated with gold. The substrate and the coating compositions were determined by energy dispersive X-ray spectroscopy (EDS) attached to FE-SEM. XPS spectra of elements on the sample surfaces were recorded using an ESCALAB250 system from Thermo VG with an Al Kα anode (λ = 1486.6 eV). The XPS analysis was conducted after the coating surfaces were etched for 1 min by argon-ion-beam to reduce the carbon contamination. All energy values were corrected according to the adventitious C 1s signal, which was set at 284.6 eV. The data were analyzed with Xpspeak 4.1 software. After anodic coatings were scrapped off from aluminum alloys with a razor, they were analyzed using a D8 ADVANCE X-ray diffractometer with Cu Kα radiation and a Nicolet 460 FTIR spectrometer in the range of 400–4000 cm^{-1}. C and H elements of anodic coatings were analyzed by a Vario MACRO element analyzer after the coating were scrapped from the sample with a razor and dried in a vacuum at 60 °C and 40 Mpa pressure.

Polarization measurement was performed using an EG&G 273 Potentiostat/Galvanostat and EG&G 5210 lock-in amplifier integrated with a PC system. The working electrode was immersed in 0.05 M NaCl solution. The test system consisted of a three-electrode cell, in which a saturated calomel electrode (SCE), a platinum foil electrode and a sample (10 mm × 10 mm × 10 mm) were used as reference, counter and working electrodes, respectively. The quiet time was 5 min and scans were conducted from −0.3 to +0.5 V/SCE with respect to E_{ocp} using a scan rate of 1 mV/s [1]. Four parallel samples were tested to check the repeatability of the results.

3. Results and Discussion

3.1. Voltage–time response

The MAO processing of aluminum alloys is characterized by three stages in the voltage–time curve and every stage is accompanied by different phenomena [6]. The curve of voltage with treating time at a constant current density of 50 mA/cm^2 is shown in Fig. 2 and the spark pictures taken in different MAO stages are shown in Fig. 3.

During the first 25 s, namely, in Stage I, the voltage increased linearly with a slope of 12 V/s (Fig. 2). Only intensive oxygen evolution could be seen on the sample surface (Fig. 3a). Since 25 s, Stage II was started, corresponding to the working voltage at 303 V. Bright,

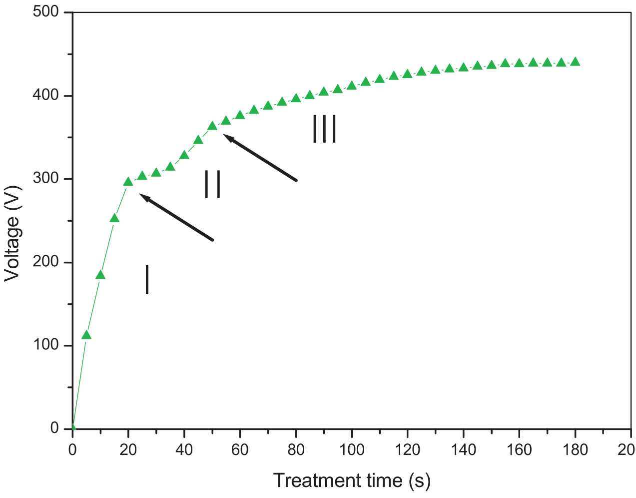

Fig. 2. The variation of voltage with time obtained under current density 50 mA/cm^2, frequency 2000 Hz and duty cycle 20%.