The correlation between the coating structure and the corrosion behavior of the plasma electrolytic oxidation coating on aluminum

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ABSTRACT

Two kinds of plasma electrolytic oxidation (PEO) coatings with different microstructures were fabricated on AA1060 pure aluminum in two kinds of electrolytes, respectively. The electrochemical behavior of the coatings was evaluated by electrochemical impedance spectroscopy (EIS) in a long term immersion in 3.5 wt.% NaCl solution. Some coatings were detached from the substrate by an electrochemical method and the microstructure of the coatings before and after the immersion was observed by SEM. A compact thin layer of ~1 μm in thickness was observed at the coating/substrate interface region. Based on the EIS results and the SEM observation, the effect of the coating structure on the corrosion process changing with immersion time is discussed, especially the effect of the coating/substrate interface layer.

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1. Introduction

Plasma electrolytic oxidation (PEO), also called micro-arc oxidation, is a relatively novel surface modification process in which a thick ceramic oxide coating quickly grows on valve metals (magnesium, aluminum, titanium, etc.) and their alloys [1,2]. The coatings formed by PEO are usually several to more than 100 μm thick and with numerous micro-pores and other defects [3–5]. No matter what substrates and electrolytes are used, the defects always exist as a result of many factors including: discharging process, solidification process, mechanical stresses, and gas evolution during the PEO process [6]. Since the porous structure of PEO coatings strongly affects the properties of the coatings, many efforts have been made to observe the microstructure of the PEO coatings, which can be concluded as a "three layer structure" [7], i.e. a porous outer layer, a more dense inner layer and a thin barrier layer at the coating/substrate (C/S) interface. For the corrosion behavior of PEO coatings, the pores and cavities in the outer layer and inner layer that make the corrosive solutions can easily permeate them. In contrast, it is known that the thin barrier layer can block the corrosive solutions and significantly improve the corrosion behavior of the PEO coatings [8]. However, the thin barrier C/S interface layer is lacking in detailed and comprehensive observations due to the good bonding strength of the coatings with the substrate. Most of the previous works provide polished cross-sections of the coatings, however, the polishing process relatively changed the original morphology of the coating [9]. So it is imperative to find a method to observe the C/S interface layer of the PEO coatings. In some previous works, the PEO coatings were detached by immersing them in saturated NaOH aqueous solution, and observed the front view of the C/S interface [9] or fracture cross-sections [10,11] of the coatings. However, the coating detachment process in saturated NaOH solution modifies the original morphology of the C/S interface because alumina, usually the main phase of the coating studied, can be partially dissolved in the solution. Therefore, the microstructure of the C/S interface region of PEO coatings is still indistinct, although it is well known that the inner portion of the coating is usually less porous than the outer portion. Some researchers believe that through-pores exist in the coating and the corrosive solutions can reach the substrate directly through these pores [12], however, some believe that there is a compact continuous thin layer at the root of the coating.

Based on microstructure observation, electrochemical tests are usually used to investigate the relationship between the coating microstructure and the corrosion behavior of the PEO coatings. Among the electrochemical methods, electrochemical impedance spectroscopy (EIS) as a nondestructive testing which does not affect the surface state of the samples is commonly used to provide information about interfaces between electrolyte/coating/substrate [13] and about pitting corrosion process [14]. Numerous studies have been made to evaluate the corrosion behavior of PEO coatings by EIS [15–19]. However, the plots obtained by EIS are various due to the various coating processing parameters, and the coating structure or chemical, electrochemical, physical processes corresponding to these plots are still not distinct, leading to difficulties to compare the results from different works. For example, the Nyquist plots provided by most previous works show two or three capacitive loops, in which some are with a inductive loop [20,21] and some are with a diffusion tail [22,23] at the low frequency

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side. The physical meaning of the two capacitive loops is differently interpreted in different works [24,25], as well as the inductive loops [12,26] and the diffusion tails [22,27].

Based on the studies made on the corrosion and electrochemical tests, the effects of the PEO coatings on the corrosion process and the evolution of the corrosion process on PEO coated samples have been investigated and summarized by some works [6,12]. It is known that corrosion resistance of the PEO coatings will degrade during long term immersion, and the effect of the microstructures in the coatings will change with immersion time [28,29]. However, the fuzziness of the microstructure of the coatings, especially of the C/S interface layer, hinders more detailed and more reasonable investigations. Also, a more detailed work is needed to reveal the relations of the EIS plots and the coating microstructures. In this study, PEO coatings were made on AA1060 pure aluminum and an electrochemical process with a neutral NaCl aqueous solution was used to detach the coating from the substrate, which helps us observe the fracture cross-section morphologies of the coatings and the front view of the original and clear coatings/substrate interface. Combined with EIS tests, the correlation between the coating microstructure and the corrosion behavior of the coatings were investigated.

2. Experimental

2.1. PEO treatment

AA1060 pure aluminum samples of size 15 mm × 15 mm × 1.5 mm were used as the substrates for the PEO treatment. The samples were ground with 500, 800, 1500 grit emery sheets successively, degreased ultrasonically in acetone, cleaned with distilled water and air dried. The PEO treatment was performed with a self-made PEO experimental setup with an asymmetric AC power supply with a frequency of 50 Hz, a duty ratio of 50% and a positive/negative pulse amplitude ratio of 5. The samples were treated in two electrolytes as shown in Table 1. The electrolyte 1 is a common basic electrolyte for PEO treatment on aluminum alloys and the electrolyte 2 is usually used to fabricate mullite coatings [30]. In the PEO treatment process, the stainless steel container served as a counter electrode. PEO samples in different electrolytes were produced at a constant current density of 4.4 A/dm^2 for different durations to form a similar thickness, ~10 μm. The temperature of the electrolyte was maintained at 298 ± 2 K using a water cooling system. After the PEO treatment, the samples were washed with distilled water and then dried in warm air.

2.2. Immersion and EIS tests

The long term immersion tests of bare aluminum and PEO treated samples were carried out in 3.5 wt.% NaCl solution (pH = 7.0) at room temperature. Electrochemical impedance spectroscopy (EIS) tests, also in 3.5 wt.% NaCl solution, were performed using a RST5200F electrochemical workstation with a three-electrode cell setup which is composed of a saturated calomel reference electrode, a platinum plate counter electrode and a PEO specimen working electrode with an exposed area of 0.5 cm^2. The EIS measurements were carried out over a frequency range from 10^5 to 10^{-2} Hz at the open circuit potential with a 10 mV sinusoidal voltage signal. The samples immersed for different durations of 0.5, 5, 10, 24, 48, 120, 360 and 720 h were measured to understand the degradation process of the PEO coatings. ZSimpWin software was used for the data fitting of impedance spectra.

Table 1
Compositions of the two electrolytes.

	NaOH (g/L)	Na$_2$SiO$_3$ (g/L)	(NaPO$_3$)$_6$ (g/L)	KF (g/L)
Electrolyte 1	2	8	–	–
Electrolyte 2	4	13.5	16.5	0.5

The chi-squared (χ^2) values of the fitting results, less than 1×10^{-3}, were employed to evaluate the fitting quality and determine whether the data obtained are consistent with the proposed equivalent circuit.

2.3. Coating detaching and characterizations

Some of the coatings (before and after immersion) were detached from the substrate by an electrochemical process which has been detailedly described in our previous work [31].After the detachment, the coatings were immersed in de-ionized water for 20 min, dried in air and analyzed into two groups. In the first group, the morphologies of the coating/substrate (C/S) interfaces were observed and measured in front view. In the second group, the coatings were fractured and then the fracture morphologies were observed. Moreover, it should be noted that all the EIS tests were performed on undetached coatings.

The morphologies and elemental compositions of the coatings, both detached and un-detached, were observed and measured by a scanning electron microscope (SEM, Hitachi S-4800) equipped with en energy-dispersive X-ray spectroscope. The phase compositions of the coatings were measured by a D/MAX-rB X-ray diffractometer at a scanning speed of 0.03 °/s and a range of 2θ from 10° to 80°. The two groups of PEO samples fabricated in the two electrolytes were tested, observed and measured in parallel.

3. Results and discussion

3.1. Phase compositional characterization

The XRD patterns of the coatings obtained in electrolytes 1 and 2 are shown in Fig. 1. It can be seen that the coating formed in the electrolyte 1 is composed of γ-Al$_2$O$_3$. For the coating treated in the electrolyte 2, besides the peaks of mullite (Al$_6$Si$_2$O$_{13}$) and γ-Al$_2$O$_3$, a broad peak at about 22° is also detected which indicates that silica-based amorphous material was formed in this coating. The relative contents of mullite, γ-Al$_2$O$_3$ and amorphous material are calculated as 30.9%, 12.5% and 56.6%. The relative contents of these phases were determined on the basis of total integral area of diffraction peaks of each phase within 2θ = 10°–80°. As the main crystal phases in the coatings treated in electrolytes 1 and 2 are alumina and mullite, the coatings obtained from these two electrolytes in this work are termed as A- and M-coatings, respectively.

3.2. Morphological characterization

Typical surface and polished cross-section morphologies of the A- and M-coatings are shown in Fig. 2. Two distinct regions can be
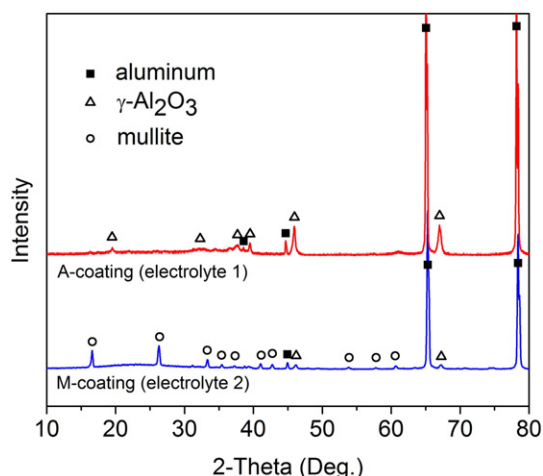

Fig. 1. Phase composition of the coatings formed in the two electrolytes.