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Phase transformation in plasma electrolytic oxidation coatings on 6061 aluminum alloy

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ABSTRACT

Oxide coatings were produced on a 6061 aluminum alloy using a pulsed unipolar plasma electrolytic oxidation (PEO) process. The effect of electrical parameters including pulse frequency, duty cycle and current density on phase formation in the coatings was revealed using conventional and glancing angle X-ray diffraction. The results show that PEO coatings are mainly composed of γ-Al_2O_3. Depending on the electrical parameters employed, the coatings can also contain α-Al_2O_3 and mullite with varying concentrations. Higher current densities and higher duty cycle were found to favor the formation of mullite. Under the experimental conditions used, the ratio of the integrated XRD peaks for α- and γ-Al_2O_3 varied from 0 to about 0.6, indicating that the relative content of α-Al_2O_3 in the PEO coatings varied over a wide range. Longer pulse on-times and higher current densities promoted the gamma to alpha-alumina phase transformation. Depth profiling of PEO ceramic coatings using glancing angle XRD with different incident beam angles revealed that mullite was more concentrated in the top surface of the coatings. No significant variation in α-Al_2O_3 concentration across the coatings could be concluded in this study, unlike the results of some other studies.

1. Introduction

Alumina ceramic coatings have great potential as hard, wear and corrosion resistant coatings on aluminum and its alloys. Various techniques including chemical vapor deposition (CVD), ionization-assisted magnetron sputtering PVD, and thermal spray are available to deposit alumina coatings, most of which involve high temperatures, but are not suitable for aluminum which has a relatively low melting point. As an alternative, coatings prepared by plasma electrolytic oxidation (PEO) are less expensive and easier to apply to components with complex geometries and large dimensions than the CVD, PVD or thermal spray processes [1,2]. PEO is a relatively new surface modification technique which can convert the surface of valve metals and alloys such as aluminum, magnesium, zirconium, and titanium into oxide ceramic coatings [3–6]. The PEO process involves complex chemical, electrochemical and plasma thermo-chemical reactions.

Despite extensive research, the mechanism of the PEO process is not comprehensively understood [7–9]. Hussein et al. [10] proposed a discharge model involving three distinct types of discharges, A, B, and C, for PEO on aluminum alloy substrates. Types A and C were thought to result from gas discharges occurring in micro-pores in the ceramic coating, and type B was attributed to dielectric breakdown through the oxide layer. More recently, an additional type of discharge has been proposed, type D, which occurs in large pores near the interface between the inner and outer layers [7]. These discharges play an essential role in the formation and properties of the resulting coatings, by influencing phase transformation, crystallization, annealing and sintering of the coating [11].

The PEO process involves multiple features. The characteristics of PEO coatings are affected by the compositions of the substrate material and the electrolyte, process parameters such as the current regime (AC, DC, and pulsed DC), current density, duty cycle, frequency and treatment time [12–14]. In addition to the type of current regime, the current polarity and application sequence could also affect the properties of the coatings. It is suggested that the pulsed bipolar current mode generally improves the properties of the PEO coatings and results in coatings with higher density [15]. In a study on a magnesium alloy substrate, it was found that applying a hybrid current mode, in which a unipolar current was applied first followed by a bipolar current, improved the coating properties in terms of microstructure and corrosion resistance [16].

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PEO coatings produced on aluminum alloy substrates in dilute silicate electrolytes are mainly composed of α- and γ-Al_2O_3 with some amorphous alumina. In electrolytes with a high concentration of silicate, mullite is also observed [1,7,17–19]. Thick coatings, with high mullite content, possess good thermal and chemical stability and are good candidates for thermal barrier applications [2,20].

PEO coatings have also been reported to have superior wear and corrosion resistance compared to untreated aluminum alloy substrates [1,14]. The hardness of the PEO coating is a function of the nature of the dominant phases present, as well as their ratio and distribution and the porosity and density of micro-cracks in the coatings. The hardness of alumina phases have been reported to be around 26 GPa for α-Al_2O_3, 17 GPa for γ-Al_2O_3, 10.5 GPa for mullite, and 7 GPa for the amorphous anodically formed alumina. However, the measured hardness in PEO coatings is lower than in dense bulk alumina due to porosity in PEO coatings [7,11,20]. Tribological studies indicate coatings composed of α-Al_2O_3 show a higher wear resistance [21].

It is believed that increasing the α-Al_2O_3 content will enhance the wear performance of PEO coatings [22,23]. This improved hardness compared to conventional coatings formed by anodization is attributed to the presence of a large proportion of crystalline material, namely α- and γ-Al_2O_3, and to a reduced porosity [24]. Controlling the α-Al_2O_3 content of the coating, which is the hardest phase among alumina phases, is a very interesting topic in PEO studies which may prove advantageous in producing coatings with higher hardness. There are a few studies in which some aspects of the phase transformation of coatings during PEO treatment on aluminum alloy substrates have been investigated, but the phenomenon is far from being well understood. Khan et al. [25] found a decreased duty cycle caused a corresponding decrease in the ratio of α- to γ-Al_2O_3 in PEO coatings on 6082 aluminum alloy produced by pulsed unipolar current, although large data scatter was observed. Xue et al. [17] investigated the phase distribution of ceramic coatings on 2024 aluminum alloy and concluded that the surface layer of coatings mainly contained γ-Al_2O_3 and the percentage of α-Al_2O_3 gradually increased from the external surface towards the inner layers of the coatings. Applying higher current densities [11,12,26] and increasing the deposition time which resulted in thicker coatings [21,27] were reported to increase the α-Al_2O_3 content in the coatings.

Hard PEO coatings mainly composed of α-Al_2O_3 could be a promising candidate to protect Al alloy substrates against wear. Here, we report possible procedures to control the α-Al_2O_3 content in alumina oxide coatings by varying the electrical parameters in the PEO process. The results of the current study provide a reference for the possible industrial applications of PEO coatings where a high hardness is required.

2. Material and methods

2.1. Sample preparation

Disk specimens were cut from a 6061 aluminum alloy bar with an average diameter of 30 mm and an average thickness of 8 mm. The specimens were then ground with 600 grit SiC paper, degreased in propanol and rinsed with distilled water. Electrical contact to specimens was made using a steel rod bolted to a threaded hole drilled in the side of each specimen.

2.2. Coating process

PEO coatings were produced using a custom built, unipolar pulsed DC source in an electrolyte containing 2 g/L $Na_2SiO_3 + 2$ g/L KOH in deionized water. Samples served as the anode and were submerged in the electrolyte in a stainless steel tank which also served as the counter cathode. During the PEO process, the electrolyte temperature was maintained below 40 °C by circulating the electrolyte through an external heat exchanger. To investigate the effect of electrical parameters on phase transformations in the coatings, two frequencies, 50 and 1000 Hz, at duty cycles of 20% and 80% with current densities (J) of 5, 10, 15, 20, and 25 A/dm^2 were used. The samples were coated under galvanostatic conditions, i.e. the current was kept constant during the entire process and the anode potential was allowed to vary. All samples were coated for 30 min. Table 1 lists the sample codes with the corresponding electrical conditions used.

During a single pulse, t_{on} and t_{off} are the periods during which the current is on and off, respectively, and the duty cycle (D_t) is defined by Eq. (1).

$$D_t = \left[t_{on}/\left(t_{on} + t_{off}\right)\right] \times 100 \tag{1}$$

The waveform and corresponding parameters of the unipolar pulsed power source are given in Fig. 1.

2.3. Coating characterization

The surface morphologies of the PEO coatings were examined using a Hitachi S-3500N scanning electron microscope (SEM). The samples were sputter-coated with gold prior to SEM examination to minimize surface charging. A Philips X'Pert_MRD diffractometer with Cu Kα (40 kV and 40 mA) radiation was used to study the composition of the coatings. The samples were scanned over the 2θ range from 15° to 90° with a 0.02° step size. To determine the distribution of different crystalline phases throughout the coating, and to minimize interference from the aluminum substrate, glancing angle XRD at incidence angles of 1, 2.5 and 5° was performed to supplement conventional (Bragg–Brentano configuration) X-ray diffraction measurements. Coating thickness was measured using an Eddy current gauge.

3. Results and discussion

3.1. Coating surface morphology and thickness

SEM micrographs of four samples showing the typical surface morphology of PEO coatings are presented in Fig. 2. Almost all samples contain two different kinds of regions: cratered regions with a central hole and lighter areas with a nodular structure. Craters are formed when molten material is ejected from the coating/substrate interface through central holes due to the high temperatures and strong electric field present during the PEO process. On contact with the electrolyte, the molten material solidifies rapidly [28].

Previously [13] the cratered regions were shown to be rich in aluminum while the nodular structures exhibited a higher concentration of Si compared to Al. Changing the electrical parameters, namely the duty cycle and frequency, was found to alter the size of the craters and also the ratio of the craters to the nodular structures on the sample surface.

The thicknesses of coatings prepared by PEO using different electrical parameters are presented in Fig. 3. For each set, the thickness of the PEO coating increases with increasing current density as a result of the increased energy input. For samples PEO coated at 1000 Hz, the difference in the thickness of the samples processed at the same current density but different duty cycles is insignificant; however, the average thickness of each sample coated at a duty cycle of 20% is slightly greater

Table 1
Electrical parameters and sample codes for PEO treatment on 6061 Al alloy.

Sample code	Frequency (Hz)	Duty cycle, D_t (%)	t_{on} (ms)	t_{off} (ms)	*: J (A/dm^2)
S12-*	1000	20	0.2	0.8	5, 10, 15, 20, 25
S18-*	1000	80	0.8	0.2	
S52-*	50	20	4	16	
S58-*	50	80	16	4	