



Micro-structures and growth mechanisms of plasma electrolytic oxidation coatings on aluminium at different current densities



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ABSTRACT

In this study, plasma electrolytic oxidation (PEO) coatings were produced on pure aluminum in an in-house developed composite electrolyte at three current densities of 2.2 A/dm², 4.4 A/dm² and 8.8 A/dm², respectively. The coatings were investigated based on the observation and measurement of the working voltage, surface microdischarges and morphologies of surface, polished cross-section, fracture cross-section and inner surface of the coatings, by using scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS), data acquisition module, single-lens reflex camera. Especially, an in-house developed electrochemical detachment technique of the coatings was employed to observe some details of the internal micro-structure and coating/substrate interface morphology of the coatings. It was noted that the results from the above investigations are much related to the current densities going through the PEO coatings and the different growth mechanisms of coatings at low and high current densities were proposed and discussed.

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1. Introduction

Plasma electrolytic oxidation (PEO) is an advanced anodizing process where ceramic-like coatings are formed on valve metals (Al, Mg and Ti) and their alloys at high voltages in low-concentrated eco-friendly alkaline electrolytes with visible short-lived micro-discharges over the specimen surface [1–3]. It is a promising novel process to form coatings of thickness ranging from tens to hundreds of microns for corrosion protection, wear resistance, biomimetic and thermal barrier properties [4]. PEO process is a complex combination of electrochemical and plasma thermochemical reactions and thermal diffusion under high discharge temperature (10³–10⁴ K) and pressure (~10² MPa), in which plasma discharge is an essential event for the coating growth [5]. The complicated physical-chemical reactions have been inferred from observed phenomena, such as a large number of short-lived microdischarges [6], surface-connected porosity in the coatings [7] and individual discharges occurring in clusters [8]. Discharge events are discrete short-lived and microscopic, and provide multiple heating-cooling cycles to the coatings that determine thermal and chemical conditions at the surface, thus playing an important role in the formation of the phase composition, structure and stress state of the coatings.

It is difficult to catch and analyze the instant discharge events due to the fact that individual discharge events are of short duration (tens to hundreds of μs) [8] and with gas liberation. Therefore, the understanding of the discharge nature has not been unified although several discharge mechanism models have been raised. Some early works believe that the micro-discharges appear as a result of oxide film dielectric breakdown [9–11] induced by the electron ‘avalanche’ effect [12] or electronic tunneling effect [13] in a strong electric field. Another group of models consider the micro-discharges as gas discharge scattered in pores [14] or in the gas sheath at the oxide-electrolyte interface [15, 16]. Recently, many researchers used the optical emission spectroscopy (OES) to investigate the plasma discharge behavior during the PEO process [8,17]. Based on the OES results, a comprehensive discharge model consisting of three types of discharge were proposed by Hussein et al. [17], i.e. type B for dielectric breakdown of the whole coating under strong electric fields type A for gas discharge near the coating surface and type C for gas discharge deep in the pores of the coating. The discharge in pores is believed to be induced by an initial dielectric breakdown of the barrier layer in the bottom of the micro-pores [15].

The micro-structure characteristics of PEO coatings are generally influenced by processing parameters including the applied power mode, voltage and current density [18,19], electrolyte composition and additives [20,21], substrate materials [22], heating treatment [23] and so on. Current density is one of the most important parameters and has a significant effect on the plasma discharge behavior and coating

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structure during the PEO process [17]. It is well known that the current density influences the growth rate and the structure (surface and cross-section morphologies) of PEO coatings. Zhijun Li et al. [24] investigated effects of current density on the surface morphology, composition, thickness, micro-hardness of PEO coatings. Large and long-lived spark discharges at high current densities tend to produce larger craters on the surface, resulting in a coarse and porous coating, lower current densities tend to form fine and less porous micro-structure. G. Rapheal et al. [25] suggested that higher current densities resulted in increased thickness of the coating, but reduced the compactness of the coatings. P. Bala Srinivasan et al. [26] came to a conclusion that the growth of coatings is influenced significantly by the operating current density in PEO processing. Increasing current density results in much earlier attainment of high voltages and therefore, longer exposure to plasma discharges with higher energy output. R.H.U. Khan et al. [27] noted that the current density used during DC PEO treatment played an important role in the coating morphology. The coatings produced at a relatively high current density showed a dense crater-like surface morphology and coatings produced at lower current densities showed a porous coral-line morphology. V. Ezhilselvi et al. [28] reported the coating prepared at lower current density exhibits a relatively uniform surface appearance with a high degree of porosity. As the current density is increased, the porosity of the coating is decreased, though the diameter of the pores is increased.

It can be found from literature [9–17] that the methods generally used to investigate the growth mechanism of PEO coatings are recording the evolution of the operating voltage and discharge characteristics, observing the morphologies of PEO coatings, and monitoring the evolution of plasma by optical emission spectroscopy (OES), etc. However, the morphology of PEO coating/substrate (C/S) interface, the forefront of dielectric breakdown of coating material, can not be observed by these methods. Lacking in such an important experimental result, some conclusions can only be drawn through deduction so that it is difficult for researchers to have an overall and objective understanding about the growth mechanism.

It is well known that PEO coatings are composed of two layers, a compact inner layer and a porous outer layer, and the compact layer is the main body of the coatings based on observation of the polished cross-section of the coatings by using SEM. In some recent works it was found that nanocrystalline or nanocrystalline + amorphous barrier layers between the coating and substrate were observed on the cross-section of the coating on some substrates by using transmission electron microscopy (TEM) [29–32]. However, the details of internal micro-structure of the coatings are still indistinct because the original structure morphologies of the coatings were mechanically distorted or damaged to a certain extent during the grinding and polishing processes. In order to observe the non-distorted cross-section and inter-layer surface of the coating, a new type of preparing sample methods [33–37] were developed, in which the substrate was removed from the PEO coated samples through a chemical corrosion process. Some researchers observed the front view of the coating/substrate (C/S) interface [34] or fracture cross-sections [35–37] of the coatings which were detached from substrates by immersing them in the saturated NaOH aqueous solution. However, the original morphology of the C/S interface was indistinct due to partial dissolution in the solution, which is not conducive to more detailed and reasonable investigations of the C/S interface. By chemically removing the substrate aluminium in a CuCl_2 -based corrosive solution [100 mL HCl (38%) + 100 mL H_2O + 3.4 g $\text{CuCl}_2 \cdot \text{H}_2\text{O}$], B. Kasalica et al. [33] observed more clearly a thin compact inner layer which is adjacent to the substrate.

In our recent work [38], the detached coating samples were prepared by using a short electrochemical process in a neutral NaCl aqueous solution [39], and the original and detailed morphology of the C/S interface was clearly observed due to non-dissolution of the coating materials in the preparing process of detached coating samples. In the present work, the new sample preparing process was used to observe and

analyze effects of current density on the micro-structure and element composition of the PEO coatings more clearly besides the observation of the surface and polished cross-section morphologies of the coatings. Further, the different growth mechanisms of coatings at low and high current densities were proposed and discussed in combination with variation features of the operating voltage, surface discharges and thickness of the coatings with the current density.

2. Experimental procedures

Commercial pure aluminium plate was used as the coating substrate material. Substrate samples (15 mm × 15 mm × 1 mm) were sliced from the plate and the surface of the samples was ground up to 3000 grit, rinsed in distilled water, degreased ultrasonically in acetone and then dried under normal atmospheric conditions prior to the PEO process. The PEO electrolyte was prepared with distilled water containing sodium silicate (13.5 g/L), sodiumhexameta phosphate (16.5 g/L), potassium fluoride (0.5 g/L) and sodium hydroxide (4 g/L). An asymmetrical pulsed AC supply set at a frequency of 50 Hz and a duty ratio of 50% was used to produce the PEO coatings in the electrolyte with the substrate acting as anode. The applied negative-to-positive voltage ratio was 1/5. The coatings are prepared at current densities of 2.2 A/dm², 4.4 A/dm² and 8.8 A/dm² for 10 s, 60 s and 600 s, respectively. The electrolyte temperature was maintained at 30 (±5) °C during the PEO processes. After the PEO treatment, the samples were washed with distilled water and then dried under normal atmospheric conditions. The peak voltage data were recorded and analyzed by using a data acquisition module with Wave Scan software (USB-4702, Advantech Co., Ltd.). Before the PEO process, the positive terminal of the data acquisition module was connected to an Al substrate sample acting as the anode, and the negative terminal was connected to the stainless steel electrolytic bath acting as the cathode. Once all the operating parameters had been set properly, the PEO process was started and the operating voltage data are recorded and measured with the data acquisition system. A number of micro-discharge images were taken by a Coolpix Nikon video camera (800K pixels CCD, 40-optical zoom and 40 mm lens filter) to record the evolution process of the micro-discharge features on the sample surface during the PEO processes. After the PEO process, the coatings on some coated samples were detached from the substrate by means of the patent electrochemical method mentioned above. Fig. 1 shows the schematics of the coating detachment method. One side of each PEO treated sample was ground

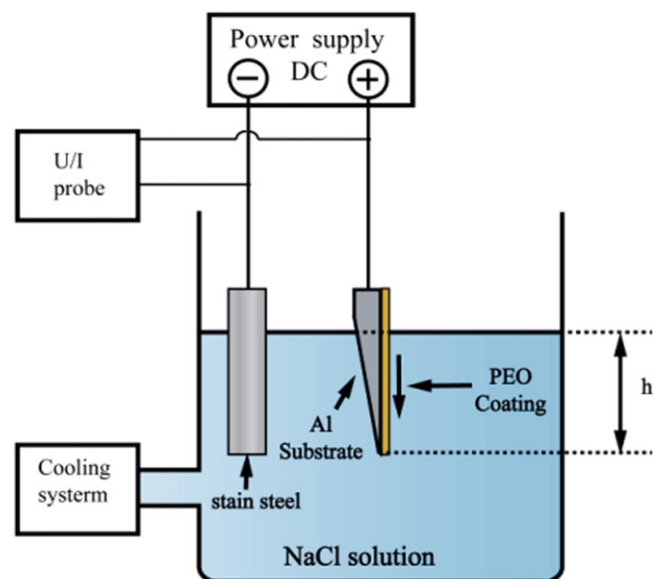


Fig. 1. Schematics of the coating detachment method.

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