

## PLASMA ELECTROLYTIC OXIDATION COATING ON 6061 AL ALLOY USING AN ELECTROLYTE WITHOUT ALKALI IONS

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### ABSTRACT

Plasma electrolytic oxidation (PEO) technique is well known to use for modifying the surface of valve metal such as Al, Mg and Ti, which improves mechanical and corrosion resistance properties. PEO is an electrochemical process of oxidation by creating micro-discharges on the surface of metal immersed in an electrolyte under applying a high voltage. Electrolyte used in PEO process is almost based on alkali ions such as Na ion. The report on PEO process using free-alkali ion is very rare. In this study, the oxide layer on 6061 Al alloy was produced in a free-alkali ion electrolyte containing calcium phosphate and ammonia water by PEO method. Microstructure, micro-hardness and corrosion resistance of PEO coated were investigated and discussed. Surface morphology analysis indicated the coating characterized by micro-pores, pan-cakes like, and micro-crakes with pore size and percentage of pores on coating surface are smaller than 1  $\mu\text{m}$  and 2.5 %, respectively. Micro-hardness and corrosion resistance of PEO coated are greatly improved compared to the bare Al alloy. Free-alkali-ions in oxide layer coated on Al alloy is important for many applications today.

*Keywords:* plasma electrolytic oxidation; free-alkali ion; 6061 Al alloy; micro-hardness; corrosion resistance.

### 1. INTRODUCTION

Al alloys are increasingly used in a variety of industries due to many their advantages such as high strength to weight ratio, good formability, low density, high thermal and electrical conductivities, and recycling potential [1, 2]. Surface treatment for components made by Al alloys which improve their mechanical and corrosion resistance properties and enhance their application. A variety surface modification methods were used for this purpose such as conventional anodizing [3], physical vapor deposition (PVD) [4], chemical vapor deposition (CVD) [5] and plasma electrolytic oxidation (PEO) [1, 2, 6, 7]. Among them, PEO is an

attractive one due to it is capable of producing thick oxide layer on Al alloy with high hardness and corrosion resistance.

The quality of coating on Al alloy formed by MAO process depends on many factors, such as kinds of metal substrate, electrolyte compositions and electrochemical parameters [8]. In which, electrolyte is one of the most important factor because it not only directly affects the properties of the coating, but also incorporating metal elements from it into the coating that might not be encouraged in some applications.

Conventional electrolytes used in PEO process are containing alkali ions such as sodium. In some applications alkali ions in PEO layers are prohibited. A typical example is the PEO coating for Al component in vacuum chambers extended for use in LCD and IC processing. This is due to the fast diffusion nature of alkali ions, once they will be the contaminants, which lead to deteriorated performance of processing devices. Thus, fabrication of PEO coating using no alkali ions electrolyte is a new research topics worthy of study.

In this study, a nonconventional electrolyte without alkali ions was used to fabricate oxide layer on 6061 Al alloy by PEO method. The electrolyte contained calcium phosphate and ammonia water. Phase composition, surface structure, element chemical, micro-hardness and corrosion resistance of PEO coated was investigated and discussed.

## 2. MATERIALS AND METHODS

6061 Al alloy plate was cut into a dimension of 20 mm × 20 mm × 3 mm and used as substrate for PEO treatment. Prior to PEO processing, substrates were polished successively using SiC abrasive papers #600, #1000 and #2000; then washed with distilled water, ultrasonically cleaned in acetone for 25 min and finally dried in air.

The substrate was used as anode and immersed in the electrolytic solution containing 0.1 M monocalcium phosphate monohydrate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , Acros Organics, 95 %) and 10 mL ammonia water ( $\text{NH}_4\text{OH}$ , Acros Organics, 28 %  $\text{NH}_3$ ) per liter of electrolytic solution. Cathode was a stainless steel tank which containing electrolytic solution. During PEO processes, electrolytic tank was placed in a cold water which maintains at 10–15 °C by circulating cooling water and electrolyte was continuously stirred thanks to a magnetic bar at the bottom of tank. A hybrid voltages was applied to the anode and cathode with a constant current density of 10  $\text{A}/\text{dm}^2$ . The hybrid voltage is set according to an our previous report with alternative voltage ( $V_{\text{AC}}$ ) of 300 V [8]. PEO treatment time is 1 hour which grows the oxide layer with thickness of  $20 \pm 1 \mu\text{m}$ .

Thickness of the oxide layer was measured at ten different locations on the sample and then averaged using an eddy current thickness meter (LZ-3730-1, Japan). Micro-hardness of un-coated and PEO coated was measured at ten different locations and averaged for each sample by a Micro-hardness Tester FM-300e using 25 g indentation weight. To ensure reproducible hardness measurements, the sample surface was slightly polished to remove soft outer layer before hardness indenting. X-ray diffraction (XRD, Bruker – D8SS with Cu  $K\alpha$  radiation) was used to determine phase composition. Surface morphology of the coating was observed using a scanning electron microscope (SEM, HITACHI/S-4800). Qualitative elemental chemical analysis was carried out by using Energy dispersive X-ray spectroscopy (EDS). Potentiodynamic polarization testing in 3.5 % NaCl solution at room temperature to evaluate the corrosion resistance of the un-coated and PEO-coated samples. The electrochemical corrosion tests were conducted using a typical three-electrode cell with a saturated calomel electrode

(SCE) as the reference, a platinum grid as the counter electrode, and the sample (with an area of  $1 \text{ cm}^2$ ) as the working electrode. The potentiodynamic polarization test was performed on a CHI-6081A Electrochemical Analyzer. Before testing, the sample was immersed in NaCl solution at an open circuit potential for 10 min to allow achieving steady state. The potentiodynamic polarization tests were performed at the scanning rate of  $10 \text{ mV s}^{-1}$  from  $-2 \text{ V}$  to  $2 \text{ V}$  versus SCE. Potentiodynamic polarization curves were taken from test samples. Electrochemical parameters including corrosion potential, corrosion current density and corrosion resistance were determined from these curves.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structural analyses of the PEO layers

XRD patterns of bare and PEO coated 6061 Al alloy formed in the electrolyte without alkali ions is shown in Figure 1. The oxide layer consisted of the main phases of Al (JCPDS # 04-0787),  $\gamma\text{-Al}_2\text{O}_3$  (JCPDS # 10-0425),  $\alpha\text{-Al}_2\text{O}_3$  (JCPDS # 10-0173) and calcium pyrophosphate ( $\text{Ca}_2\text{P}_2\text{O}_7$ , JCPDS # 10-0173). The strong peaks of Al are came from the substrate because of the low thickness and porosity of oxide layer which permits easy penetration and diffraction of the X-rays.

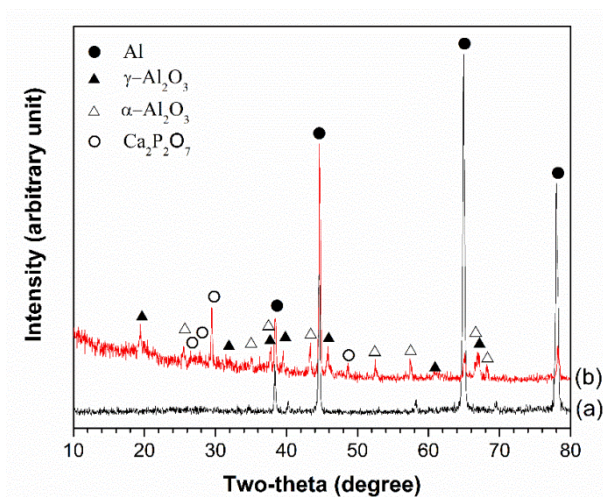


Figure 1. X-ray diffraction spectra of bare and PEO coated on 6061 Al alloy using free-alkali-ion electrolyte: a) Bare 6061 Al alloy and b) PEO coated.

It is known that the alumina is formed due to plasma thermal chemical reactions during PEO process. The meta-stable phase of  $\gamma\text{-Al}_2\text{O}_3$  formed easily in the coating during PEO process due to the solidification of oxide layer at high cooling rate when the layer surface is intact with a cool solution [9 – 11].  $\gamma\text{-Al}_2\text{O}_3$  phase starts to be transformed into  $\alpha\text{-Al}_2\text{O}_3$  phase at the temperature range from  $800$  to  $1200 \text{ }^\circ\text{C}$  [9 – 11]. The appearance of  $\text{Ca}_2\text{P}_2\text{O}_7$  phase indicated that the incorporation of Ca and P in oxide layer. This is also confirmed by the result of EDS analysis as show in Figure 2.

Figure 3 shows the surface morphology of PEO coated in the electrolyte without alkali ions at different magnification and corresponding surface porosity. The surface is characterized by micro-pores, pan-cake-like and micro-cracks (Figure 3a, b). It is typical of oxide-layers by

common PEO processes [12]. The nature of the formation of PEO coating is based on the sparks on the surface oxide layer, which extracts metal ions from the substrate, passing through the oxide layer and generating the discharge tunnels (discharge channels).

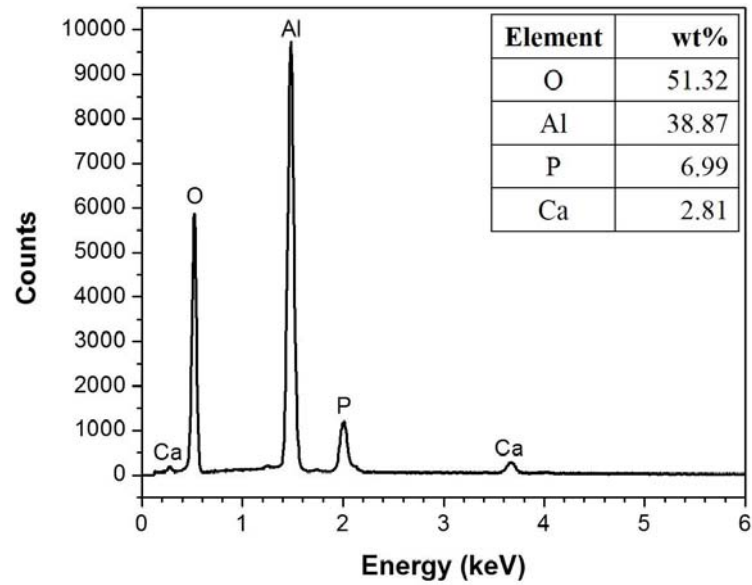


Figure 2. EDX spectra of PEO coated in free-alkali-ion electrolyte.

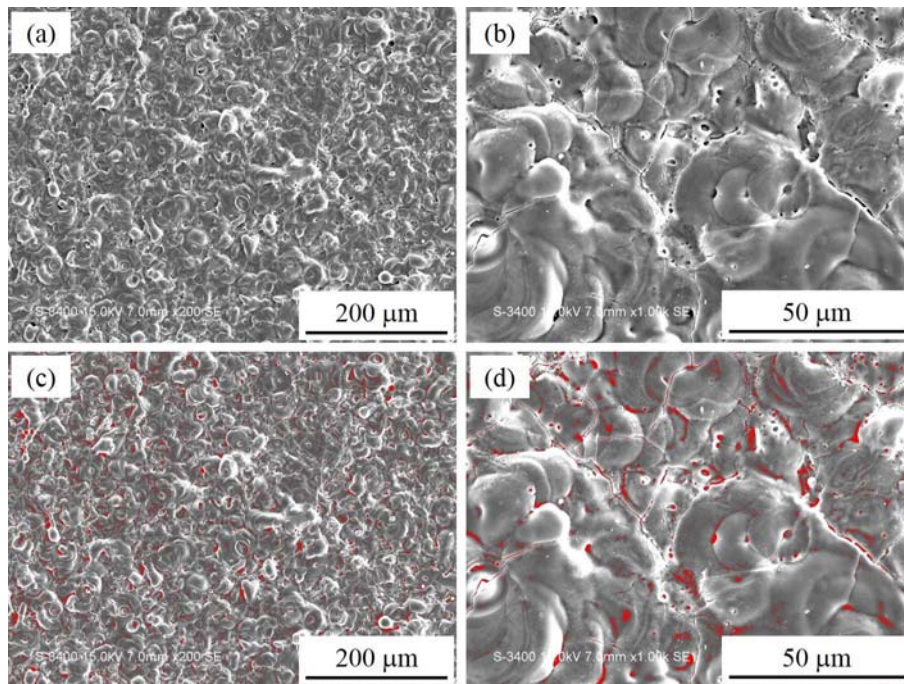


Figure 3. Surface morphology of PEO coated on 6061 Al alloy using free-alkali-ion electrolyte at the magnifications of  $\times 200$  (a) and  $\times 1K$  (b). Figure (c) and (d) corresponding to Figure (a) and (b), respectively, show the area of the pores and are characterized by red areas.

Thereby pores form on the coating surface. At the discharge sites, the temperature is very high (several thousand degrees), the metal from substrate and its oxide are melted and spilled over from discharge tunnels. The transiently molten liquid is quickly solidified leaving distinct boundaries around the pores to form the pan-cake-like morphology. Thermal stress arises from rapid solidification of transiently molten oxide exposing to cold electrolyte induce the micro-cracks appearance on the surface of oxide-layer.

The distribution of micro-pores on the surface is relatively homogeneous with average pore size smaller than 1  $\mu\text{m}$ . The area of pore is extracted from SEM images (Figure 3a and b) and marked as the red in color in Figure 3c and d, respectively. The percentage of pores on the coating surface is defined as porosity and is almost the same 2.5 % for both cases (Figure 3c, d).

### 3.2. Coating hardness

It is well known hardness of 6061 Al is around 70 HV, which is greatly increased to 940 HV after PEO treatment. The significantly increase of micro-hardness can be attributed to the phase composition and porosity of coating [9, 13, 14] and the presentation of hard phase  $\alpha\text{-Al}_2\text{O}_3$  in the coating is the main reason of the enhancement of micro-hardness.

### 3.3 Corrosion behavior of the PEO coatings

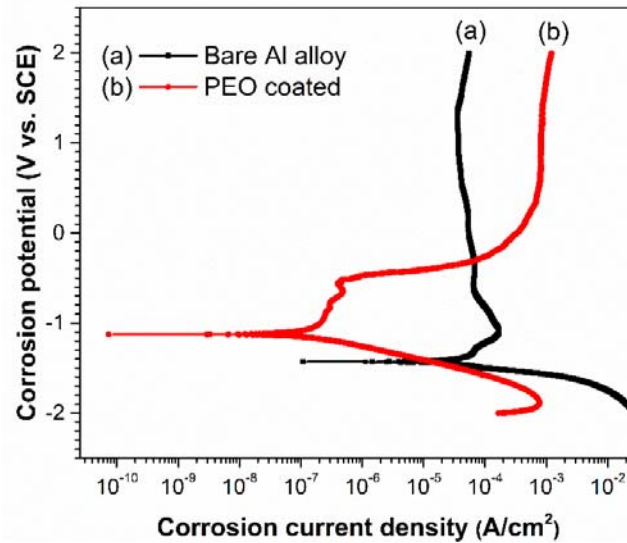


Figure 4. Potentio-dynamic polarization curves of bare and PEO treated 6061 Al alloy samples in 3.5 wt% NaCl solution.

Figure 4 shows the potentio-dynamic polarization curves of the bare and PEO-coated 6061 Al alloy samples. From polarization curves, the corrosion potential ( $E_{Corr}$ ) and corrosion current density ( $i_{Corr}$ ) were determined by using Tafel extrapolation. The polarization resistance value ( $R_p$ ) is calculated by using Sterne Geary equation as follow [15]:

$$R_p = \frac{\beta_c \times \beta_a}{2.302 i_{corr} (\beta_c + \beta_a)} \quad (1)$$

where  $\beta_c$  and  $\beta_a$  are cathodic and anodic Tafel slopes, respectively [15]. The analysis results of polarization curves are collected in Table 1. From Figure 4 and Table 1, it is clear that corrosion resistant of Al alloy improved significantly after treatment by PEO process. The corrosion potential and corrosion current density of bare Al alloy are  $-1.433$  V and  $3.24 \times 10^{-5}$  A/cm<sup>2</sup>, respectively; after PEO treatment, the corrosion potential increases to  $-1.127$  V and corrosion current density reduces to  $1.30 \times 10^{-7}$  A/cm<sup>2</sup>. These lead to the increase two orders of corrosion resistant, from  $2.11 \times 10^4$   $\Omega$  cm<sup>2</sup> for un-treated to  $7.05 \times 10^6$   $\Omega$  cm<sup>2</sup> for PEO coated sample.

Low corrosion current density and/or high corrosion voltage and/or high polarization resistance, suggest a good corrosion resistance [16].

Table 1. Electrochemical parameters related to potentiodynamic polarization curves of bare and PEO-coated 6061 Al alloy samples at different added amounts of ammonia water.

Sample	$E_{corr}$ (V)	$i_{corr}$ (A/cm <sup>2</sup> )	$\beta_c$ (V/decade)	$\beta_a$ (V/decade)	$R_p$ ( $\Omega$ cm <sup>2</sup> )
Bare Al alloy	-1.433	$3.24 \times 10^{-5}$	15.105	1.752	$2.11 \times 10^4$
PEO coated	-0.127	$1.30 \times 10^{-7}$	7.946	2.861	$7.05 \times 10^6$

#### 4. SUMMARY

In this study, a nonconventional electrolyte containing calcium phosphate and ammonia water was used in PEO process to produce the oxide layer on 6061 Al alloy. XRD, EDS and SEM analysis were used to investigate the phase composition, elemental chemical and surface microstructure, respectively, of PEO coated. Micro-hardness and corrosion resistance of bare and PEO coated samples were measured and discussed. XRD diffraction patterns show the main phase of Al,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. The incorporation of Ca and P in oxide layer is confirmed by the result of EDS analysis. SEM analyzed results indicate the PEO coated is characterized by micro-pores, pan-cakes like, and micro-cracks with pore size and percentage of pores on coating surface are smaller than 1  $\mu$ m and 2.5 %, respectively. Micro-hardness of PEO coated is 940 HV which increased significantly in comparing with the hardness of 6061 Al alloy (70 HV). Corrosion resistance increased two orders after bare 6061 Al alloy was treated by PEO process.

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## TÓM TẮT

### TẠO LỚP PHỦ TRÊN HỢP KIM AL 6061 BẰNG PHƯƠNG PHÁP Ô-XI HÓA ĐIỆN PHÂN PLASMA SỬ DỤNG DUNG DỊCH ĐIỆN PHÂN KHÔNG CÓ ION KIỀM

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Phương pháp ôxi hóa điện phân plasma (Plasma electrolytic oxidation-PEO) được biết đến như một kỹ thuật sử dụng cho việc sửa đổi bề mặt của các kim loại nhẹ như Al, Mg, Ti và các hợp kim của chúng với mục đích cải thiện đặc tính cơ học và chống ăn mòn. PEO là một quá trình điện hóa của quá trình oxy hóa bằng cách tạo ra các phóng điện cỡ mi-crô-mét trên bề mặt của kim loại ngâm trong một chất điện phân dưới sự áp dụng của một điện áp cao. Chất điện phân sử dụng trong quá trình PEO hầu hết là dựa trên các ion kiềm như ion  $\text{Na}^{+1}$ . Các báo cáo về quá trình PEO sử dụng dung dịch điện phân không chứa ion kiềm là rất hiếm. Trong nghiên cứu này, lớp ô-xít phủ trên hợp kim Al 6061 được hình thành bằng phương pháp PEO. Dung dịch điện phân sử dụng trong quá trình PEO này không chứa ion kiềm, bao gồm calcium phosphate và dung dịch a-mô-ni-ắc. Cấu trúc, độ cứng và khả năng chống ăn mòn của lớp phủ PEO được nghiên cứu và thảo luận. Phân tích hình thái bề mặt chỉ ra rằng, lớp phủ PEO được đặc trưng bởi các lỗ, các cấu trúc dạng hình bánh, và các vết nứt với kích thước cỡ mi-crô-mét. Các lỗ có kích thước nhỏ hơn 1  $\mu\text{m}$  và chiếm một diện tích 2.5 % trên toàn bộ bề mặt lớp phủ. Độ cứng và khả năng chống ăn mòn của lớp phủ PEO được cải thiện đáng kể so với hợp kim Al 6061 chưa được xử lý. Lớp phủ oxit trên bề mặt hợp kim nhôm không chứa các ion kiềm là rất quan trọng đối với nhiều ứng dụng hiện nay như sử dụng các buồng chân không phún xạ để chế tạo các linh kiện điện tử.

*Từ khóa:* ôxi hóa điện phân plasma, ion kiềm; hợp kim nhôm 6061; độ cứng; chống ăn mòn.