Journal of Ceramic Processing Research. Vol. 17, No. 8, pp. 831~836 (2016)

J O U R N A L O F
Ceramic Processing Research

Influence of process time on microstructure and electrochemical characteristics of ceramic oxide coating produced on Al alloy by pulsed plasma electrolytic oxidation

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Plasma electrolytic oxidation of Al alloy 5083-O was carried out in a dilute alkaline electrolyte with a unipolar pulsed DC condition. The coatings were fabricated with different process time (10, 20, 30 and 40 min) and were characterized for surface morphology, phase composition, and corrosion resistance. It was found that increasing process time resulted in an increase in thickness of the coating. However, longer duration of coating period did not result in an improvement of corrosion resistance. In this study, 10 min of process time is determined to be the optimum condition to improve corrosion resistance, resulting in two orders of magnitude lower corrosion current density compared to the substrate.

Key words: Plasma electrolytic oxidation, Ceramic oxide, Alumina, Process time, Corrosion resistance, Surface modification.

Introduction

With more fuel-efficiency regulation, application of lightweight material is rapidly increasing in the field of transportation equipment such as automobile, aircraft and ship. Al alloys are particularly gaining attention for lightweight material due to its high strength-to-weight ratio, corrosion resistance, durability and machinability. To meet this trend, Al alloys require a new metal forming technology and surface treatment to provide multi-functionality for a broad spectrum of applications. Anodizing is the most common surface treatment technique for Al to improve corrosion resistance of surface. However, the anodizing releases various toxic substances during or after process. Moreover, the process related to wastewater treatment involves complicated processes and costs. Plasma electrolytic oxidation (PEO) is receiving increased attention from various industries as a surface modification technique for Al alloys, using a similar principle to anodizing. The PEO technology is an environmentally friendly process which utilizes non-hazardous alkaline aqueous solution as compared to the anodizing. The PEO process introduces micro-discharge on material surface by applying a voltage higher than dielectric breakdown voltage to form ceramic oxide layer having various characteristics including corrosion and wear resistance, optical and dielectric properties. The surface characteristics of the PEO ceramic coating layer can be easily manipulated by controlling process parameters, such as applied current mode, composition and concentration of electrolyte.

Recently, there have been a number of research activities worldwide in terms of revealing mechanism of PEO and improving functionality of PEO coating layer. Most researches are concentrated on the effects of PEO process parameters, such as power source (DC, AC, and pulse), electrolyte (composition and concentration), electrical parameters (unipolar or bipolar pulse) and substrate composition, on the characteristics of resultant coating. In the meanwhile, process time is considered as an important parameter of PEO coating process, and it is the governing factor for good quality of PEO coating including coating thickness, adhesive property, hardness, corrosion resistance and wear resistance [1]. Therefore, it is of paramount importance to determine and optimize process time in the PEO coating process. In particular, there are a few research works addressing the influence of process time on the electrochemical characteristics of PEO coating layer. In related literatures, J.B. Bajat et. al investigated the effects of process time on the corrosion resistance of PEO coating formed on pure Al, and found that the surface morphology and porosity of the PEO coating have more significant effects on the corrosion resistance than coating thickness [2]. P.B. Srinivasa et. al conducted the similar study with PEO-treated Mg alloy, and claimed that the superior corrosion resistance of PEO coating with thinner thickness is attributed to better pore morphology and compactness of the coating layer [3]. However, their investigations were carried out with constant DC current mode. Taking into account the practical and operational aspects of pulsed PEO process, the related research should be targeted to reveal the effects of process time on the characteristics of PEO coating.

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In this paper, pulsed PEO process was performed on a commercial Al alloy 5083-O, and the effects of PEO process time were investigated on surface morphology and crystalline phase of PEO coating as well as relationship between coating thickness and corrosion resistance.

Experimental Details

The substrate material was a commercial Al alloy 5083-O plate with a dimension of 20 mm × 20 mm × 5 mm (t). The rectangular sample was mounted with epoxy resin in order to expose the surface area of 4 cm^2, and the copper wire was connected to the opposite side of the exposed area. Prior PEO coating, one side of the sample was polished with SiC paper up to 1000 grit, and rinsed ultrasonically with acetone and deionized water, followed by hot air drying. The PEO coating system was custom built for this study, and it was comprised of DC pulse power supply for electric source, acrylic bath and cooling system for electrolyte. During PEO process, it is important to suppress temperature rise of electrolyte, and this syzstem employed a magnetic pump to circulate the electrolyte from the bath through a heat exchanger equipped with a chiller to maintain the electrolyte temperature at 20 ºC. The electrolyte was prepared by dissolving 2 g/L of potassium hydroxide (KOH) and 2 g/L of sodium silicate (Na_2SiO_3) in deionized water. The positive terminal of DC power supply was connected to the Al substrate, which served as the anode, while the negative terminal was connected to the stainless steel plate (exposed area: 100 cm^2), which was served as the cathode. The two electrodes were immersed in the electrolyte and a pulsed unipolar DC current (frequency: 100 Hz, duty cycle: 20%) with a current density of 0.1 A/cm^2 was applied for 10, 20, 30 and 40 min. After PEO coating process, the coated samples were thoroughly rinsed with deionized water and dried in a stream of hot air to avoid possible contamination by the electrolyte. The surface morphology of the PEO coating was observed with SEM and the elemental composition for the surface part of interest was analyzed using spot EDS analysis. The crystalline phase analysis for the PEO coating was carried out using HR-XRD. The cross-section of the PEO coating was mounted with epoxy resin and ground up to 2000 grit SiC paper with 0.1 μm size diamond suspension. The coating thickness was measured with eddy current type thickness gauge, and the average of 20 measurements was determined to be the thickness. The electrochemical experiments for PEO coating were carried out in a typical flat cell and natural seawater as electrolyte solution. A three-electrode system was used consisting of the sample (exposed area: 1 cm^2) as working electrode, Ag/AgCl reference electrode and platinum counter electrode. The rest potential with time variation was monitored for 3600 s in seawater solution. In addition, potentiodynamic polarization experiment was carried out in the applied potential range of –0.25 V to + 3.0 V (vs open circuit potential) at a scan rate of 2 m/V. From the polarization curves, electrochemical investigation for PEO coatings was carried out, including observation of passivity and determination of corrosion potential and corrosion current density.

Results and Discussion

Fig. 1 presents a typical voltage-time response and the corresponding micro-discharge evolution for the PEO coating process under pulsed galvanostatic condition. In the PEO process, four stages could be distinguished, each representing a different micro-discharge phenomenon [4]. The stage 1 is characterized as a rapid linear increase of voltage, giving rise to formation of thin insulating oxide film on surface. Upon further increase of voltage, the critical point is reached and the dielectric breakdown occurs at weak parts of the oxide film. It is referred as 'dielectric breakdown voltage', which in this study was observed around 450 V at 14 s after application of current (stage 2). Such dielectric breakdown is accompanied by fine and uniform distribution of micro-discharges with a gradual increase of voltage thereafter. The PEO process reaches the stage 3 with further decrease of voltage growth rate, where the micro-discharge phenomenon intensifies, showing whitish micro-discharges turning into yellowish discharge, consequently orange arc. Finally, the voltage increase tends to be stabilized (stage 4) and the discharge was localized with higher intensity than the previous stages. With the oxide layer growing, a higher breakdown voltage is required to sustain discharge, leading to larger discharge with higher intensity. Such presence of large discharges with high intensity may result in destruction of the coating layer achieved by PEO [5]. It was observed that the size and spatial density of discharge changed with PEO stage. Uniform

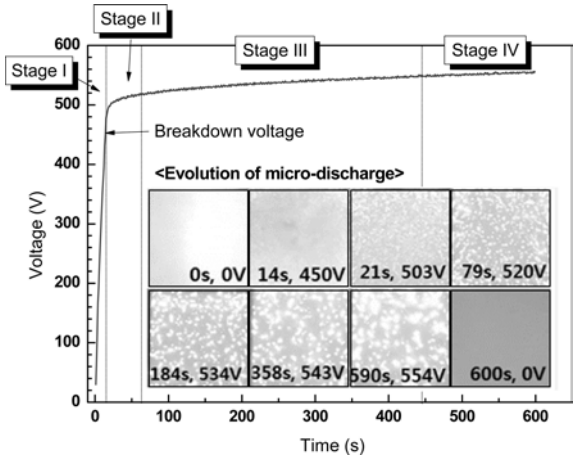
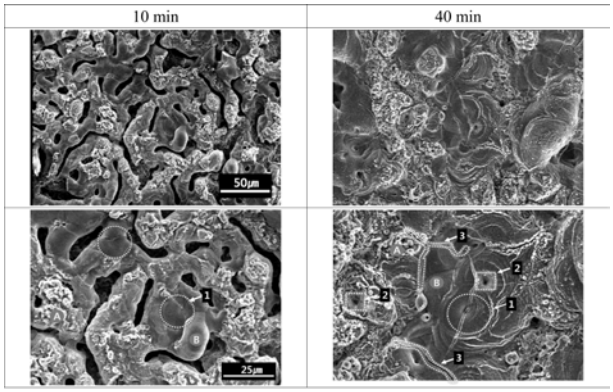


Fig. 1. Voltage-time response during pulsed plasma electrolytic oxidation at applied current density of 0.1 A/cm^2 and the evolution of micro-discharge during 10 min of PEO coating.



(a)

10 min					40 min				
Elem.	A		B		Elem.	A		B	
	wt.%	at.%	wt.%	at.%		wt.%	at.%	wt.%	at.%
O K	68.07	78.48	64.10	75.06	O K	69.48	80.15	66.66	77.12
Mg K	3.51	2.66	0.67	0.52	Mg K	-	-	1.48	1.12
Al K	13.78	9.42	34.05	23.64	Al K	1.71	1.17	27.97	19.19
Si K	13.64	8.96	1.17	0.78	Si K	26.00	17.08	3.89	2.57
K K	1.00	0.47	-	-	K K	2.01	0.95	-	-
Total	100.00		100.00		Total	100.00		100.00	

(b)

Fig. 2. (a) Surface morphology for ceramic oxide coating treated for 10 min and 40 min (b) EDS analysis for spot A and B.

distribution of micro-discharge over surface was observed in the early stage, and the size of discharge increased but the spatial density decreased with the elapse of time. In the final stage, large and localized discharge (arcs) was observed. Such voltage-time behavior with the corresponding micro-discharge phenomenon is an important characteristic of PEO process and it may exert significant influence on the PEO coating growth mechanism [6].

Fig. 2 depicts SEM surface morphology (a) and the EDS elemental composition (b) for the PEO coatings produced for the PEO process time 10 min and 40 min in pulsed galvanostatic mode. As a general rule, surface microstructure of PEO coatings could be controlled by electrolyte composition and electrical parameters such as applied voltage, current and power mode. In this study, a reticulate structure with nodules and pores was dominant in PEO coating during 10 min of process time, while a pan-cake structure was observed mainly for PEO coating with 40 min. In this study, the pan-cake structure (marked No. 1), also referred as a crater, was observed in both PEO coatings. They were formed by melting of substrate or coating in the vicinity of weak part of the oxide layer, followed by subsequent rapid solidification of molten oxide by the relatively low temperature electrolyte. The central sinkhole (marked No. 2) of the carter indicates the discharge channel through which the plasma discharge occurs, and the molten substrate or oxide layer is erupted to form the crater structure [7]. It is generally admitted that the dielectric breakdown becomes impeded with the increase of PEO coating thickness, and this results in growth of diameter for the

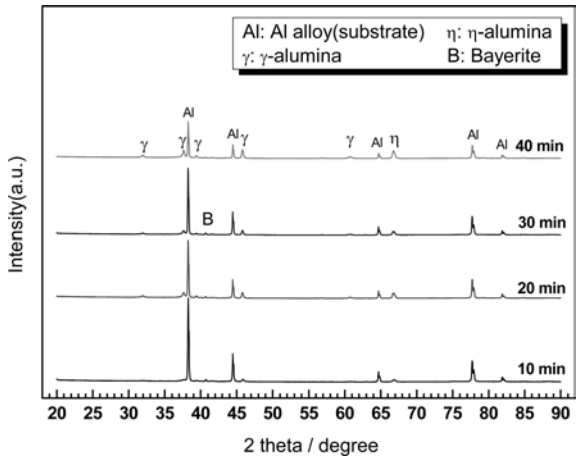


Fig. 3. X-ray diffraction pattern of ceramic oxide coatings treated by PEO with different process times.

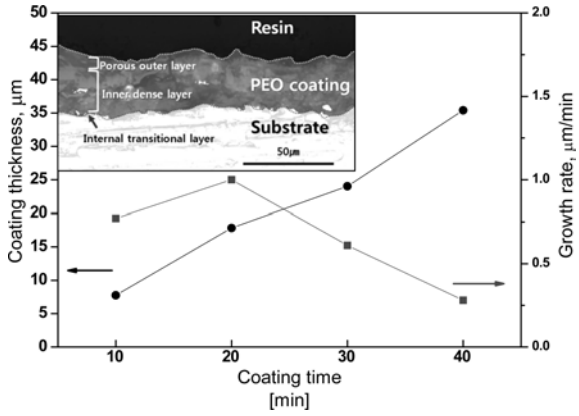


Fig. 4. Thickness and growth rate of PEO coating with time. The inset shows the cross-section of PEO coating for 40 min.

discharge channel and the reduced spatial density of discharges [8]. The diameter of craters was measured to be 12 μm and 20 μm for 10 min and 40 min of process time, respectively, and this indicates the increasing tendency with time. The micro cracks (marked No. 3) was also observed in the vicinity of craters. This indicates that the accumulated residual stress during PEO process was relieved by the crack formation process [9]. Two points of the surface of interest were selected for spot-EDS analysis, and the result is summarized in Fig. 2(b). The EDS analysis confirmed the white particles (marked as 'A') to be Si-rich compounds, which was formed by an electrolyte constituent, Na_2SiO_3. The craters (marked as 'B') were confirmed to be Al-rich oxides.

Fig. 3 displays X-ray diffraction patterns for PEO coatings produced with different process time under pulsed galvanostatic condition. It is observed that alumina peaks by PEO coating as well as the substrate peak due to X-ray penetration, regardless of process time. With the increasing of PEO process time, there was an increasing tendency of alumina peak intensity. This suggests that the alumina layer grows during growth of PEO ceramic coating layer possibly due to

repetition of micro-discharge and chemical reaction. Generally, the PEO ceramic oxide layer formed on Al alloys has α-alumina and γ-alumina as main crystalline phases [10]. In this study, the primary crystalline phase was γ-alumina, which is metastable phase with face-centered cubic structure. It is acknowledged that the outermost region of PEO coating has γ-alumina due to rapid cooling by relatively cold electrolyte, while phase transformation of γ-alumina into α-alumina is favored in the inner region due to high-temperature plasma discharge compared with the outer region [5]. In this research, α-alumina peak was not detected, and this does not indicate the absence of such a phase, but X-ray did not reach the inner layer, which is believed to possess α-alumina phase. Aside from γ-alumina, η-alumina (2θ = 67.034) peak was observed, suggesting that the thermal transformation of Al oxide-hydroxides, such as bayerite or gelatinous hoehmite, into ç-alumina [11]. The trace amount of bayerite peak indicates that transition of alumina could have been commenced by formation of bayerite.

Fig. 4 demonstrates the thickness and growth rate of PEO coating layer with process time under pulsed galvanostatic regime, and the inset shows the cross-section of the PEO coating achieved for 40 min. In PEO coating process, it is natural that the coating thickness will increase with process time. It is observed that the average coating thickness was measured to be 7.7 μm and 35.4 μm for 10 min and the 40 min process time, respectively. The thickness growth rate depends heavily on the electrolyte composition and the characteristics of applied current mode [12]. It is common that PEO coating thickness increases with the increasing of process time but the growth rate decreases. In this study, the growth rate showed an increasing tendency in the early stage, showing 0.77 μm/min for 10 min and 1.0 μm/min for 20 min of process time. However, after then it decreased to 0.28 μm/min for 40 min of process time. The cross-sectional observation indicates that the PEO coating layer is comprised of outermost porous layer, inner dense layer and transition layer. In the microstructure, the outermost layer accounted for about 30% of the coating with porous structured layer and high amount of γ-alumina. It is considered that such porous layer has poor mechanical properties and thus requires removal by polishing. From the other aspect, the porous structure can facilitate the application of other coatings onto PEO coating, which increases adhesive strength due to anchorage effect [13]. Furthermore, pores and cracks in PEO coating can serve as reservoirs for lubricant to form stable lubricative film, which may result in beneficial effects on tribological performance under boundary-lubricated conditions [5]. The inner dense layer, which is also referred to as 'functional layer', has a relatively high ratio of á-alumina and thus determines the mechanical properties of PEO coating. The transition layer forms the interface between the substrate and ceramic oxide, which

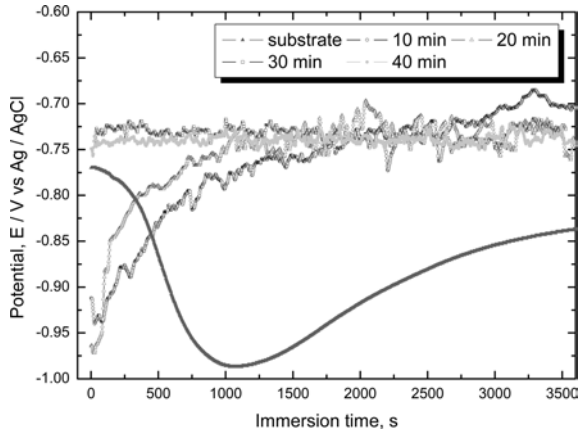


Fig. 5. Variation of rest potential in seawater for substrate and PEO coatings produced with various process times.

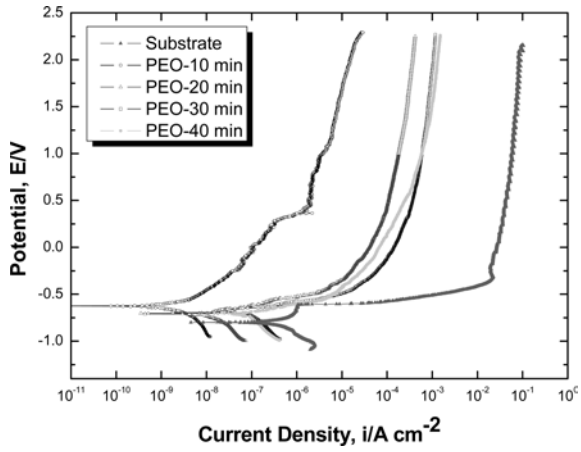


Fig. 6. Potentiodynamic polarization curves in seawater for substrate and PEO coatings produced with various process times.

gives excellent adhesive strength to PEO coating [14]. It needs to be stressed that the process time is one of important process parameters to control coating properties such as thickness, roughness, hardness, wear resistance and corrosion resistance. Along with the optimization of process time, identification of the characteristic change on PEO coating with process time is as important as the optimization of electrolyte and electrical parameters.

Fig. 5 exhibits rest potential behavior during 3600 s in seawater solution for PEO coatings and substrate (non-PEO processed). In the case of the substrate, the potential shifted in the active direction with immersion in seawater until 1071 s, after then reversed gradually in the noble direction, consequently −0.838 V of potential in the end. This implies that the immersion of the substrate caused breakdown of the natural oxide layer on Al alloy by Cl^- ions in seawater, followed by subsequent reconstruction of the oxide layer. In the case of process time 10 min and 20 min, more active potential was observed in the early stage of immersion than other specimens, but after then they shifted gradually towards noble direction, indicating growth of passive film in thickness. Different behavior was observed

for process time 30 min and 40 min, which is characterized by periodic fluctuation of potential with time but showing relatively stabilized behavior. This is attributed to thicker PEO coating which retards the initiation and propagation of corrosion by lowering supply and accumulation rates of Cl^- ions at PEO coating or PEO coating/substrate interface [15]. The final potentials of all PEO coatings with process time represented more noble potential than that of the substrate. Regardless of process time, the rest potential for PEO coatings presented a certain degree of fluctuation in potential. This would be related to the depassivation and repassivation of the Al constituent from the substrate by penetration of seawater into through-thickness pores.

Fig. 6 presents polarization curves for PEO coatings and substrate after potentiodynamic polarization experiment in seawater solution. The polarization curve can be readily obtained by polarizing a specimen from equilibrium potential and measuring corresponding change of current density, and it provides useful information on electrochemical corrosion characteristics of the specimen. The corrosion potential and corrosion current density, which were determined by Tafel extrapolation method, are summarized in Table 1. All PEO coatings represented more noble corrosion potential and lower current density than the substrate, and it is noticed that the lower corrosion current density was obtained for the PEO coating with shorter process time. Particularly, the PEO coating with 10 min of process time showed about two orders of magnitude lower corrosion current density than the substrate. This result is contrary to the belief that prolonged process time might improve the corrosion resistance of the coating. The degradation of corrosion resistance with PEO process time can be elucidated as follows: repetition of discharge with longer process time may deteriorate the interface between PEO coating and substrate, the transition layer; this weakens the interfacial adhesion strength; the formation of through-thickness pores may be then promoted, where corrosive solution is permeated into the substrate. Generally, the inner dense layer is known to act primarily as a barrier layer to suppress the penetration of corrosive solution from the outermost porous layer to the substrate [16]. However, the result of this study indicates that the effect of deterioration of transition layer might be more pronounced than the thickness of inner dense layer. In the related literature, P. Bala Srinivasan et. al investigated the corrosion behavior of the PEO-processed Mg alloy AM50 for different applied current density and process time. In their research, higher applied current density formed thicker PEO coating, but with degradation of corrosion resistance. They claimed that the corrosion resistance of thin PEO coating could be attributed to better pore structure and compactness of the coating. Other researchers also pointed out that longer process time produced thicker coating but at the same time large discharge channel, which allows a fast ingress of a corrosive solution was also formed, resulting in decreased corrosion resistance [6]. The anodic polarization behavior of the substrate showed that at first pseudo-passive behavior was observed in the potential range from the open circuit potential to about −0.6 V with the increasing of polarization in the anodic direction, but later rapid anodic dissolution reaction occurred. After the anodic current density increased sharply, it soon reached the limiting current density at the potential of about −0.3 V, from which the increase of current density was retarded. On the other hand, the PEO coating with 10 min of process time showed pseudo-passive behavior in the potential range from the open circuit potential to about 0.3 V. This indicates much broader pseudo-passive behavior range of PEO with 10 min of process time than the substrate, but no such phenomenon was observed in the PEO coating with other process times (20, 30 and 40 min). Furthermore, the PEO coating with 10 min of process time had the lowest anodic limiting current density, and thus was determined to have the most enhanced corrosion resistance than other PEO coatings.

Table 1. Electrochemical parameters determined by Tafel extrapolation for substrate and PEO coatings treated with various process times.

	Corrosion potential (V vs Ag/AgCl)	Corrosion current density (A/cm^2)
Substrate	−0.800	3.49×10^{-7}
10 min	−0.625	3.98×10^{-9}
20 min	−0.708	1.80×10^{-8}
30 min	−0.697	9.10×10^{-8}
40 min	−0.705	7.92×10^{-8}

Conclusions

In this paper, plasma electrolytic oxidation was performed on a commercial Al alloy under pulsed galvanostatic condition with different process times, and the influences of process time on surface characteristics, elemental composition of surface, crystalline phase, thickness and corrosion resistance were investigated. With the increasing of process time, the surface morphology was changed from a porous reticulate structure to a dense pan-cake structure. The coating thickness increased, while the growth rate decreased. The PEO coatings had more noble corrosion potential and lower corrosion current density than the substrate, indicating improved corrosion resistance of the substrate. The rest potential measurement indicated that the PEO coatings with longer process time represented the stabilized rest potential behavior throughout the experiment. However, the PEO coating with shorter process time exhibited lower corrosion current density. In PEO process, process time was proved to have significant effects on the coating properties and

electrochemical characteristics, and therefore optimization of process time should be established base on this consideration.

Acknowledgments

This research was a part of the project titled 'Construction of eco-friendly Al ship with painting, and maintenance/repairment free', funded by the Ministry of Oceans and Fisheries, Korea.

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