

Article

Effects of Processing Parameters on the Corrosion Performance of Plasma Electrolytic Oxidation Grown Oxide on Commercially Pure Aluminum

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Abstract: The plasma electrolyte oxidation (PEO) process has been considered an environmentally friendly surface engineering method for improving the corrosion resistance of light weight metals. In this work, the corrosion resistance of commercially pure Al and PEO treated Al substrates were studied. The PEO layers were grown on commercially pure aluminum substrates using two different alkaline electrolytes with different addition concentrations of Si_3N_4 nanoparticles (0, 0.5 and 1.5 gL^{-1}) and different duty cycles (25%, 50%, and 80%) at a fixed frequency. The corrosion properties of PEO coatings were investigated by the potentiodynamic polarization and electrochemical impedance spectroscopy test in 3.5 wt.% NaCl solutions. It showed that the weight gains, layer thickness and surface roughness of the PEO grown oxide layer increased with increasing concentrations of Si_3N_4 nanoparticles. The layer thickness, surface roughness, pore size, and porosity of the PEO oxide layer decreased with decreasing duty cycle. The layer thickness and weight gain of PEO coating followed a linear relationship. The PEO layer grown using the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ contained electrolyte showed an excellent corrosion resistance and low surface roughness than other PEO coatings with Si_3N_4 nanoparticle additives. It is noticed that the corrosion performance of PEO coatings were not improved by the addition of Si_3N_4 nanoparticle in the electrolytic solutions, possibly due to its detrimental effect to the formation of a dense microstructure.

Keywords: plasma electrolytic oxidation; pure aluminum; Si_3N_4 nanoparticle; borax; corrosion resistance

1. Introduction

Aluminum and its alloys have been extensively used in different industrial applications (shipbuilding, marine, automotive, aerospace, and in innumerable other areas) due to their high quality of properties, i.e., high strength to weight ratio, low density, light weight, noble ductility, and non-magnetic properties. However, the relatively poor corrosion resistance and low surface

hardness restrict their wider application in crucial environments [1,2]. One of the efficient approaches to improve these disadvantages of aluminum is by surface modification for enhancing its anticorrosion performance, such as plasma electrolytic oxidation (PEO), ion implantation, laser surfacing, diffusion treatment, thermal spraying, physical vapor deposition (PVD), chemical vapor deposition (CVD) and conversion coatings such as anodizing, etc. Among several kinds of surface modification techniques, PEO is one of the most promising surface treatment methods [3], because it is an environmentally friendly and cost-effective technique for surface engineering and a suitable method for producing thick, hard and dense ceramic coatings on light metals.

PEO, also known as micro-arc oxidation (MAO) [4], is an electrochemical induced plasma surface treatment process for creating oxide ceramic coatings on light metals [5,6]. PEO is a relatively new surface modification technique which can significantly improve the hardness, corrosion and wear resistance, adhesion strength, thermal and other desirable properties of Al alloys by efficiently growing thick alumina rich ceramic coatings [7–10]. During this process, plasma discharge can cause the formation of a highly adhesive and dense oxide layer on the substrate [11,12]. PEO is also considered an environmentally friendly and cost-effective coating process with real industrial applications [3,13–18]. Several parameters, including duty cycle, process time, current density, frequency, and electrolyte, can influence the PEO ceramic oxide coating growth process and its corrosion resistance performance [19–21]. Since the addition of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in the electrolyte can reduce the pore depth on the PEO coating, the corrosion resistance of the PEO coating was better than that of PEO coating developed in the base electrolyte system [22]. It is also reported that, as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was added to the electrolyte, both the coating formation rate and coating density increased [23]. Therefore, the corrosion resistance of the D16 aluminum alloy increased due to less porosity formed on the PEO layer [23]. For modifying the electrolyte solution to impart desirable properties in PEO coatings, especially for a better corrosion performance, a variety of inorganic, organic compounds and other different additives are used in addition to the primary electrolyte additives [24].

The addition of nanoparticle in the electrolyte solution was an important factor for improving corrosion resistance. The most nanoparticle studied on corrosion performance of PEO coatings were Al_2O_3 [25,26], CeO_2 [27,28], TiO_2 [29,30], SiO_2 [31], ZrO_2 [32,33], and Y_2O_3 [34]. However, the research of Si_3N_4 nanoparticles on the anti-corrosion properties of the PEO layer on pure aluminum is seldom reported in the literature. Si_3N_4 has been widely applied as structural ceramic material, which has good high temperature stability, low thermal expansion coefficient, excellent fracture resistance, high strength of flexural and toughness, comparatively high hardness, and wear resistance [35]. Nevertheless, only limited researchers used Si_3N_4 nanoparticles in the electrolyte for PEO coatings and different results were reported [36–38]. In our previous work, the addition of Si_3N_4 nanoparticle in the base electrolyte can improve the corrosion resistance of PEO layer on AZ31 magnesium alloy substrate [36]. On the other hand, no improvement on the corrosion performance of PEO layer on AM50 magnesium alloy by the addition of Si_3N_4 nanoparticle was reported by Lu et al. [37]. They found that the addition of Si_3N_4 nanoparticle does not produce dense PEO coatings [37]. Qin and co-workers revealed that the addition of $\text{TiO}_2 + \text{Si}_3\text{N}_4$ nanoparticles into the PEO electrolyte of 5052 aluminum alloy can decrease the surface roughness, improve the density and hardness of PEO layer [38]. Because no research works has been done by using both the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and Si_3N_4 nanoparticle in electrolytes, we plan to make a dense and compact surface morphology of PEO oxide by the combination of these two additives in electrolyte.

In this study, a systematic investigation of PEO coatings fabricated on pure aluminum by using two different alkaline electrolytes with different concentrations of Si_3N_4 nanoparticle additives and different duty cycles at a fixed frequency was conducted. The influences of Si_3N_4 nanoparticle additives, electrolytes, and duty cycles on the corrosion resistance of PEO grown oxide layers on pure aluminum were studied.

2. Experimental Procedures

2.1. Preparation of the Samples

The PEO experiments were carried out by using a pulse DC power controller (YSTC-600-005HD, Taiwan). The upper voltage limit of the power supply is 600 V and the experiments have been carried out at a maximum current density of $100 \text{ mA}\cdot\text{cm}^{-2}$. The PEO treatment were operated under a unipolar mode and fixed at a frequency of 1 kHz for 10 min. Three different duty cycles of 25%, 50%, and 80% were selected. A duty cycle is the fraction of one period in which a signal or system is active. Duty cycle is commonly expressed as a percentage or a ratio. A period is the time it takes for a signal to complete an on-and-off cycle. Thus, a 25% duty cycle means the signal is on 25% of the time but off 75% of the time. The specimen designations and parameters of the PEO treatment are shown in Table 1. In this study, commercially pure aluminum plates with the dimensions of $5 \times 5 \times 0.1 \text{ cm}^3$ were selected as the substrate for the PEO processes. The substrates were cleaned by an ultrasonic cleaner in the deionized water, acetone, and ethanol for 5 min, respectively. The PEO process used two different alkaline electrolytes with and without borax. In addition, Si_3N_4 nanoparticles, (average size of 20 nm, Serin International, Morehead, KY, USA) with three different concentrations of 0, 0.5, and 1.5 g L^{-1} were added respectively into the PEO processes to form the PEO coatings. A water cooling system was used to maintain the temperature of electrolyte at 25°C throughout PEO process. After the PEO process, the PEO grown oxide coatings were cleaned by the ultrasonic cleaner in deionized water and then dried in air.

Table 1. Specimen designation and plasma electrolytic oxidation (PEO) process conditions.

Specimen Designation	APA	APB	APC	APD	APE	APF
Size (cm)	$5 \times 5 \times 0.1$					
Si_3N_4 concentration in electrolyte (g L^{-1})	0	1.5	0	0.5	0.5	0.5
Electrolyte concentration	$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (g L^{-1})					
	7					
	KOH (g L^{-1})					
	2.5					
	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (g L^{-1})					
	5					
	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (g L^{-1})					
	0	0	5	5	5	5
Duty cycle (%)	80				50	25
Frequency (Hz)	1000					
Voltage (V)	600					
Current density ($\text{mA}\cdot\text{cm}^{-2}$)	100					
Time (sec)	600					
Breakdown voltage (V)	382.3	385.0	397.1	396.0	399.5	417.2
The time to reach breakdown voltage (s)	16.5	18.5	22.0	34.5	24.5	22.0

2.2. Sample Characterization

The phases of the PEO coatings were analyzed by a grazing angle X-ray diffractometer (GAXRD, PANalytical, X'pert, Almelo, The Netherlands). The radiation source was from the Cu target ($\text{Cu } \alpha$, $\lambda = 1.540 \text{ \AA}$) with an incidence angle of 2° , and the power of X-ray generation was fixed at 30 kV and 40 mA. A scanning electron microscope (SEM, S3400N, Hitachi, Fukuoka, Japan) was used to study the surface and the cross-sectional microstructure of PEO coatings. The chemical compositions of PEO coatings were examined by field emission-electron probe micro-analyzer (FE-EPMA, JXA-8500F, JEOL, Akishima, Japan). The average pore size and the percentage of porosity were measured by SEM and calculated by ImageJ software. The average thickness of each PEO coating was measured according to the SEM observations from ten different regions. The surface roughness of the coatings was measured by a surface profilometer (Surfcorder ET3000, Tokyo, Japan) from ten measurements. The corrosion performance of PEO coating in 3.5 wt.% NaCl aqueous solutions was studied by a potentiodynamic polarization experiments using a potentiostat (PGSTAT30, Autolab, Utrecht, The Netherlands). A

pure aluminum plate without PEO treatment was used as a reference. Electrochemical impedance spectroscopy (EIS) was also carried out in a 3.5 wt.% NaCl solution by using an electrochemical workstation (Bio-Logic SAS, SP-200, Seyssinet-Pariset, France). EIS measurements were prepared after allowing the sample to stabilize at the corrosion potential (E_{corr}) after immersion for 6 h. A standard three-electrode cell arrangement was used with a saturated calomel reference electrode (SCE), with a platinum plate as the counter electrode and the coated samples serving as the working electrode. The frequency ranging from 0.01 Hz to 100 kHz were acquired for obtaining the impedance spectra. An alternative current potential amplitude of 10 mV at the E_{corr} was applied to the working electrode. The equivalent electrical circuits were fitted by Bio-Logic software to interpret the impedance data for each sample.

3. Results and Discussion

3.1. Voltage-Time Response of PEO Coatings

Figures 1 and 2 depict the voltage–time responses of all PEO coatings. The breakdown voltage and the time for reaching the breakdown voltage for each sample were obtained from Figure 1 and listed in Table 1. Breakdown voltage is the potential of the oxide film produced on the surface of the substrate, which results in the formation of plasma micro-discharge events. This allows the formation of coatings composed of not only predominant substrate oxides but of more complex oxides containing the elements present in the electrolyte. Many dispersed discharge channels are produced as a result of micro-regional instability when the breakdown voltage is reached. Figure 1a shows the voltage–time curves of APA, APB, and APC, which can be used to study the effect of Si_3N_4 concentrations and borax in the electrolytic solution. The enlarged plots from 0 to 100 s of the voltage–time responses indicated with the breakdown voltage values are shown in Figure 1b. As compared with APA, the breakdown voltage of APB increased slightly from 382.3 V to 385.0 V which contained 1.5 g L^{-1} Si_3N_4 nanoparticle in electrolyte. Meanwhile, the time to reach breakdown voltage also increased from 16.5 s to 18.5 s with the addition of Si_3N_4 nanoparticle. As compared with APA, the breakdown voltage and the time to reach breakdown voltage of APC further increased from 382.3 V to 397.1 V and from 16.5 s to 22 s, respectively, with the addition of borax in electrolyte. The voltage–time responses of APD, APE and APF are illustrated in Figure 2a, which can tell the effect of duty cycle. Figure 2b presents the enlarged plots from 0 to 100 s of the voltage–time responses indicated with the breakdown voltage values. When the duty cycle increased from 25% to 80%, the breakdown voltage and the time to reach breakdown voltage decreased from 417.2 V to 396.1 V and increased from 22 s to 34.5 s, respectively. It is reported that the lower duty cycle of PEO treatment can generate higher voltage than the higher duty cycle one [39]. In this work, the lower duty cycle (25%) of PEO operation, APF, reached the maximum voltage around 500 V and required a higher breakdown voltage of 417.2 V. In addition, the addition of borax in electrolyte also increased the breakdown voltage of the PEO process.

The relationships between breakdown voltage and duty cycle, Si_3N_4 and borax concentrations are presented in Figure 3. It is obvious that the breakdown voltage increased with decreasing duty cycle in Figure 3a. Meanwhile, no direct relationship between breakdown voltage and the concentration of Si_3N_4 nanoparticle is obtained in Figure 3b. The higher breakdown voltage values can be seen for the PEO coatings with borax addition as depicted in Figure 3c.

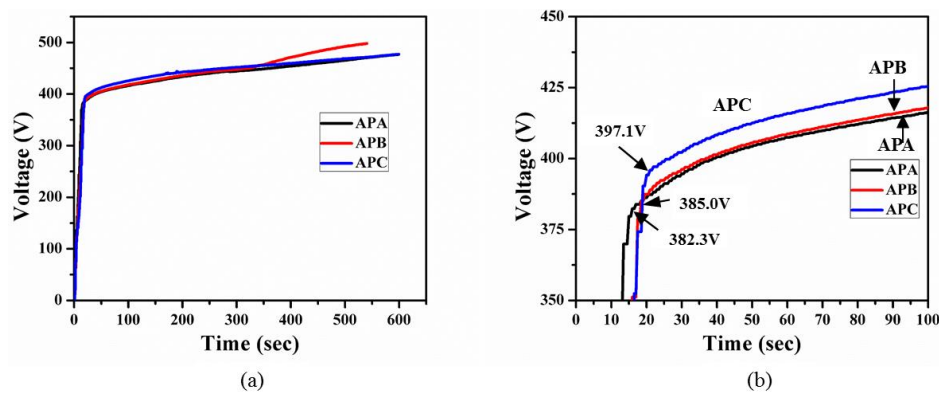


Figure 1. The voltage-time responses of PEO processes (a) with different concentrations of Si_3N_4 and borax, and (b) the enlarged plots from 0 to 100 s indicated with the breakdown voltage values.

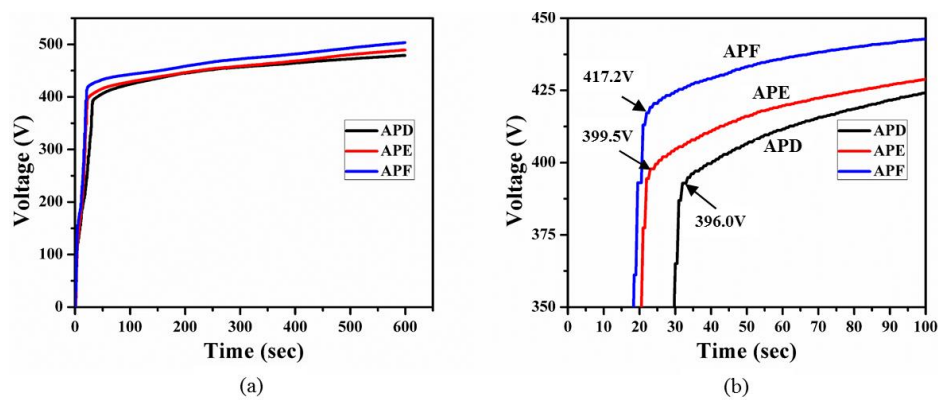


Figure 2. The voltage-time responses of PEO processes (a) with different duty cycles and (b) the enlarged plots from 0 to 100 s indicated with the breakdown voltage values.

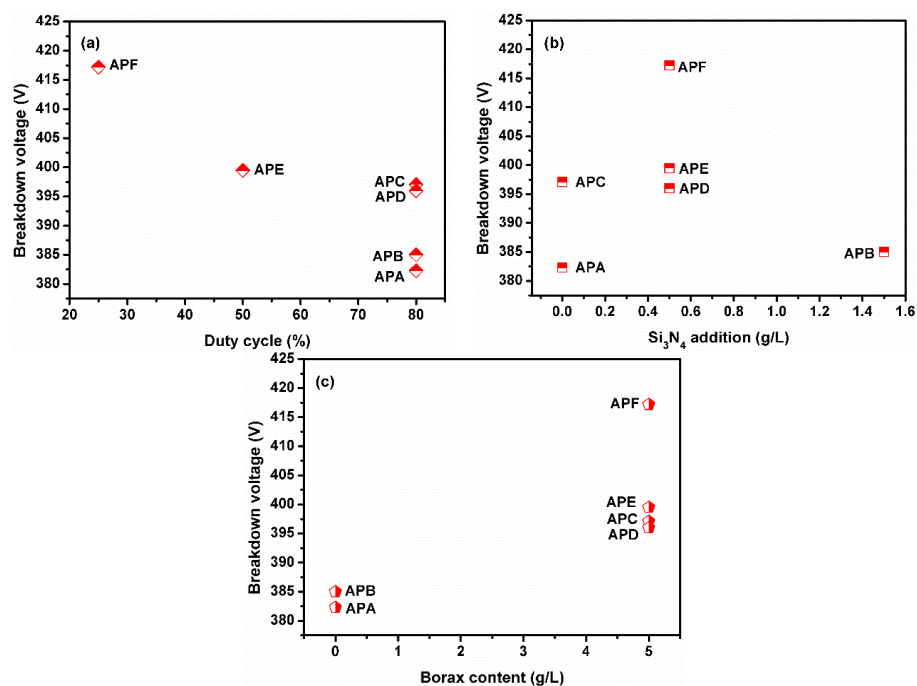


Figure 3. The relationships between breakdown voltage and (a) duty cycle, (b) Si_3N_4 and (c) borax concentrations.

3.2. Phase and Composition Analysis

Figure 4 represents the GAXRD results of PEO coatings and the pure aluminum. By analyzing the results of X-ray diffraction patterns of PEO samples, it is shown that γ - Al_2O_3 is the primary phase for all PEO coatings. In addition, α - Al_2O_3 and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) phase were also observed for APB sample. Dehnavi et al. [40] reported that mullite can be produced when more concentration of Si was formed on the surface and at higher duty cycle. Some literatures mention that one factor that affects formation of α - Al_2O_3 is the addition of impurity in the electrolyte [41,42]. Yurekturk et al. [43] also reported that increasing the concentration of Si_3N_4 nanoparticle in the electrolyte can increase the occurrence of α - Al_2O_3 . The other process for increasing the PEO coating oxide layer thickness and enhancing the phase transformation of γ - Al_2O_3 to α - Al_2O_3 is the application of higher duty cycle [40,44,45]. Because the APB was grown using 1.5 gL^{-1} Si_3N_4 nanoparticle in electrolytic solution and 80% duty cycle, we suggest that by applying a greater concentration of Si_3N_4 nanoparticles and higher duty cycles, the mullite and α - Al_2O_3 phases can be generated in the PEO coating.

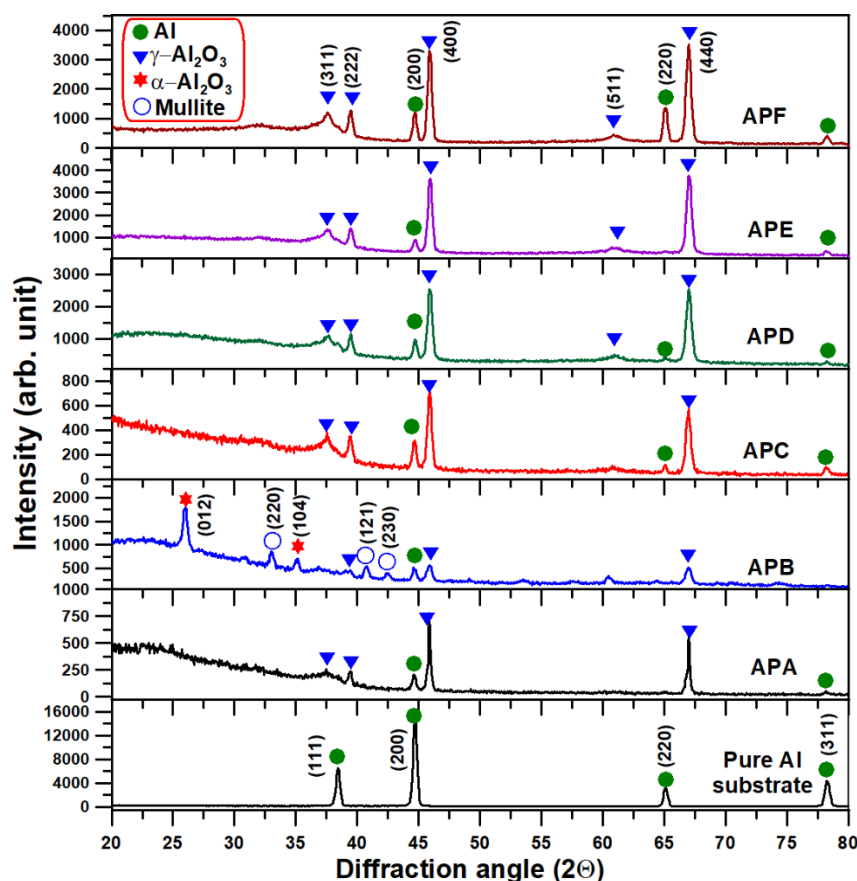


Figure 4. X-ray diffraction patterns of pure aluminum without PEO coating and PEO coatings with two different alkaline electrolytes with different Si_3N_4 nanoparticle addition concentrations and different duty cycles at a fixed frequency.

In Figure 4, the diffraction peaks of Al substrate are also found due to the strong penetration power of X-rays. A similar result was also reported in the GAXRD analysis of PEO coating on AA7020-T6 aluminum alloys [46]. There is no presence of Si_3N_4 peaks in the GAXRD pattern because of its broad peak nature of nano size particles in XRD. Another possible reason is due to its lower addition amount in electrolyte. In addition, the reaction between the Si_3N_4 nanoparticles and the molten aluminum oxide for forming the mullite phase during the plasma discharge also reduce the amount of Si_3N_4 nanoparticle in the PEO layer, which was also reported elsewhere [37].

Table 2 lists the chemical compositions of PEO coatings analyzed by FE-EPMA. We can confirm that the Al content is from the substrate and O, Na, Si, P, and K are from the electrolytic solutions, while Si and N elements are from the Si_3N_4 nanoparticles. The chemical composition results show that the Si contents increase with increasing amounts of Si_3N_4 nanoparticles. The Al content depends on the oxide layer thickness, which increases with decreasing thickness of the oxide layer. The highest Si and N contents can be found for APB sample with 1.5 gL^{-1} Si_3N_4 concentration additives in the electrolyte.

Table 2. Chemical compositions of PEO coatings analyzed by FE-EPMA (unit: at. %).

Sample	APA	APB	APC	APD	APE	APF
Composition						
O	62.37	60.97	61.13	59.56	60.88	58.98
Na	0.14	0.20	0.08	0.06	0.11	0.12
Al	36.29	30.77	36.15	34.36	35.30	35.33
Si	1.15	5.85	1.37	4.03	1.63	3.29
P	0.02	1.33	0.08	0.19	0.09	0.34
K	0.03	0.13	0.06	0.03	0.24	0.13
N	0.00	0.75	0.00	0.25	0.33	0.19
B	0.00	0.00	1.13	1.52	1.42	1.62

The dependence between sum of Al and O contents and duty cycle, Si_3N_4 and borax concentrations are depicted in Figure 5. There is no direct relationship between the sum of Al and O contents and duty cycle as shown in Figure 5a. In Figure 5b, the sum of Al and O contents increased with decreasing Si_3N_4 concentration. Meanwhile, no direct relationship can be seen between the sum of Al and O contents and borax contents in Figure 5c.

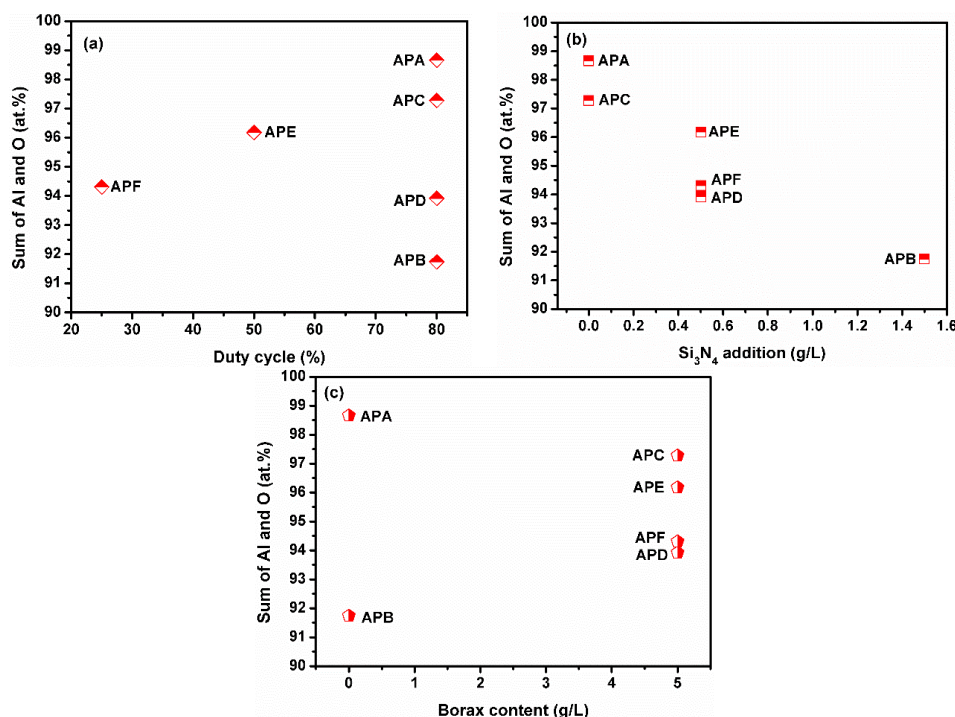


Figure 5. The dependence between sum of Al and O contents and (a) duty cycle, (b) Si_3N_4 and (c) borax concentrations.

3.3. Microstructure Analysis of PEO Coatings

Dehnavi and coworkers [47] reported that the PEO coatings had quite different surface morphologies if they were prepared by different kinds of electrolytic solutions, concentrations of Si_3N_4 nanoparticle and duty cycles. Particularly the duty cycles and frequencies showed greater effects on changing the surface structures of the PEO coatings. Figure 6 depicts the surface morphologies of all PEO samples. It appears that the APC sample has more compact, less crack and pores feature which was grown using the electrolytic solution with borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and without Si_3N_4 nanoparticle. The high magnification images of white dashed rectangular areas on APB, APC and APD coatings in Figure 6 are shown in Figure 7a. The APB coating has more pores and deep cracking than these of APC and APD. In addition, some clusters of Si_3N_4 nanoparticles indicated by white arrows can be seen on the surface of APB coating as illustrated in Figure 7b.

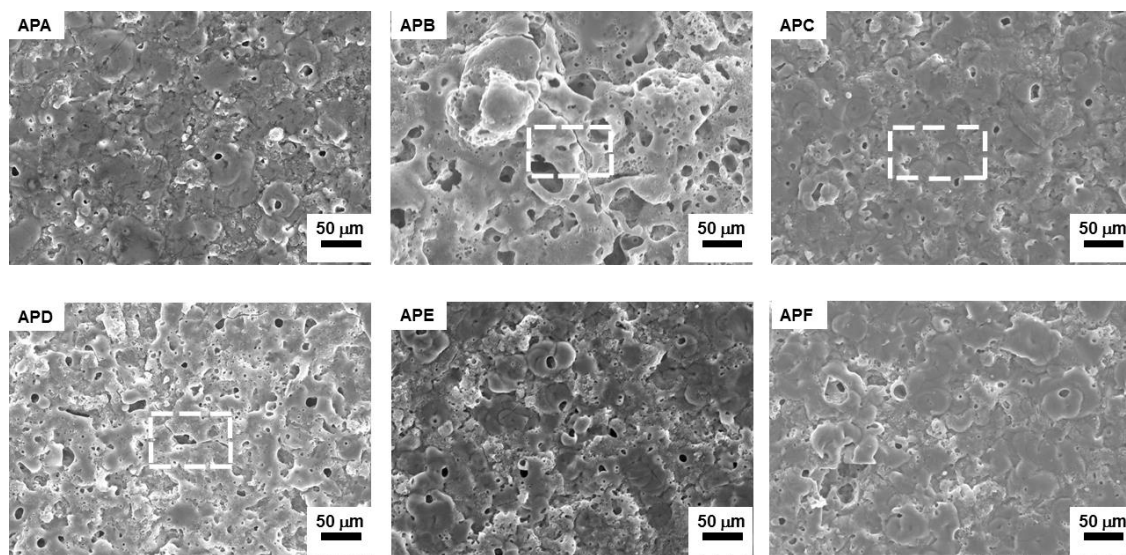


Figure 6. Surface morphologies of PEO samples prepared under different process parameters.

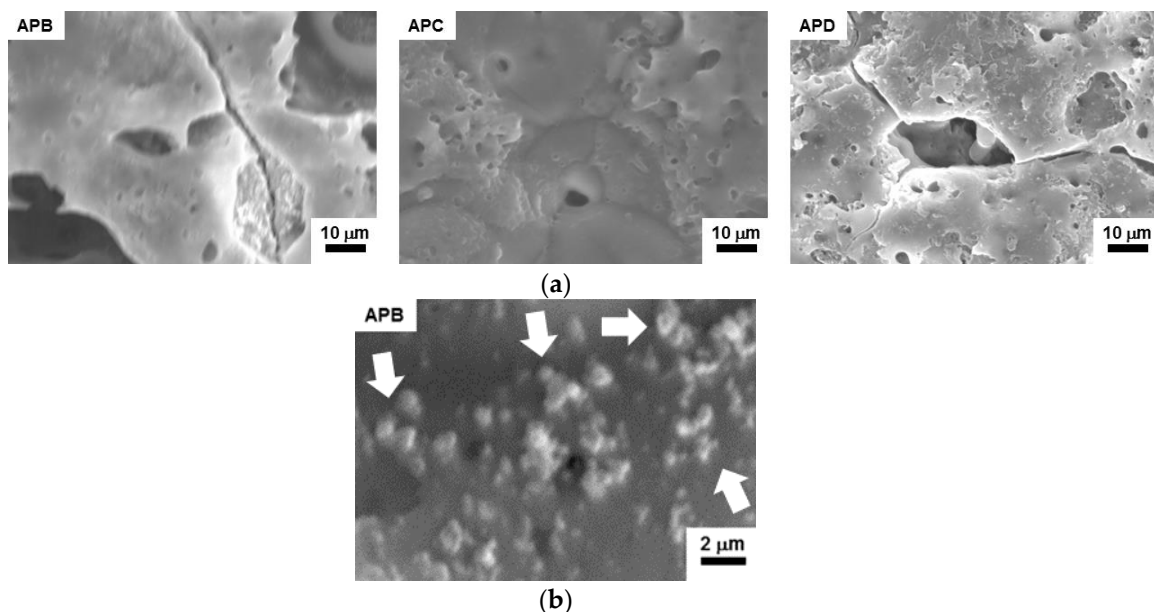


Figure 7. High magnification surface morphologies of (a) APB, APC and APD coatings on the highlighted sections in Figure 6 and (b) clusters of Si_3N_4 nanoparticles (indicated by arrows) on APB coating.

The average pore size and average porosity ratios of each sample are listed in Table 3. It is obvious that the average size of the micropores as well as the porosity ratios were lower for the coatings formed with addition of borax and without Si_3N_4 addition. The largest average pore size of $6.532\text{ }\mu\text{m}$ and the highest average porosity ratio of 19.06% are found for the APB sample, which was grown with the electrolyte without borax and with 1.5 g/L^{-1} Si_3N_4 additive. Meanwhile, the lowest average pore size of $0.662\text{ }\mu\text{m}$ and the lowest average porosity of 0.201% can be found for the APC sample under a borax contained electrolyte and without Si_3N_4 particle additive. It appears that the addition of borax into the electrolyte can generate a compact microstructure with less structural defects as shown in Figure 6 for APC sample. From the high-magnification SEM images, as depicted in Figure 7, the significant difference of surface morphologies for the three coatings can be clearly seen. The PEO coatings grown without borax (APB), grown with borax and Si_3N_4 additives (APD) exhibited severe cracking as compared to the coatings formed in electrolyte containing borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and without any Si_3N_4 additive (APC). Figure 8 describes the correlation between average pore size, duty cycle, Si_3N_4 , and borax concentrations. There is no direct correlation between duty cycle, pore size and borax contents as shown in Figure 8a,c. In Figure 8b, the pore size of the PEO coating increased with increasing Si_3N_4 concentration.

Table 3. Weight gain, layer thickness, surface roughness, average pore size, and average porosity of the PEO coatings.

Sample No.	APA	APB	APC	APD	APE	APF
Weight gain (g)	0.048	0.121	0.041	0.062	0.054	0.047
Layer thickness (μm)	7.55 ± 0.58	25.5 ± 52.02	8.10 ± 0.62	14.35 ± 1.13	10.8 ± 1.05	9.88 ± 1.01
Surface roughness (μm)	1.01 ± 0.11	4.88 ± 0.2	1.44 ± 0.13	2.2 ± 0.17	1.83 ± 0.12	1.54 ± 0.09
Average pore size (μm)	0.804	6.532	0.662	1.647	0.859	0.850
Average porosity (%)	0.229	19.057	0.201	3.888	0.769	0.717

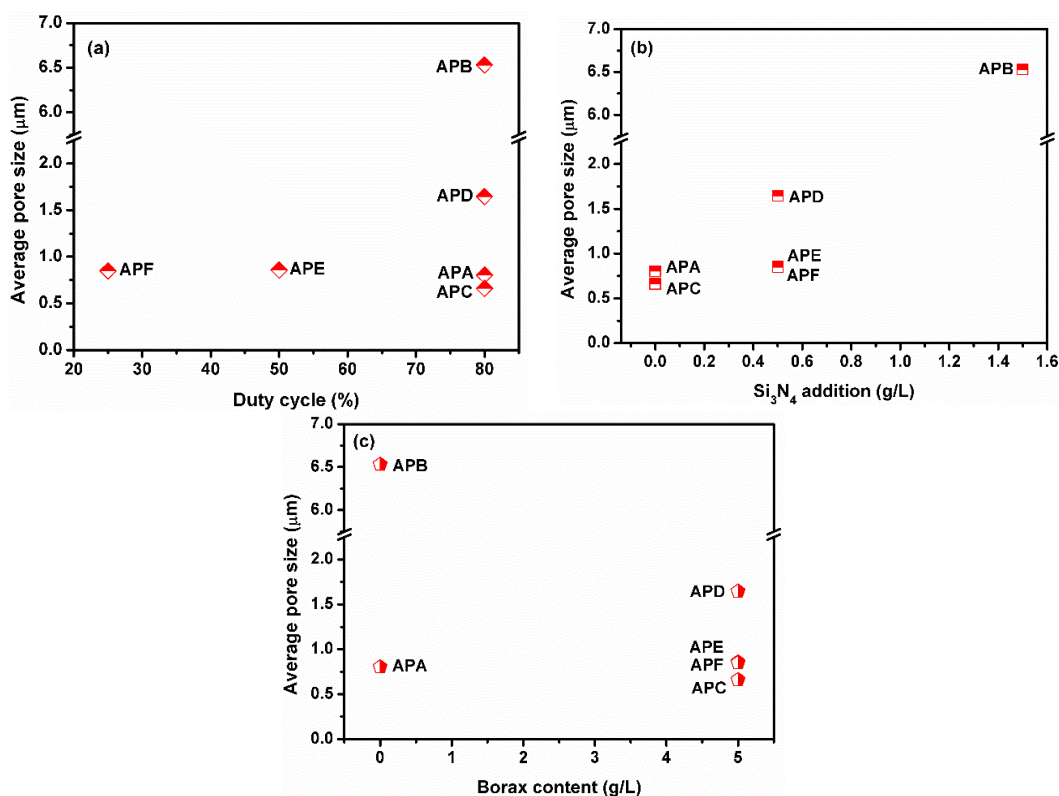


Figure 8. The correlation between average pore size and (a) duty cycle, (b) Si_3N_4 and (c) borax concentrations.

Figure 9 defines the relationships between average porosity, duty cycle, Si_3N_4 , and borax concentrations, which show very similar tendency as depicted in Figure 8. There is no direct relationship between porosity, duty cycle, and borax contents, as shown in Figure 9a,c. In Figure 9b, the porosity of the PEO coating increased with increasing Si_3N_4 concentration. According to these results shown in Figure 9 and listed in Table 3, the PEO coating grown with addition of borax and without Si_3N_4 in electrolyte exhibited a low porosity. However, the coating with a higher concentration of Si_3N_4 (APB) showed a higher porosity.

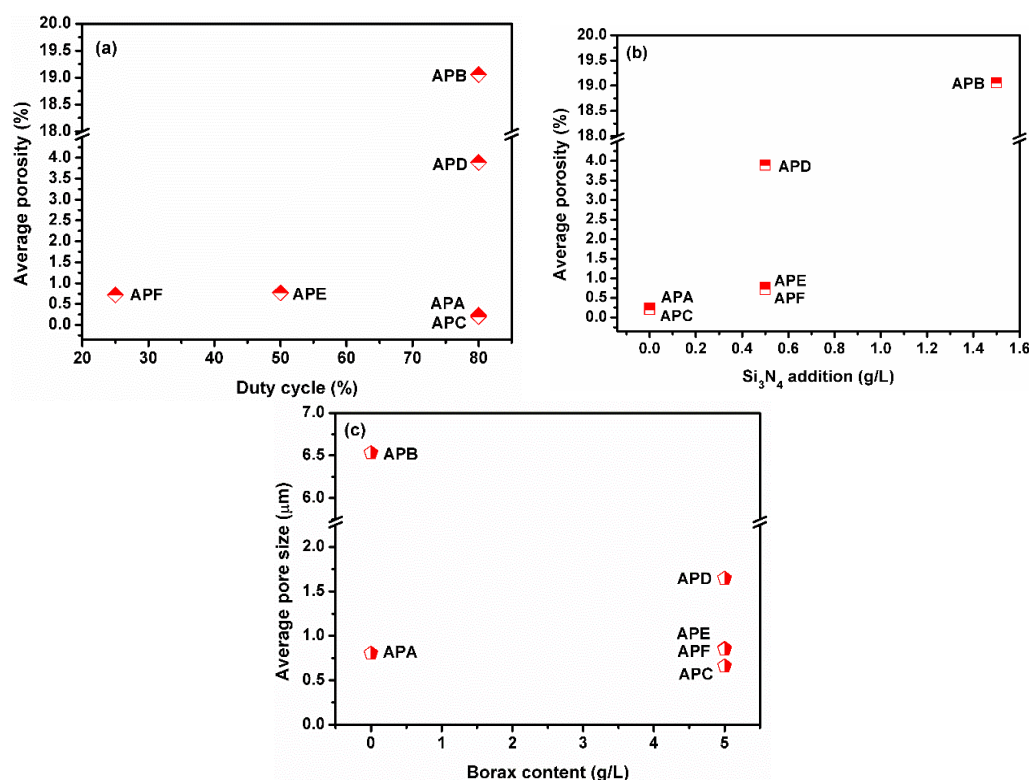


Figure 9. The relationships between porosity and (a) duty cycle, (b) Si_3N_4 and (c) borax concentrations.

The cross-sectional morphologies of all PEO coatings were illustrated in Figure 10. The oxide layer is indicated by white arrow in each coating. All PEO coatings consisting of some tiny pores and cracks were found due to the strong micro discharges across the PEO coating. The quality of PEO coating can be determined by the parameters of electrolytic concentrations [48]. The cross-sectional morphology of the APC sample shows that a relative uniform coating structure, less micro cracks and micro pores was formed on the cross-sectional morphology. A thin and non-uniform structure of oxide layer was produced on pure aluminum by the PEO electrolyte containing borax and different concentrations of Si_3N_4 nanoparticles. Most of the coatings include some large defects as well as the micro-crack networks. It is obvious that the microstructure containing pores and cracks are presented in all PEO samples. It is noticeable that some deep cracks and pores are occurred in the oxide layer of APB coating. The inner part of the APC coating is more compact than other oxide layers.

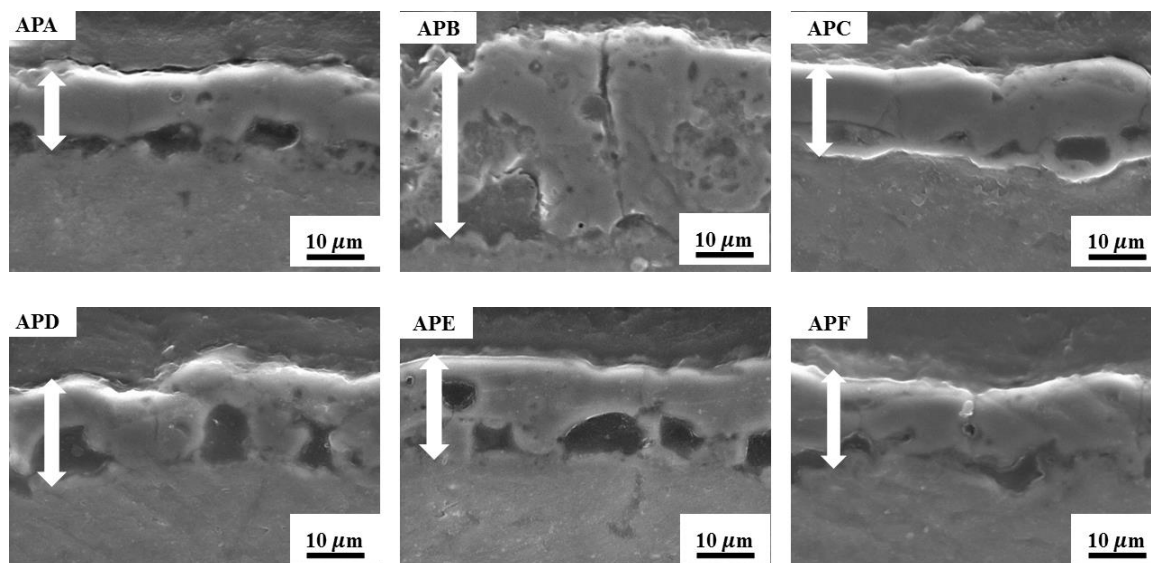


Figure 10. Cross-sectional micrographs of PEO coatings.

3.4. PEO Layer Thickness and Weight Gain

The layer thickness values of PEO coatings calculated from twenty various regions of each PEO coating are listed in Table 3. A relatively non-uniform layer thickness can be seen in this work. For the PEO coating grown at the same duty cycle (80%) with different Si_3N_4 additive concentrations, the oxide layer thickness increases with increasing Si_3N_4 concentration. For example, the PEO coating layer thickness of APB reaches $25.5 \pm 2.02 \mu\text{m}$ which contains 1.5 gL^{-1} Si_3N_4 nanoparticle additives in electrolyte. Whereas the thickness values of APA and APC are $7.55 \pm 0.58 \mu\text{m}$ and $8.10 \pm 0.62 \mu\text{m}$ respectively, which were grown under an electrolyte without Si_3N_4 . Compared to Si_3N_4 nanoparticle addition, the addition of borax has no significant influence on the PEO coating thickness [16]. The PEO oxide layer thickness increases with increasing duty cycle when the Si_3N_4 concentration in electrolyte was the same.

The weight gains of PEO coatings are shown in Table 3. Since the plasma discharge in the PEO coatings leads to the growth of adhesive oxide coating and the partial fusion of oxide film on the substrate [49], the weight of pure aluminum substrate increases due to the oxide formation of PEO coating process. Different weight gains are obtained for PEO coating using different electrolytes and process parameters. In general, the weight gains of the PEO coatings increase with increasing Si_3N_4 concentration when the duty cycle is 80%. In addition, the weight gain increases with increasing duty cycle when the Si_3N_4 concentration is the same. The weight gain of APC is the lowest than other PEO coatings when the electrolyte contains borax and without Si_3N_4 addition. The relationship between the weight gain and the layer thickness of PEO coating can be seen in Figure 11. The following equation can be used to describe the linear relationship between weight gain (Y) and layer thickness (X). The accuracy of this fitting is 95.53%.

$$Y = 0.0048X \quad (1)$$

It appears that all data points, except APA, follow this equation very well. We suggest that the fabrication of APA coating without the addition of Si_3N_4 nanoparticle and borax in electrolyte makes the relationship between weight gain and layer thickness differ from other five PEO coatings, which were grown with the addition of Si_3N_4 nanoparticle or borax in electrolyte.

The surface roughness values of all PEO coatings are presented in Table 3. The surface roughness is affected by the concentrations of Si_3N_4 nanoparticle, duty cycle and the chemistry of electrolytic solutions. In previous work, the nanoparticle additives in the PEO electrolyte solution can affect the properties of the PEO ceramic coatings [29,36,37,50,51]. Li et al. [52] reported that the surface roughness

of the PEO oxide increased with an increasing amount of Si_3N_4 nanoparticles. The surface roughness increased with increasing duty cycle from 25% to 80% when the concentration of Si_3N_4 nanoparticles was the same. In this work, the surface roughness values of APA and APC are low because of no Si_3N_4 additives in electrolyte.

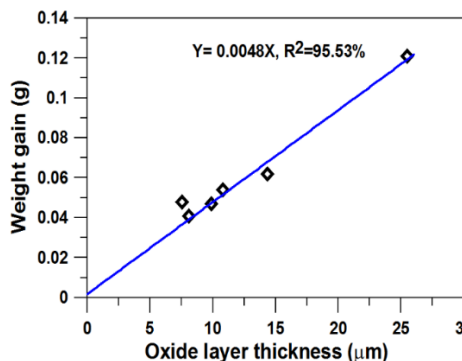


Figure 11. The relationship between the weight gain and the layer thickness of PEO coatings.

3.5. The Anti-Corrosion Performance Evaluation of PEO Coatings

3.5.1. Potentiodynamic Polarization Tests

The corrosion resistance of each PEO coating was evaluated by the potentiodynamic polarization tests in 3.5 wt.% NaCl solution as shown in Figure 12. There are signatures of stable and metastable pittings in the case of APF, APB, and APA coatings. The corrosion potential (E_{corr}), corrosion current density (I_{corr}) and polarization resistance (R_p) derived from the potentiodynamic polarization curves are summarized in Table 4. It is reported that the process parameters of PEO treating including duration time and the chemistry of electrolytes have influences on microstructure of PEO coatings and their anti-corrosion performance [14]. Meanwhile, the corrosion resistance of PEO coating depends on the coating thickness and the compactness of its microstructure [53]. However, Dehnavi and coworkers reported that the PEO layer thickness did not show any significant influence on its corrosion performance [54]. In this work, although the addition of Si_3N_4 nanoparticle in the electrolytic solution increases the thickness of the PEO coating, however, the corrosion resistance of this thick oxide coating, for example, APB, is not improved. Therefore, we can conclude that the corrosion resistance cannot be enhanced by the thicker PEO layer in this study.

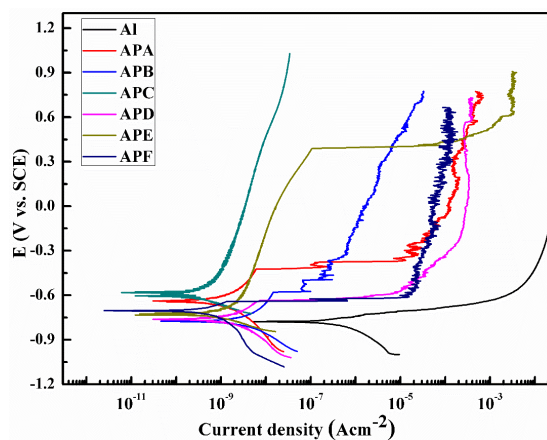


Figure 12. Potentiodynamic polarization curves of PEO coatings and pure aluminum sample.

Table 4. Corrosion properties of pure aluminum and PEO coatings.

Sample No.	Al	APA	APB	APC	APD	APE	APF
I_{corr} ($\text{A}\cdot\text{cm}^{-2}$)	4.97×10^{-7}	8.49×10^{-10}	2.70×10^{-9}	4.83×10^{-10}	1.43×10^{-9}	1.01×10^{-9}	7.17×10^{-9}
E_{corr} (V)	−0.773	−0.639	−0.775	−0.599	−0.762	−0.727	−0.706
R_p ($\Omega\cdot\text{cm}^2$)	8.15×10^3	3.07×10^7	9.66×10^6	5.40×10^7	1.83×10^7	2.60×10^7	3.64×10^7

According to the data listed in Table 4, the PEO coating grown in the electrolyte containing borax ($\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$) and without Si_3N_4 nanoparticle additive has the highest corrosion resistance in the present work. Gu et al. [55] reported that the PEO layer grown on Mg with borate and NaAlO_2 contained electrolytes had improved corrosion resistance. Apparently, the electrolytic compositions play a great role on the anticorrosion performance of PEO coating [56–58]. Therefore, in this work, the borax ($\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$) additive can greatly improve the corrosion resistance of the pure aluminum due to the formation of a more compact oxide layer with efficiently reduced cracking and less porosity [16,22,59–61]. It is suggested that the addition of borax in the electrolyte can produce a compact microstructure and a less defective structure. The addition of borax causes intensive and fixed spark discharge. In addition, increasing the concentration of borax can continuously decrease the spark number [62].

For the APC sample, the highest corrosion potential of −0.599 V and the lowest corrosion current density of $4.83 \times 10^{-10} \text{ A cm}^{-2}$ are obtained due to its less average pore size, less cracks and relatively dense surface microstructure. For the APC coating, the growth of oxide layer can reduce the I_{corr} from $4.97 \times 10^{-7} \text{ A cm}^{-2}$ of pure Al to $4.83 \times 10^{-10} \text{ A cm}^{-2}$, which is about 1028 times lower as compared with that of pure aluminum. The PEO coating on the pure aluminum substrate in this work has a better corrosion resistance than that reported in different studies. The comparison of corrosion resistance for PEO coatings on pure aluminum and alloys are shown in Table 5. We can observe that the corrosion resistance of PEO coating is not improved by the addition of Si_3N_4 nanoparticle in this work. Similarly, Lu and coworkers [37] also reported that the addition of Si_3N_4 did not make a dense and thick PEO coatings due to initiating of pores on the oxide surface by the collapsed plasma bubbles.

Table 5. Comparison of corrosion resistance for PEO coatings on pure aluminum and alloys substrate in literature [63–66].

Substrate	Electrolyte	NaCl Solution	I_{corr} ($\text{A}\cdot\text{cm}^{-2}$)	E_{corr} (V)	Ref.
Al-Mg-Si alloy	alkaline-phosphate-based electrolytes and Na_3AlF_6	3.5 wt %	9.40×10^9	−0.659	[63]
pure aluminum	NaOH , Na_2SiO_3 and $(\text{NaPO}_3)_6$		4.32×10^{-9}	−1.390	[64]
7050 Al	Sodium hexametaphosphate, Sodium silicate, Sodium tungstate and Sulfuric acid		2.10×10^{-10}	−0.665	[65]
LY12 aluminum alloy	NaAlO_2 and with and without NaF		0.88×10^{-7}	−0.602	[66]

The relationships between the corrosion current density, duty cycle, Si_3N_4 , and borax concentration are demonstrated in Figure 13. In Figure 13a, The PEO coating grown using 25% duty cycle has the highest corrosion current density. According to Figure 13b,c, the PEO coatings grown in the electrolyte without Si_3N_4 nanoparticle and with more concentrations of borax exhibit lower corrosion current density.

The surface morphologies of PEO coatings after potentiodynamic polarization tests are shown in Figure 14. Delamination and cracking of PEO oxide layer can be seen for each sample, which are indicated with white arrows. However, the spallation region and the length of the cracks are different. It can be clearly seen that the APC coating has a relatively lower spallation appearance than other samples. Meanwhile, large corrosion pits and the delamination of PEO layers can be seen in the APB coating.

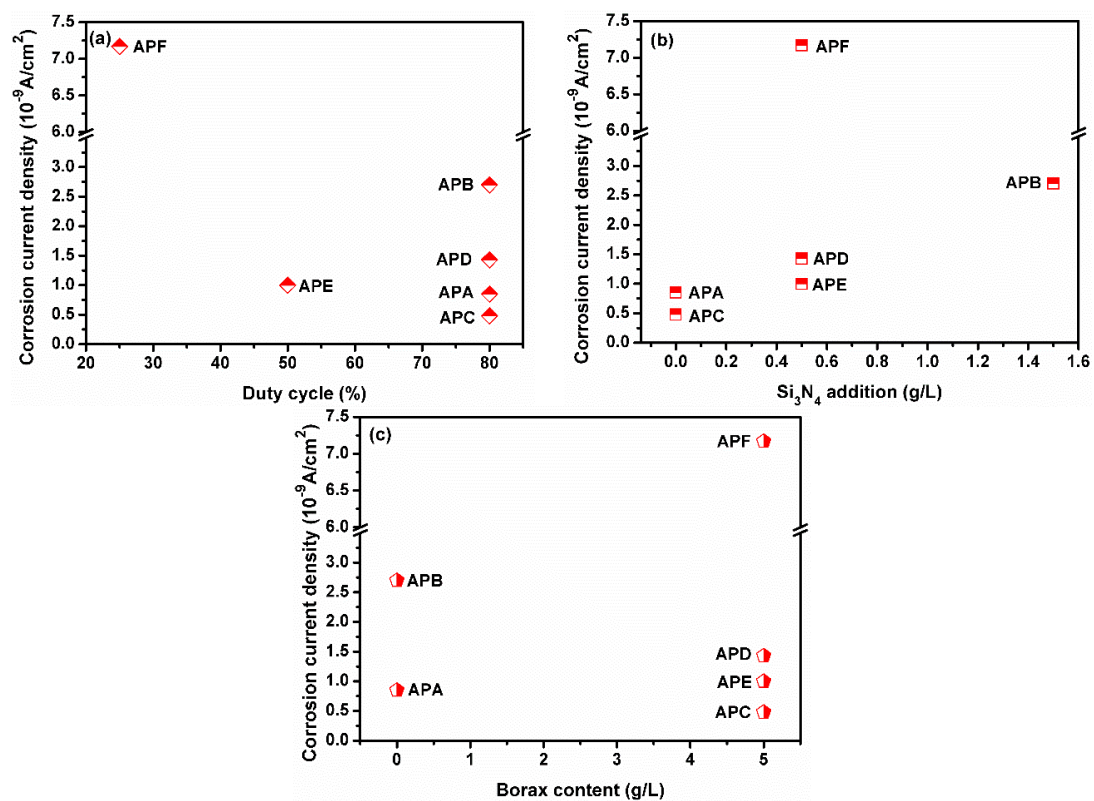


Figure 13. The relationships between corrosion current density and (a) duty cycle, (b) Si_3N_4 and (c) borax concentrations.

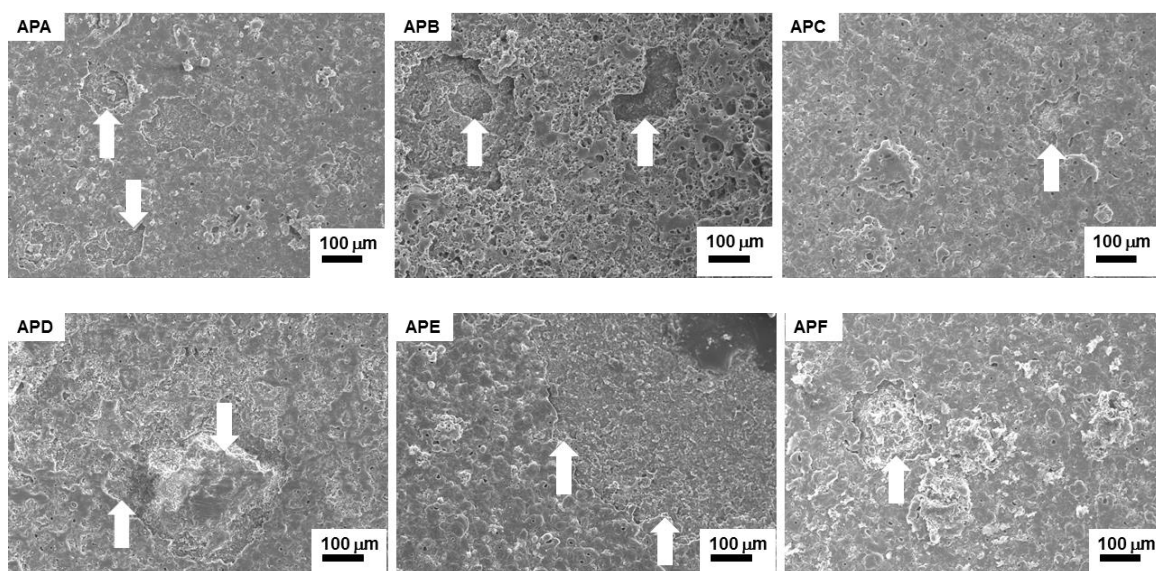


Figure 14. The surface morphologies of PEO coatings after potentiodynamic polarization test.

3.5.2. Electrochemical Impedance Spectroscopy (EIS) Test

According to the results of the potentiodynamic polarization test, the coating grown in the electrolyte containing borax and without Si_3N_4 nanoparticle additive shows the best corrosion resistance. Then, in the following study, the anti-corrosion performance of each coating is further investigated by EIS test. The Nyquist and Bode plots for uncoated pure aluminum and PEO coatings are shown in Figure 15. The equivalent electrical circuits for modeling the experimental EIS data

of pure Al substrate and PEO coatings are presented in Figure 16a,b, respectively. The EIS fitting parameters, i.e., resistance, capacitance, corrosion reaction, diffusion reaction and electrolyte interface, etc., of all coatings were obtained from the equivalent electrical circuits [67–69]. In this equivalent electrical circuit model of pure Al, R_1 is the electrolyte resistance, R_2 is the resistance due to the oxide formation on the surface. Q_1 is the non-ideal capacitor, i. e, a surface morphology with defects at the interface. On the other hand, for the PEO coatings, R_2 is the resistance of corrosive media in the pores and defects of PEO layer and paralleled with a constant phase element (CPE_1, Q_1), R_3 is the resistance of PEO layer with a parallel constant phase element (CPE_2, Q_2), and R_4 is the resistance of the interlayer between PEO layer and substrate paralleled with a constant phase element (CPE_2, Q_3). A Warburg impedance related to the diffusion process is also connected with R_4 , which is related to the microstructure of PEO coatings for representing semi-infinite length diffusion and has higher influence at lower frequency [70]. The fitted results of all sample were also plotted in Figure 15, which show a very good match to the experimental data points. Based on the proposed equivalent electrical circuit model, the corresponding values of parameters are listed in Table 6.

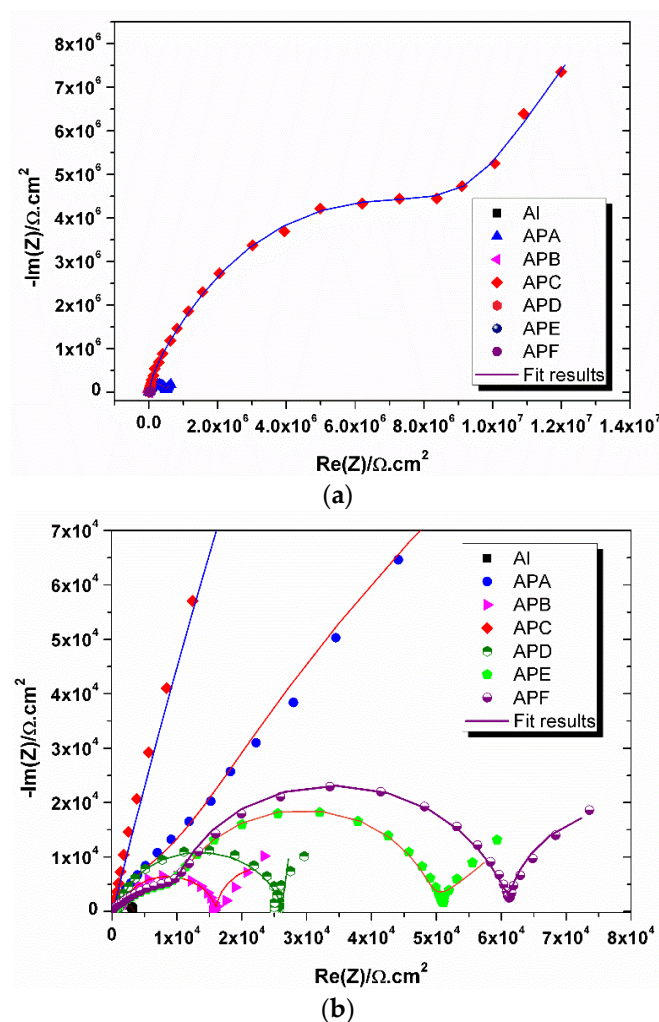


Figure 15. Cont.

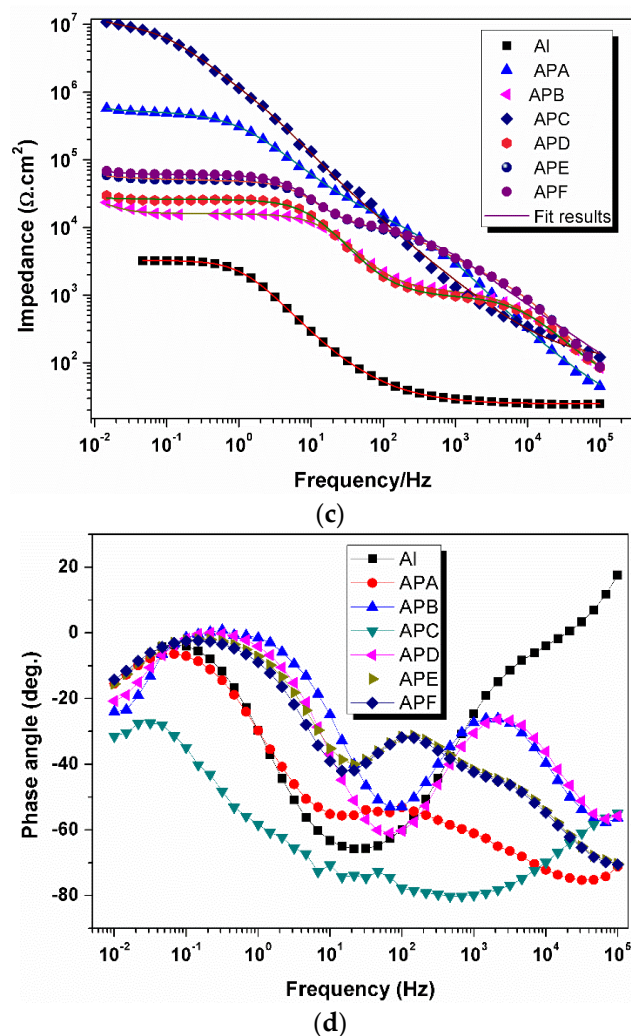


Figure 15. Nyquist plots of (a) PEO coatings and uncoated pure aluminum for 6 h immersion time, (b) the enlarged plots of the lower left region in Figure (a), and the (c) Bode modulus and (d) Bode phase plots of PEO coatings and uncoated pure aluminum.

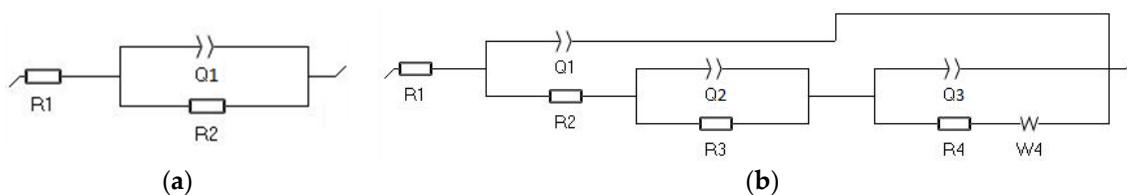


Figure 16. Corresponding equivalent electrical circuits for fitting the impedance data of (a) uncoated pure aluminum and (b) PEO coatings.

To better describe the interfacial heterogeneities of the coatings, the more general constant phase element (CPE) is used instead of a rigid capacitive element. The CPE is defined by the following equation: [69]

$$Z_{CPE} = 1/[Y(j\omega)^n] \quad (2)$$

where j is the imaginary unit, ω is the angular frequency, and n and Y are the CPE parameters. The n values are ranging from 0 to 1. For $n = 0$, the CPE describes an ideal resistor, and for $n = 1$, the CPE describes an ideal capacitor. We can confirm that in the formation of PEO coating, the addition of borax without Si_3N_4 nanoparticle to the electrolyte can improve the corrosion properties by significantly

decreasing the value of average porosity. These results are consistent with the microstructure analysis results depicted in Figure 6 and the average porosity analysis in Table 3.

Table 6. EIS fitting parameters of all PEO coatings and Al substrate obtained from the equivalent electrical circuits.

Parameter	Al	APA	APB	APC	APD	APE	APF
R1 ($\Omega\cdot\text{cm}^2$)	25.36	20.96	28.87	29.3	28.83	30.92	29.66
Q1 ($\text{S}\cdot\text{s}^{n1}$)	5.13×10^{-5}	8.31×10^{-8}	1.3×10^{-7}	6.45×10^{-8}	1.22×10^{-7}	1.77×10^{-8}	0.22×10^{-6}
n1	0.839	0.85	0.81	0.87	0.82	0.80	0.72
R2 ($\Omega\cdot\text{cm}^2$)	3.40×10^3	2.02×10^4	1.42×10^3	3.26×10^6	1.54×10^3	2.18×10^3	1.01×10^4
Q2 ($\text{S}\cdot\text{s}^{n2}$)	–	6.51×10^{-6}	8.76×10^{-4}	8.98×10^{-9}	7.01×10^{-7}	5.03×10^{-8}	0.76×10^{-6}
n2	–	0.90	1.00	0.77	0.92	0.80	0.82
R3 ($\Omega\cdot\text{cm}^2$)	–	4.38×10^5	1.72×10^4	7.49×10^6	2.51×10^4	2.97×10^4	4.25×10^4
Q3 ($\text{S}\cdot\text{s}^{n3}$)	–	0.32×10^{-6}	7.93×10^{-7}	1.56×10^{-6}	9.49×10^{-4}	5.83×10^{-7}	0.49×10^{-3}
n3	–	0.74	0.91	0.89	0.93	0.80	0.80
R4 ($\Omega\cdot\text{cm}^2$)	–	5.05×10^5	1.49×10^4	2.85×10^7	2.70×10^4	3.66×10^4	1.42×10^5
W ($\Omega\cdot\text{s}^{-1/2}$)	–	1.09	1.05×10^{-8}	2.23×10^5	9.39×10^{-7}	0.26×10^{-4}	6.78×10^{-6}

The corrosion resistance of the PEO coating samples can be quantitatively compared from the EIS spectra, where larger semicircles commonly show a higher corrosion resistance. The smallest semicircles can be observed in the EIS spectrum of the pure aluminum, suggesting that the corrosion resistance of the pure aluminum in 3.5 wt.% NaCl solution is the poorest one. The larger sizes of semicircles for the PEO coatings indicate the obvious corrosion resistance improvement of pure Al substrate by the oxide layer formation. In addition, the PEO coating grown in the electrolyte containing borax and without Si_3N_4 nanoparticle additive exhibits the largest capacitive loop of all, implying the excellent anticorrosion properties of this coating, which is in good agreement with the potentiodynamic polarization results shown in Figure 12.

According to the EIS data for all coatings and untreated Al, as listed in Table 6, the R_1 , R_3 , or R_4 value increases from $3.40 \times 10^3 \Omega\text{ cm}^2$ for untreated pure Al substrate to $2.85 \times 10^7 \Omega\text{ cm}^2$ for APC. When the PEO coating with Si_3N_4 , the R_3 value of PEO coating increases with decreasing duty cycle. The PEO coating grown with borax addition and without Si_3N_4 nanoparticle, an increase of R_4 value up to 8382 times higher comparing to Al substrate can be obtained in this work. The coatings which created by the addition of Si_3N_4 and borax exhibited different EIS result and the changes mainly considered by the low frequency (LF) range of bold plots (Figure 15c,d). The difference between the bold plots of coatings in the range of LF explains that the variation in corrosion performance. The main difference in corrosion resistance is the nature of the inner barrier layer, from the figure represented in bold plot illustrating that APC has better corrosion resistance in the LF range.

4. Conclusions

The plasma electrolytic oxidation (PEO) treatment on the pure aluminum substrates using electrolytes with different Si_3N_4 nanoparticle, different borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) (0 and 5 g L^{-1}) and different duty cycles were studied in this work. The $\gamma\text{-Al}_2\text{O}_3$ was the primary phase for all PEO coatings. The breakdown voltage of the PEO coatings increased with decreasing duty cycle. The PEO coatings with borax addition in electrolyte had higher breakdown voltage than these coatings without borax. The sum of Al and O contents increased with decreasing Si_3N_4 concentration in electrolyte. Lower value of sum of Al and O contents was obtained for the coating grown in the electrolyte containing higher Si_3N_4 nanoparticle concentrations. A linear relationship can be found between the layer thickness and weight gain of the PEO layers grown with the addition of Si_3N_4 nanoparticle or borax in electrolyte. The pore size and porosity of the PEO coating increased with increasing Si_3N_4 concentration. The addition of borax in the electrolyte reduced the pore size and porosity of PEO

coatings. The PEO coatings without Si_3N_4 addition in electrolyte had lower pore size and porosity values. We can conclude that the addition of borax can significantly improve the corrosion resistance of the pure aluminum due to the formation of a more compact and less defective oxide layer. Although the addition of Si_3N_4 nanoparticle in the electrolytic solution increased the thickness of the oxide layer, no significant enhancement of the densification of microstructure of PEO coating was obtained, possibly due to the initiation of pores on the surface.

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