Original Article

Effect of duty cycle and treatment time on electrolytic plasma oxidation of commercially pure Al samples

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ABSTRACT

Plasma electrolytic oxidation (PEO) is an environmentally friendly anodizing technique that produces ceramic coatings using high voltage discharges. To the present work this technique was applied to treat aluminum surfaces using a pulsed current supply and sodium silicate electrolyte. The effect of the duty cycle and treatment time on the morphology, phase composition and tribomechanical properties of the formed layer was investigated. The current density was maintained at 12 A/dm², with two different duty cycles, 30% and 50%, for total period of 100 µs. For each duty cycle two different treatment times (2 min and 12 min) was used. During each treatment, the voltage was monitored to determine the start of the rupture of the passive oxide layer. It was demonstrated that the increase in the duty cycle from 30% to 50% influenced the thickness and porosity of the film, verified by scanning electron microscopy (SEM) images. Phase γ-Al₂O₃ was predominant on the surface of the samples treated by PEO, although occurrence of mullite and α-Al₂O₃ were also observed. There was an inversion in the intensities of the diffraction peaks Al (200) and Al (111) after the formation of the oxide phase, suggesting a preferential oxidation in the Al (111) direction. The PEO process allows tuning of the hardness, yield strength and wear resistance by controlling film thickness, porosity and phases present.

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1. Introduction

PEO is a technique that leads to the formation of ceramic coating on surfaces of metals such as aluminum, magnesium, titanium and its alloys [1]. Several studies report improvements with respect to the increase in surface hardness, wear resistance and surface corrosion of these PEO coated metals [2–12]. The principle of the technique is based on applying a high voltage in the range of 400–700 V, capable of creating micro-arcs discharges on the metal surface immersed in an electrolytic bath. These plasma discharges are responsible for the localized melting of the metal and subsequent oxidation, solidification and deposition of the oxide [13]. Therefore, they play a fundamental role in the phase composition, structure and morphology of the coating [14]. The process is more environment-friendly than conventional anodization because it uses low concentration electrolytes and is free of heavy metals like Cr, Ni and V [11,15]. The mechanism of the film growth is sensitive to changes in the treatment time and the electrical parameters such as the type of current used in the system, current density and duty cycle [15]. Akbar et al. [16] have investigated the influence of frequency and duty cycle on PEO coatings. By varying these electrical parameters, they found that it is possible to modify the microstructure, morphology and growth rate of the coatings. Chen et al. [17] studied the effect of the duty cycle and treatment time on the characteristics of a PEO coating on a magnesium alloy. They obtained porous surfaces and found that the number of pores decreases as their size increases with increasing treatment time. In addition, the increase in duty cycle from 10% to 50% resulted in thinner and less porous layer which provided better corrosion resistance. Considerable research effort has focused on understanding the influence of the PEO processing parameters in modifying surfaces of aluminum and its alloys, in order to extend their lifespan [18–21]. However, Yang et al. [18], studying PEO in an aluminum alloy 7570, observed that some alloying elements present in the alloy participated in the mechanism of the oxide layer formation, making it difficult to analyze the influence of the electric variables on the process. The present study used commercially pure aluminum (Al-1050) as an anode to investigate the influence of the processing variables on the characteristics of PEO-produced oxide layers. The effect of the duty cycle and treatment time on the microstructure and tribomechanical properties of the oxide layer were investigated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duty cycle (%)</th>
<th>Current density (A/cm²)</th>
<th>Treatment time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Al30/2</td>
<td>30</td>
<td>12</td>
<td>2</td>
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<tr>
<td>Al30/12</td>
<td>30</td>
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<tr>
<td>Al50/2</td>
<td>50</td>
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<tr>
<td>Al50/12</td>
<td>50</td>
<td>12</td>
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2. Materials and methods

2.1. Sample preparation

Commercial-purity aluminum Al-1050 disks (99.5% Al), dimensions 30 mm × 3 mm (diameter × thickness), electrically connected by copper wire on one side, were embedded with resin and prepared metallographically with final polishing of alumina 0.05 μm. These samples were washed with enzymatic detergent solution in ultrasonic vibration for 10 min. Finally, the surfaces were dried with the aid of a thermal blower.

2.2. PEO treatments

PEO was performed using an experimental apparatus as depicted schematically in Fig. 1A. An electrolytic solution of 2 g/L Na2SiO3 was prepared in a 500 mL becker. In addition, Fig. 1B shows the experimental apparatus used in the treatment, where it is possible to observe the action of the electrolytic plasma on the surface of the sample. Plasma comes in the form of small micro-discharges (or micro-arcs), which are visible to the naked eye, but difficult to capture for chemical and physical analysis due to the speed at which it occurs and cease, making it an obstacle to its study and generating different theories about its formation, as outlined by Hussein and Northwood [22].

It was used as the cathode a stainless-steel plate of 50 mm × 50 mm and the sample as the anode. Between the two electrodes pulsed current were applied using two different duty cycles, 30% (Ton = 30 μs; Toff = 70 μs) e 50% (Ton = 50 μs; Toff = 50 μs) and treatment time of 2 min and 12 min (Table 1). The solution was agitated by a stirrer with rotation of 60 rpm, for homogenization and thus to avoid loss of conductivity of the medium.

![Fig. 1 – Experimental apparatus used in the PEO process. (A) Schematic drawing and (B) photograph illustrating micro-arcs on the aluminum sample during the electrolytic plasma oxidation process.](image-url)
2.3. Surfaces characterization

The size, number and pore distribution of the oxidized surfaces were determined from scanning electron microscopy images (SEM, VEGA3, Tescan) with the aid of image processing software ImageJ. The thicknesses of the oxidized layers were determined by the oxygen composition profile, obtained by electron dispersive energy spectroscopy (EDS), transversally to the layer. The crystalline phases of the coatings were investigated by X-ray diffraction (XRD 6000, Shimadzu) using Bragg-Brentano and Seeman-Bohlin geometry. The mechanical behavior of the PEO layers was evaluated by using a nanoindenter UNAT, ASMEC. Indentations with a Berkovich pyramidal tip were performed in 20 different positions on the surface of the coating, with a maximum load of 300 mN. Depth-dependent hardness and elastic modulus were evaluated through the QCSM (Quasi Continuous Stiffness Measurement) method [15]. Load-penetration depth curves obtained with this test allowed to measure the elastic moduli of the surfaces. Wear test was performed using free ball micro-abrasion tester CSM Calowear, where a 25.4 mm diameter ball was pressed against the surface of the samples with a load of 0.2 N, rotating at 150 rpm. An abrasive suspension of silicon carbide (~4 µm particle size) at a concentration of 750 g/L in distilled water was applied. The test was performed for four different runner radii, corresponding to different numbers of ball turns (200, 400, 600, 800), respectively. The wear crater diameters were measured by light microscopy. From this data, the sliding distance (L) and the wear rate (k) were calculated, using Eqs. (1) and (2) respectively:

\[ L = n_c\pi D_c \]  
\[ k = \frac{\pi \left( \frac{M_v}{n} \right)^{\frac{4}{3}}}{32L^{\frac{2}{3}}F D_c^{\frac{4}{3}}} \]  

where \( n_c \) is the number of turns of the sphere; \( D_c \) is the diameter of the sphere; \( M_v \) is the average value of the wear crater and \( F \) is the normal load applied by the sphere.

3. Results and discussion

Fig. 2 shows the voltage-time curve during a PEO coating process for the two duty cycles studied. In both curves, a rapid increase in voltage can be observed at the initial instants of the process, until they reach critical values (between 500 and 550 V), followed by a plateau. According to Dehnavi et al. [3], the initial stage, called stage 1, is responsible for the formation of a passive layer, where the voltage reaches its critical value corresponding to the point at which the dielectric rupture of the oxide occurs. After this, the process reaches stage 2 (see detail), where the first micro-discharges are observed throughout the material’s surface. This behavior, typically seen in atmospheric plasmas, is also fundamental for the formation of the films. A third stage is still observed, where the micro-discharges are more intense and spaced, due to the larger dielectric barrier of the film, already thicker and more compact.

As expected, the second stage for the process with the highest duty cycle (50%) was reached faster (40 s) than the process with the shortest duty cycle, (30%) Al30/2 and Al30/12, which reached the second stage only after 55 s. Despite, the third step was achieved earlier for samples with lower duty cycle. This stage starts between 150 and 240 s of treatment to 30% and 50% respectively (Fig. 2), i.e. the samples Al30/2 and Al50/2 did not complete this stage because they were treated for 120 s. Characteristics of the formed oxide film can be influenced by this parameter. By comparing the micrographs of samples treated for 12 min (Fig. 3C and E) with untreated samples (Fig. 3A), the presence of pores, roughness, cracks and pancake-like structures can be observed. Note that cracks and pancake-like structures do not appear on samples treated for 2 min (Fig. 3B and D). Dehnavi [14] suggested that pores arise due to gases dissolved in the liquid metal that are trapped after solidification. Chen et al. [17], studying oxidation of magnesium alloys, claimed that the pores are traces of the discharge channels through which the molten material are produced and then expelled to the surface of the coating.

According to Hussein and Northwood [22], pancake-like structures are typical of PEO coatings, where a large pore is found in the center of each pancake. Pores act as discharge channels, through which metal from the coating-substrate interface is ejected, melted due to the high plasma temperature, and rapidly solidified in contact with the electrolyte, leaving distinct contours that define each pancake. In the micro-discharge regions, the temperature is high enough to melt the metal and metal oxide. Besides that, there is high pressure and local evaporation of the electrolyte. Under these conditions a high stress state is generated, which eventually relieves with the appearance of microcracks [10]. It is therefore evident that such structures are characteristic of those surfaces which have undergone stage 3 of the process. The more intense the local micro-discharges were, the higher temperatures and states of tension were, also giving rise to microcracks. These topographical features can be quantified by the layer thickness, pore size and distribution (Fig. 4).

It was found that the pore size was not influenced by the duty cycle when the treatment time was kept constant, whereas the layer thickness and the porosity were directly
proportional and inversely proportional to it, respectively. On
the other hand, thickness, pore size and porosity were directly
proportional to the treatment time. Larger duty cycles will
produce higher amounts of molten material that will spread
over the surface; since it comes from the interior of the oxide
layer, the fused metal or oxide can close pores, thus justifying
the lower porosity. Egorkin et al. [23] studied the effect
of the duty cycle produced by pulsed PEO on an aluminum alloy.
They observed that the increase in the duty cycle from 12% to
21% led to a reduction in the porosity of the oxide films. The
effect of the treatment time was discussed by Erfanifar et al.
[24]. According to these authors, when the treatment is pro-
longed, the tendency is that the oxide film becomes thicker
and compact, with increased dielectric strength. Therefore,
higher voltages should be observed for processes with longer
duration. X-ray diffraction analyzes using Bragg-Brentano
govern geometry and grazing incidence of 7° (Seeman-Bohlin geom-
try) are shown in Fig. 5. In diffractograms with Bragg-Brentano
geometry (Fig. 5A), as expected, the peaks related to the

Fig. 3 – SEM micrographs of the (A) untreated aluminum surface, and those after the PEO treatment: (B) Al30/2; (C) Al30/12;
(D) Al50/2; (E) Al50/12.

Fig. 4 – Surface topographic aspects of the PEO treated
samples: layer thickness, pore size and porosity.

Fig. 5 – X-ray diffractograms of the untreated aluminum
surface, and those treated under conditions Al30/2;
A130/12; Al50/2 and Al50/12, (A) using Bragg-Bretano
geometry and (B) using Seeman-Bohlin geometry under 7
degrees grazing incidence. M = mullite; \( \gamma = \gamma-Al_2O_3 \);
\( \alpha = \alpha-Al_2O_3 \).
aluminum phase were much more intense than those ascribed to the oxides. Two peaks of the oxide phase should be highlighted in this diffractogram, namely: $\alpha$-Al (113) and mullite. Considering that solidification should be rapid in the process, it was expected that $\alpha$-Al$_2$O$_3$ (113) disclosed low crystallinity; however, it was not the case, since this phase presented sharp peaks in the diffractograms. Displacement of the peak from 42.58$^\circ$ (present on the untreated surface) to 42.68$^\circ$ was observed, as the duty cycle was reduced and/or treatment time increased. In addition, the peak intensity was reduced in that same order. Regarding mullite, this phase peaks were more intense for the condition (Al30/2), while the less intense peak was the one corresponding to the longest duty cycle and treatment duration. Therefore, the presence of this phase is associated with low energy plasmas. These phases were also observed in PEO films reported by other authors [25–29]; they asserted that these phases were more amorphous near the surface of the coatings. Looking at the diffractograms obtained with 7$^\circ$ grazing incidence (Fig. 5B), it is possible to observe that these peaks practically disappeared or became broadened, featuring an amorphous structure.

Based on the JCPDS card no. 4-0787, the Al (200)/Al (111) intensity ratio is 47%. An interesting fact observed in our result is the inversion of this relative intensity, in which the peak Al (200) is higher than the Al (111), excepted only for the Al50/2 condition (Fig. 5B). This result suggests preferential oxidation in the Al (111) direction. By further exploring these results, one can estimate the thickness of the oxide film through the ratio $\gamma$-Al$_2$O$_3$ (400)/Al (200). The observed result is consistent with that observed by electron microscopy (Fig. 4), except for the Al50/12 condition that was smaller than the film thickness produced in the Al30/12 condition. This apparent inconsistency may be explained by the higher film density, corroborated by the hardness results (Fig. 6A). All the PEO treated surfaces revealed superior hardness values than the polished aluminum surface. This increase is mainly due to the $\gamma$ phase aluminum oxide layer. The treatment time (2 or 12 min) was more decisive for the surface hardening than the duty cycle employed. The condition Al30/12 presented the higher hardness value of 2.57 GPa, followed by the Al50/12, with 2.3 GPa. This result can be justified not only by the greater amount of gamma phase observed, but also can be attributed to the presence of mullite, which was higher on these surfaces. However, all hardness values of Fig. 6A are lower than those presented by a dense Al$_2$O$_3$ ceramic bulk, of about 20 GPa [6]. The reason is the typical porous morphology of PEO layers, as shown in Fig. 3. Under an increasing load $P$, the indenter smashes pores, leading to deeper penetration depths $h_c$ than it would be possible in a nonporous material. Cracks nucleated during the tip incursion also contribute to the loss of bearing strength. As a result, the contact projected area $A_c$ is overestimated, since $A_c = 24.5h_c^2$ for Berkovich tips, whereas hardness $H$ is underestimated ($H = P/A_c$). In addition, this low hardness value, compared to the hardness values of the alpha, gamma and mullite phases (approximately 26 GPa, 17 GPa and 10.5 GPa, respectively [13]) confirms the presence of aluminum in the superficial part of the oxidized layer, as identified in the XRD. The influence of artifacts on indentation results obtained in PEO layers were discussed in detail elsewhere [30].

Other differences among the studied surfaces were inferred from indentation tests, as shown in the loading curves of Fig. 6B. The elastic behavior of the surface give insights for the wear resistance, since abrasion involves both plastic and elastic deformations of the surfaces in contact [31]. While the elastic recovery for the untreated sample was approximately 10%, on the oxide-coated surface it reached values ranging from 15% to 39%, as demonstrated by samples Al30/2 and Al50/12, respectively. Abrasive wear was examined from the results obtained in a calotester. The results showed that the values of the wear rate ($k$) of the samples treated by PEO were lower than those of the untreated surface (Fig. 7). The sample Al50/2, with higher duty cycle and shorter treatment time, presented the lowest $k$ ($3.3 \times 10^{-12}$ m$^2$/N). Although this surface did not show the highest hardness and elastic recovery values, it presented the smallest values of pore size and porosity (Fig. 4), being the most compact of all. Moreover, this.

![Fig. 6](image1.png)  
**Fig. 6** – (A) Hardness values measured at $\sim$3 $\mu$m depth, still inside the oxide coating and (B) average loading curves of the reference (polished) aluminum surface and those PEO treated at the indicated conditions.
surface still presented an intermediate hardness value among the samples. The combination of these characteristics resulted in greater wear resistance. It is also worth noting that the samples treated for the longest time showed microcracks, which can reduce their resistance to wear. It is noteworthy that in the present work the commercial aluminum is being studied in its pure form, unlike the other works of the literature that use aluminum with alloying elements. Then, of course, no significant improvement in hardness and wear resistance was expected. Li and Di [26] studied the influence of pulse width, \( t_{on} \), on a pulsed bipolar PEO process on the tribological characteristics of coatings in 2024-T4 aluminum alloys. They observed that the increase in pulse width resulted in lower wear resistance of the coating and attributed this result to the greater amount of microcracks and porosity obtained with the larger \( t_{on} \).

4. Conclusions

Commercially pure aluminum samples were treated by PEO using two duty cycle values (30% and 50%) and treatment times (2 min and 12 min). Influence of these parameters on the microstructure, crystalline phases and tribo-mechanical characteristics were investigated. From the obtained results it can be concluded that:

The pancake-like structure was observed only to the longest treatment time, where the third plateau of more intense micro-discharges occurred. The layer thickness is directly proportional to the duty cycle, the reverse happens for porosity. The pore size was not influenced by this parameter.

The oxides present on the surface treated were predominantly \( \gamma \)-Al\(_2\)O\(_3\). However, mullite peaks and \( \alpha \)-Al\(_2\)O\(_3\) were observed, mainly in the low plasma energy condition. Al\(_{200}\)/Al\(_{111}\) ratio was inverted to treated surfaces, suggesting preferential oxidation in the Al\(_{111}\) direction of the oxide film.

Hardness of the commercially pure aluminum surface increased for all the treatment conditions. The highest value was 2.57 GPa for the Al30/12 sample, representing approximately 83% increase in the substrate hardness (1.4 GPa). Elastic recoveries improved as well, increasing from 9% to \( \sim \)30% after PEO.

Samples with the longest working cycle and the shortest treatment time were those with the highest wear resistance. This result was attributed to having smaller pores and the lower porosity among the studied samples, besides not presenting microcracks, which contributed positively to the surface wear properties.

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REFERENCES


