Growth of PEO ceramic coatings on AA 2024-T3 aluminium alloy

S Forero Sotomonte1, C Blanco Pinzon2 and S García Vergara1
1 Universidad Industrial de Santander, Bucaramanga, Colombia.
2 Instituto Colombiano del Petróleo (ICP), Piedecuesta, Colombia.

E-mail: sagarver@uis.edu.co

Abstract. The growth of PEO ceramic coatings on AA 2024-T3 aluminium alloy in an aqueous Na2SiO3 (10.5g/l), KOH (2.8g/l) solution at 310 and 400V for 500 and 710s, was investigated. The morphology, roughness and thickness of the coatings were determined by SEM, digital microscopy, XRD diffraction analysis and thickness measuring instrument. The results show that thicker coatings are produced with longer process times and high applied voltages. Due to the nature of the PEO process, the roughness of the surface coatings increases as the coating become thicker, due to the development of sparks. The coatings are porous, with a crater like morphology and they are mainly amorphous.

1. Introduction
Aluminium alloys are widely used in aerospace and automotive industry due to their excellent properties such as high strength, low density, non-magnetic properties and good formability [1,2]. However, the corrosion performance of these alloys is low due to presence of alloying elements like copper. Plasma Electrolytic Oxidation (PEO), a relatively new surface modification technique, can be used to provide the corrosion resistant of these aluminium alloys [3,4]. Additionally, the PEO coatings can improve wear, thermo-optical, dielectric and thermal barrier properties [5-7]. PEO coatings exhibit a superior performance, cost effectiveness and environmental friendliness, compare to conventional methods used on aluminium-copper alloys [8-9]. The PEO coatings formation mechanism starts when the natural, very thin and passive film of the substrate begins to dissolve. With increasing the applied voltage, gas bubbles are produced which result in a porous film with a columnar structure perpendicular to the substrate. Plasma micro-discharge begins when the applied voltage exceeds the breakdown voltage of the oxide film [10,11]. The properties of the PEO coating mainly depend on electrolyte concentration and composition [12], the alloying elements of substrate [13], the applied current density [14] and type of power source [15].

In the present study, PEO treatment was performed on AA 2024-T3 aluminium alloy in an aqueous Na2SiO3-KOH electrolyte under DC conditions, in order to determine the influence of applied voltage and treatment time on the morphology, thickness and crystallinity of the coatings.

2. Experimental
Rectangular samples with dimensions of 35x20x1.76mm of AA 2024-T3 (wt%: 4.476 Cu, 1.207 Mg, 0.582 Mn, 0.189 Fe, 0.163 Si, 0.037 Zn, 0.039 Ti, 0.013 Cr) aluminium alloy were used in the present study. The surface of samples was ground with 400#, 800#, 1000# and 1200# SiC abrasive papers consecutively, cleaned with distilled water and acetone, and then dried by cool air flow.
The electrolyte was an aqueous solution of Na$_2$SiO$_3$ (10.5g/l) and KOH (2.5g/l) in distilled water. DC power supply with approximate 500V of the maximum output voltage was used for PEO treatment. PEO treatment was performed under constant sparking voltages of 310 and 400V for 500 and 710s. A stainless steel electrode sheet was used as cathode. After coating, the samples were removed from the electrolyte, washed in distilled water and acetone and then dried by cool air flow.

Microstructure and surface roughness were studied by scanning electron microscopy (SEM) (Quanta FEG 650) and digital microscopy (Hirox KH-7700). The coating thickness was determined using a gauge (PosiTector 6000). XRD diffraction analysis was used to study the crystallinity of the coatings.

3. Results
The formation of PEO coatings observed on the current density-time curves, showed an initial increase of the current density followed by a current drop, which corresponds to uniform establishment of “soft sparking” over the entire sample surface. Such current drop is attributed here, to an increased thickness and density of the coating over the entire sample surface and consequently the higher resistance of the oxide material to mass transfer.

The thickness and roughness of the PEO coatings are presented in Table 1. The PEO treatment was applied at 310 and 400V for 500 and 710s. It is clear, that with the increase in the treatment time and applied voltage, the thickness of the PEO coating increases. The roughness of the sample surface increases for the thicker coatings, as reported for other researchers [10,16]. This increase in roughness is due the fact that the sparking on the surface produces many discharge channels and craters.

| Coating Thickness (µm) | Average Roughness (µm) |
|------------------------|------------------------|
| A1 (310V, 500s)        | 1.62                   | 6.949                  |
| A2 (310V, 710s)        | 2.72                   | 5.838                  |
| B1 (400V, 500s)        | 9.48                   | 9.387                  |
| B2 (400V, 710s)        | 13.90                  | 27.741                 |

Figure 1 presents the SEM micrographs of the surface of PEO treated AA 2024-T3 aluminium alloy at conditions used in the present work. Pores of corresponding discharge channels distributed all over the surface can be distinguished. The surface of the coatings formed at higher conditions (410V, 710s) presents a crater-like morphology. The discharge channels are the result of localized discharge, and the pores are possibly the result of escaping gases during PEO process [5,17]. Through these channels, the molten alumina flows out of the channel and rapidly solidifies, and at the same time anionic components such as SiO$_3^{2-}$ enter the channels, leaving the sharp and distinctly visible boundaries. The craters are the result of cooling and deposition of molten material on the surface. As the voltage of the process increases and also the time, the surface of the coatings showed the presence micro-cracks.

The X-ray diffraction patterns of PEO coatings formed on AA 2024-T3 aluminium alloy are presented in Figure 2. The X-rays can easily penetrate through the coating because of its porosity, thus the diffraction peaks of substrate are strongly detected. It can be seen that coating formed at 400V consists mainly of γ-Al$_2$O$_3$, which is a typical phase in PEO coatings of aluminium alloys [12]. There is not presence of α-Al$_2$O$_3$. The oxide layer that ejected out from the channel is objected to high cooling rate in immediately contact with surrounding electrolyte and promotes the formation of γ-phase during solidification of alumina droplets. However, the coatings formed at 310V are mainly amorphous. Signals corresponding to mullite and cristobalite are also detected. The presence of these phases is due to the electrolyte used for the PEO treatment. It has been reported that the amorphous
phase can be formed as a result of rapid localized quenching around each individual discharge during the formation of the layer. The presence of such amorphous material influences the thermal conductivity of the coating.

![Figure 1](image1.png)

**Figure 1.** SEM micrographs of PEO coatings formed on AA 2024-T3 aluminium alloy in Na₂SiO₃ (10.5g/l) and KOH (2.5g/l) in distilled water solution. (a) 310V-500s, (b) 310V-710s, (c) 400V-500s, (d) 400V-710s.

![Figure 2](image2.png)

**Figure 2.** The XRD pattern of PEO treated 2024-T3 Al alloy in Na₂SiO₃ (10.5g/l) and KOH (2.5g/l) in distilled water solution.
4. Conclusions

Thick porous ceramic coatings are developed on AA 2024-T3 aluminium alloy by PEO process in a Na$_2$SiO$_3$ (10.5g/l) and KOH (2.5 g/l) in distilled water solution. The thickness of the PEO coatings is about 13.9 µm when a 400 V is applied for 710 s. At these conditions, the coatings are composed by γ-Al$_2$O$_3$, mullite and cristobalite phases. Generally the thickness and the roughness of the coatings increase as the time and the voltage applied increase. The surface of the coatings showed a crater-like morphology.

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