



Microstructure and phase composition of surface layers formed on aluminium alloys by plasma electrolytic oxidation

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Abstract: This paper presents elaboration and structural characterization of surface layers formed on aluminum alloys by plasma electrolytic oxidation (PEO). The electrolyte is a mixture consisting: sodium metasilicate and sodium hydroxide. The coatings obtained by PEO were investigated with: scanning electron microscopy (SEM) with Energy dispersive X-ray spectrometer (EDX) and X-ray diffraction (XRD) techniques.

Keywords: coatings, plasma electrolytic oxidation, aluminum alloys, surface analysis

1. Introduction

Plasma electrolytic oxidation, also known under the names of micro-arc oxidation, spark anodic oxidation or spark anodization has experienced increasing interest in recent years for the oxidation treatment of alloys. light metals (Ti, Al, Mg alloys). It covers several processes, based on the anodization of a metal substrate in an electrolyte, with the applied potential high enough for electrical discharges to occur.

PEO is a relatively new method to produce ceramic layers on the surface. This process was first developed by Gunterschulze and Betz and has been widely used in the surface treatment of metals in recent years [1].

PEO is a process for producing oxide coating with high hardness, strong adhesion, excellent corrosion strength and high wear resistance on the surface of aluminum alloy in aqueous electrolyte. The properties of the PEO coating will depend on the process parameters used, the chemical composition of the anodized materials, and the electrolytes used. The composition of the PEO coating comes from both the substrate and the electrolyte. Thus, the composition of the electrolyte plays a key role, and which could be used for the preparation of the desired PEO coating.

As a result, many types of electrolyte, for example, silicate, aluminate, phosphate, silicotungstic acid, etc. were used for the prepared PEO coating on aluminum alloys. Moreover, the effects of certain additives with small amount in the electrolyte, such as sodium tungstate, ammonium metavanadate, rare earth, lead mine, have also been studied. However, these PEO coatings have been found to be composed primarily of Al_2O_3 , or mulite [2].

The PEO process is commonly practiced in weak alkaline electrolytes containing anions such as silicate, phosphate, aluminate, which are environmentally friendly. Because the electrolyte substances participated in the film-forming reaction during the PEO process, the structure, composition, and other properties of PEO films would vary with the electrolyte compositions [3].

Plasma electrolytic oxidation is an efficient technique allowing the production of relatively thick oxide layers on the surface of valve metals (Mg, Al, Ti and many others) and their alloys. While for the "conventional" anodizing typically direct low voltage currents are used and the formation of oxide layers takes place in a quiet state, significantly higher voltages and alternating currents generally applied for the PEO cause intensive sparks due to discharges. micro-arc breaking the oxide layer. Extreme temperatures and pressures are developed in the discharge channels and cause complex phase transformation processes leading to the production of dense, thick and hard coating often having attractive abrasion and corrosion resistance [4].

The PEO coatings are utilized in various applications such as anti-corrosion, anti-friction, and photoactive layers [5-7].

2. Experimental details

2.1. Materials and methods

The alloy used in our study is an Al-Cu-Mg type alloy (AA2024-T351), a time-hardening alloy. The AA2024 aluminum alloy was supplied in metallurgical state T351, which corresponds to solution, quenching, controlled tensile (1.5-3%) and maturation at room temperature. The chemical composition is given in table 1.

Table 1. Chemical composition of the 2024 alloy

Composition	Al	Cu	Mg	Mn	Fe	Zn	Si	Ti	Zr
Alloy 2024	based	4,6	1,5	0,6	0,14	0,12	0,08	0,04	0,01

Before starting the PEO treatment, aluminum alloy samples were degreased and cleaned in an ultrasonic bath successively with alcohol and distilled water.

The PEO equipment was design and manufactured at the University of Pitesti (Figure 1). The experimental set-up consists of: an insulated stainless steel electrolyte cell with a stirrer and a pulsed bipolar DC power supply. The aluminum alloy was used as anode, while a stainless steel cell was used as cathode.

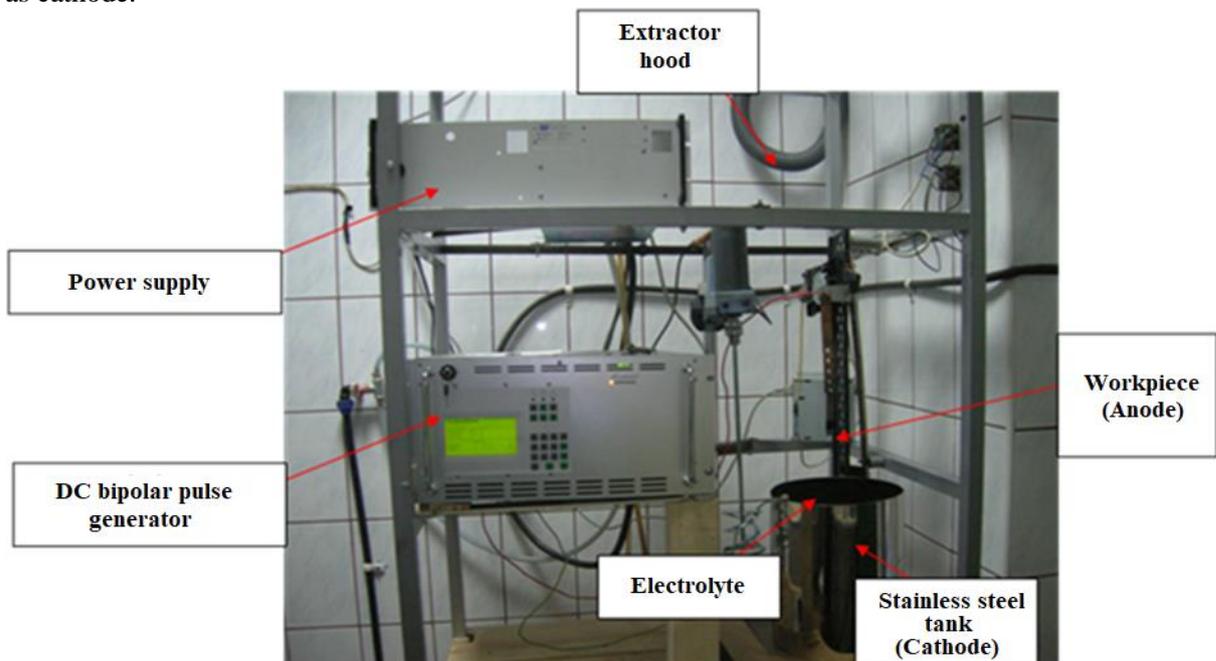


Figure 1. The plasma electrolytic oxidation equipment

The choice of the electrolyte is made according to the substrate alloy involved and the desired properties of the coating. Furthermore, electrolytes used in PEO process are weak alkaline solutions and are friendly to environment. Weak alkaline electrolytes such as silicate, aluminate and phosphate systems are usually used as the base electrolytes [8-9].

To carry out this treatment, an aqueous solution of sodium metasilicate and sodium hydroxide in distilled water was used.

PEO was carried out at an applied voltage of 400 V and a processing time of 20, 30 and 40 minutes. The PEO treatments were obtained using a pulsed current regime. During the oxidation, the temperature of electrolyte was less than 50°C. After the PEO treatment, the samples were washed with distilled water and dried at room temperature.

2.2. Evaluation techniques

The coatings obtained by PEO and immersed in SBF solution were investigated with: scanning electron microscopy (SEM) with Energy dispersive X-ray spectrometer (EDX) and X-ray diffraction (XRD) techniques.

The surface morphology of treated surfaces was observed on a Scanning Electron Microscope (SEM, Low-vacuum Inspect S – FEI Company).

The elemental composition was studied with energy dispersive X-ray spectrometer (EDX, Genesis-XM2) incorporated into the scanning electron microscope. EDX was performed at an acceleration voltage of 20 kV.

The surface structure of the films was analyzed by X-ray diffraction (XRD; Rigaku Ultima IV) using $\text{CuK}\alpha$ radiation, with Parallel Beam optics, in grazing incidence geometry (angle of incidence was kept constant at 2°). The measurements were conducted in the 2θ range 20° - 73° , step width 0.05° and 2s as counting time. The divergence angle of emitted beam from the multilayer mirror is approximately 0.05° . This kind of optics is suitable for analysis because of increased beam intensity and significant reduction of instrumental aberrations.

3. Results and discussions

For the electrolyte solution mentioned in the previous section were made a series of experiments, in a pulsed current regime. The experiments were carried out at a voltage of 400V and a treatment time of 20, 30 and 40 minutes.

The morphology of the surface was examined using scanning electron microscopy shown in Figure 2. The structure of the coatings is porous. On the surface of the coatings one can see pores of different sizes and microcracks produced due to electrical discharges on the surface of the sample during the deposition process. The pores on the surface are probably caused by the oxygen bubbles produced in the anodic reaction during the PEO process.

PEO coatings develop a two-layer morphology, with an amorphous outer layer with a coarse porous morphology and an inner crystalline layer with numerous fine pores. The cavities are due to the generation of oxygen which may be associated with the crystallization of the amorphous component in the inner layer [10].

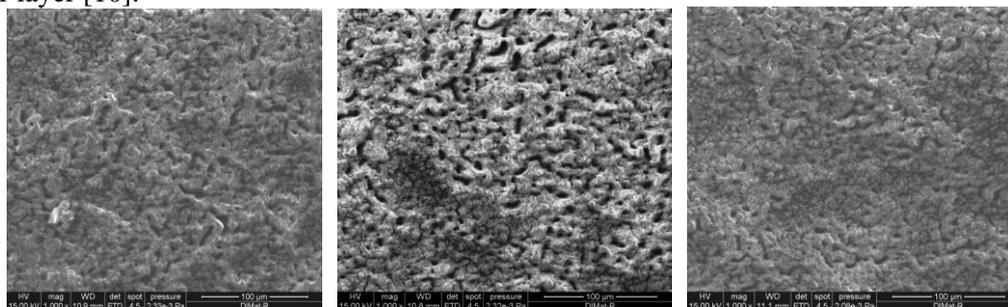


Figure 2. The SEM morphologies of Al_2O_3 obtained at: a.20 min, b. 30 min, c. 40 mins

The elemental composition and the phase proportion of coatings were evaluated using energy X-ray dispersion spectroscopy and X-ray diffraction, respectively.

In Figure 3 are present the EDX spectrums obtained for the treatments carried out at 400 V.

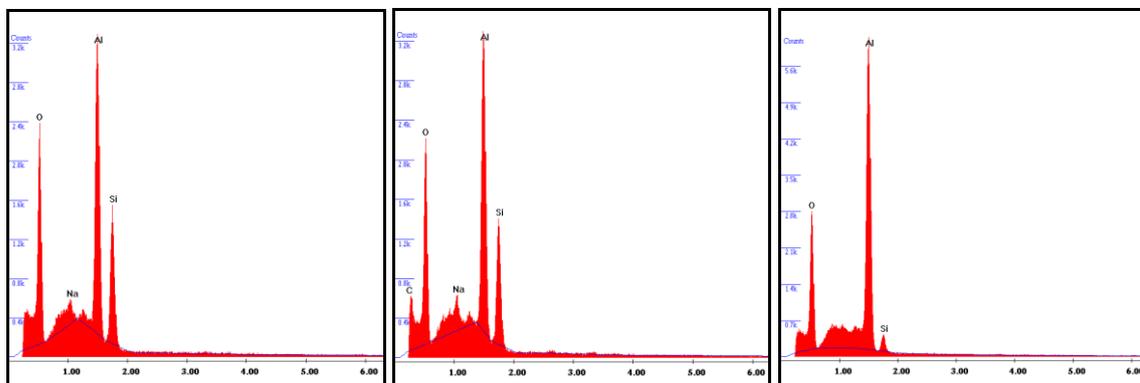


Figure 3. EDX spectrums of PEO oxidation film prepared at: 20, 30, 40 minutes

All layers contain aluminum and oxygen. In the oxide film, silicon and sodium were detected, which are supplied by the electrolyte. As the oxidation time increased, the oxygen and aluminum content changed (table 2). The content of Na is little. There is little variation in the composition profile of the coatings.

Table 2. Relative content of Al, O, Si of the surface PEO treatments

Sample	Relative content			
	Al (at.%)	O (at.%)	Si (at.%)	Na(at.%)
400V, 20 min	26,82	53,97	16,18	3,03
400V, 30 min	17,34	40,51	9,10	2,81
400V, 40 min	32,00	51,07	13,36	3,57

Figure 4 represents the $\theta / 2\theta$ X-ray diffraction spectra for PEO coatings obtained by varying the oxidation time. Intensity is represented in arbitrary units.

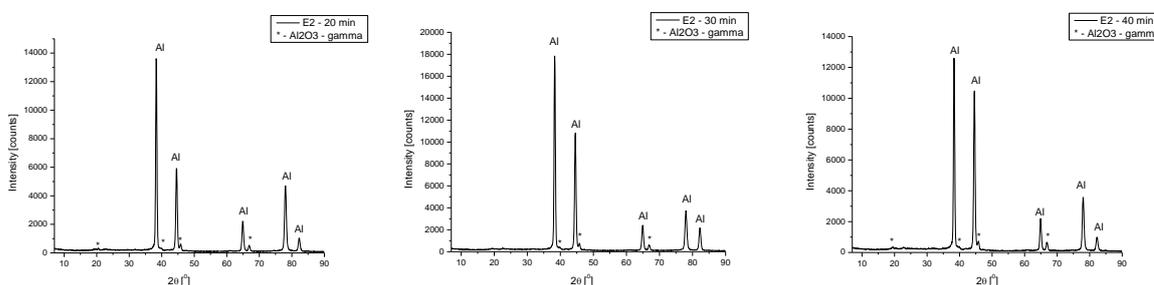


Figure 4. XRD diffraction spectra processed at 400 V and 20, 30, 40 minutes

The coatings consist of fine grains of gamma alumina and a significant proportion of amorphous material.

Strong elemental Al diffraction peaks are detected. It seems impossible that the characteristic diffraction peaks of aluminum originated from the substrate below the coating, as some coatings

prepared in this study are fairly thick and these peaks do not reduce in height with increasing coating thickness.

Therefore, the presence of elemental Al in the coatings could be attributed to the high temperature and pressure produced by a plasma discharge.

The element Al which is present in the alloy of the substrate melts at high temperatures and pressures, and then some of the molten aluminum solidifies on the coated surface, during the cooling of the electrolyte, before it can react with an oxygen atom to form Al_2O_3 . Therefore, some of the aluminum atoms can be found on the coating surface.

PEO coatings are formed at high stresses. These stresses provide very high surface energy. This could play the role of heat treatment and cause crystallization of amorphous metal oxides. So, the oxide film that forms at first is amorphous and then crystallizes [11].

4. Conclusions

The Al_2O_3 coatings obtained by the PEO technique on an aluminum alloy substrate were made in one type of electrolyte solution: sodium metasilicate (Na_2SiO_3) and sodium hydroxide (NaOH), in distilled water.

The morphology and chemical composition of Al_2O_3 coatings obtained by the PEO technique depends on the treatment time and the electrolyte solution.

The results obtained by scanning electron microscopy of the oxide layers formed demonstrate the strong influence of the process parameters on the evolution of the arcs and on the ceramic film formation mechanisms. These studies are currently continuing in order to better understand the understanding of the mechanisms involved, in particular through the coupling of plasma and material studies.

The structure of the coatings obtained by electrolytic plasma oxidation is porous. The formation of pores in coatings obtained by plasma electrolytic oxidation is inevitable and depends on the parameters of the electric discharge.

Protective coatings on aluminum alloy have better mechanical and anti-corrosion properties, when the substrate materials are obtained in a mixed electrolyte, using microsecond polarization of the current pulses.

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