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ELECTROCHEMICAL TREATMENT OF THE ALUMINUM SURFACE BY ELOXATION

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The work presents the effects of eloxation processing parameters on aluminum surface thicknesses employed by electrochemical treatment in a sulphuric acid solution. The parameters of the electrochemical deposition process were: temperature and concentration of the electrolyte bath, reaction time, in order to obtain on the surface of the Al samples an adherent, uniform and bright layer of alumina. The protective deposited alumina layer is morphological and compositional characterized by SEM and EDS. After the analysis of the results, it was verified that the electrochemical treatments provide a good adherent and uniform interface layer with role of anti-corrosion protection.

Keywords: aluminum, alumina oxide layer, electrochemical deposition, eloxation

1. Introduction

The surface of the aluminum, in contact with the atmosphere, is usually covered with a layer of aluminum oxide, with a thickness of less than 1µm. Due to its low thickness, high porosity and low mechanical strength, this coating does not protect the metal against corrosion. In the case of aluminum, the use of other methods of protection (coating with paints) is difficult due to the poor adhesion of the paints to the aluminum surface.

Aluminum and its alloys are characterized by a high corrosion resistance under standard atmospheric conditions and in the environment of several acids due to the layer of aluminum oxide (Al_2O_3) that develops on their surface. Therefore, the corrosion resistance of aluminum depends on the solubility of its protective layer. Its tightness and good adhesion to the substrate, determining the corrosion resistance, are dependent on the purity of aluminum or its alloys [1].

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It is known, the alumina is the most well-known fine ceramic material for chemical and physical stability with good thermal properties. The specific mechanical properties indicate a high strength and high hardness. Other properties of the alumina are the high electrical insulation, high corrosion resistance and biocompatibility. Some metals and alloys are protected against corrosion by coatings with inorganic layers, made by chemical or electrochemical means. Oxide, phosphate and chromate films are frequently applied industrially. Coating with layers of oxides and phosphates improves some qualities of metal surfaces such as hardness, wear resistance, electrical insulating properties, etc. Oxide and chromate films are used for the decorative finishing of parts, casings of measuring and control devices [2].

Eloxation is an electrochemical surface treatment method as applied to metallic surfaces by electrolyte treatment in a suitable solution, the metal being the anode. Aluminum may be protected by artificial formation of oxide film on the surface in an electrolytic cell having a suitable acidulated electrolyte; the commonest being the sulphuric acid [3-9].

Electrochemical oxidation or anodizing is an electrochemical process used to thicken a naturally occurring oxide layer on aluminum, aluminum alloys and other industrially important metals [10]. As the name suggests, the process involves passing an anodic current or imposing a positive potential on the metal/solution interface. The process oxidizes metal to metal ion which in turn reacts with water in the bath solution to form the oxide coating.

In general, the electrochemical reaction forming aluminum oxide on pure aluminum and aluminum alloys proceeds as:

$$2A1 + 3H_2O \rightarrow Al_2O_3 + 3H_2 \qquad (1)$$

Although this adequately describes the overall cell reaction during aluminum anodizing it offers no insight into the complex system of reactions taking place at multiple reaction interfaces [10].

Potentiostatic anodizing requires a positive potential in the range of 10 V to more than 200 V depending on cell conditions. Galvanically produced films result from controlling the anodic current across the metal/oxide interface. Both potential and galvanic anodizing oxidize the metal to metal ion by stripping electrons from the material

$$Al^o \rightarrow Al^{3+} + 3e^- \qquad (2)$$

Electrons flow through the external circuit and are available at the cathode. Hydrogen ions in solution are reduced at the cathode and form hydrogen gas

$$2H^+ (aq) + 2e^- \rightarrow H_2 \qquad (3)$$

These oxidation-reduction reactions describe the processes at the anode and cathode respectively. The reaction forming aluminum oxide must be regarded while considering multiple reaction planes. There are two reactants in the formation of aluminum oxide, aluminum and oxygen. Aluminum ions originate in the metal where it is oxidized [10]. Oxygen ions are provided by water as it breaks down at or near the oxide/electrolyte interface.

Four reactions take place simultaneously at the oxide/electrolyte interface. The previously formed oxide is dissolved by the acid electrolyte

$$Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-} \qquad (4)$$

Whether this reaction is accelerated during eloxation and to what extent this reaction influences the formation of porous oxides is a point of contention and will be addressed in a following section.

Reactant oxygen is ejected into the oxide as water dissociates at the interface

$$H_2O \leftrightarrow 2H^+ (aq) + O^{2-}(ox) \qquad (5)$$

The oxygen anion is a mobile charge carrier in the film and accounts for 60 % of the ionic current. The other 40 % is carried by metal cations [10, 11].

During porous oxide growth metal cations that reach the oxide/electrolyte interface dissolve into the bath solution by ion transfer [10, 12].

$$Al^{3+}(ox)-+Al^{3+}(aq) \qquad (6)$$

This ejection and loss of metal cations appears during porous oxide growth only.

In barrier type films, metal cations at the oxide/electrolyte interface may react directly with water molecules through the following reaction

$$2Al^{3+} + 3H_2O \rightarrow Al_20_3 + 6H^+ \qquad (7)$$

During porous growth, new oxide is formed primarily at a reaction plane nearby the metal/oxide interface. The production of oxide material follows

$$2Al^{3+}(ox)+3O^{2-}(ox) \rightarrow Al_2O_3 \qquad (8)$$

where oxidized aluminum reacts with migrating oxygen ions.

Regions mentioned as sites of enhanced dissolution create non-uniformity in the interfaces. Where the non-uniformity is a region of thinning, it will be amplified by the electrostriction pressure. The region of thinning is pulled toward the metal/oxide interface and displaces oxide material.

The obtained anodic oxide layer has porous structure and mainly consists of amorphous Al_2O_3 [13-15]. Owing to this porosity, anodic oxide layer is very beneficial for tribological application as they can be used as a reservoir for lubricants to form self-lubricating structures [15-18].

These are some of specific properties and advantages of the surface treatment of the aluminum by eloxation:

-the anodizing layer is made of metal itself, is fully integrated into it and there are no adhesion problems;

-the anti-corrosion performance of the eloxation is very good, if all the rules of production, application and use procedures are observed;

-aluminum anodizing products have a metallic appearance.

The aim of this paper is to examine the surface of aluminum samples deposited with Al_2O_3 in an aqueous solution of 20% concentration H_2SO_4 using a lead cathode, following the influence of eloxation parameters: electrolyte solution concentration, voltage, time and electrolyte temperature. The surface coatings and the thickness of the deposited alumina on the aluminum substrate are analyzed by SEM and EDS.

2. Materials and methods

The commercial chemical composition of the pure aluminum plate used for this study is presented in table 1:

Table 1

Chemical composition of AA 1050 plate used as substrate

Element	% weight
Aluminum	99.5 min
Iron	0.4 max
Copper	0.05 max
Iron	0.4 max
Magnesium	0.05 max
Manganese	0.05 max
Silicon	0.25 max
Titanium	0.03 max
Vanadium	0.05 max
Zinc	0.05 max

Figure 1 and 2 show the rectangular shape aluminum plate samples with dimensions of 160 x 120 x 1 mm and a laboratory design and fabricated electrochemical cell used for experiments.

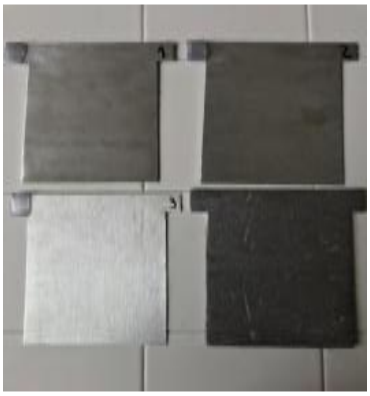


Fig. 1. Aluminum samples and lead cathode used for experiments

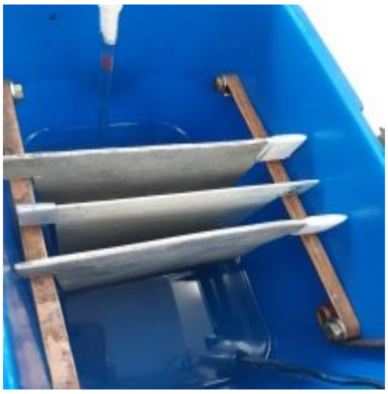


Fig. 2. Laboratory electrolysis bath

The anode was an aluminum plate and the cathode a lead plate with surface ratio to 1:1. Before eloxation the surface of the samples was prepared by grounding with silicon carbide paper and chemically degreased. The electrochemical processing conditions (table 2) for this study are: the concentration of the sulphuric acid used for the experiments was 20 %, the homogenization of the electrolyte solution by stirring with the rotation speed between 100-600 rpm, the eloxation time varies from 30, 60 and 90 minute, with different voltages and controlled electrolyte temperature. After anodic oxidation, the samples were sealed in distilled water at 95 ^{o}C for 10 minutes for decreasing of the porosity of the alumina layer.

Table 2

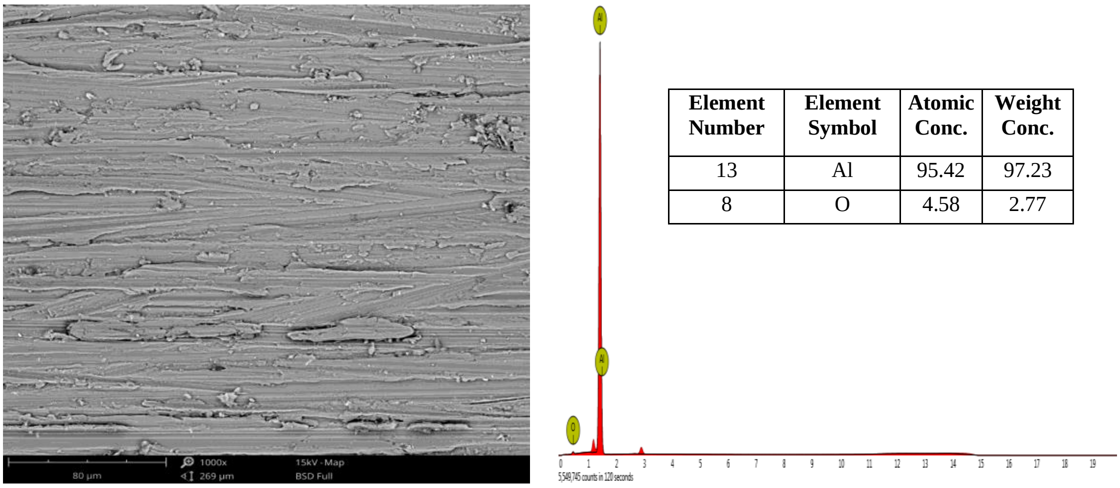
The experimental condition for aluminium eloxation

Sample no.	Concentration of the H_2SO_4 electrolyte solution, %	Temperature of the H_2SO_4 electrolyte solution, ^{O}C	Supply Voltage	Eloxation time, minute
1	20	15	25 V	90
2	20	10	15 V	60
3	20	25	12 V	30

The morphology and microstructure of the eloxated aluminum samples were analyzed by SEM (Phenom ProX, with a field emission gun - FEG with 1.2 nm resolutions and an Energy Dispersive Spectrometer - EDS having ≤ 140 eV resolutions at MnKα).

3. Results and discussion

The morphology of the aluminum plate subjected to experiments before eloxation is observed with SEM image and EDS analysis (figure 4). The low kV scanning electron microscopy images reveal an ultrafine grain disturbed layer caused by processing of aluminum plate and the presence of oxidized zone with aluminum oxide. The topography of the aluminum surface will influence the quality of the electrochemical oxidation processes.

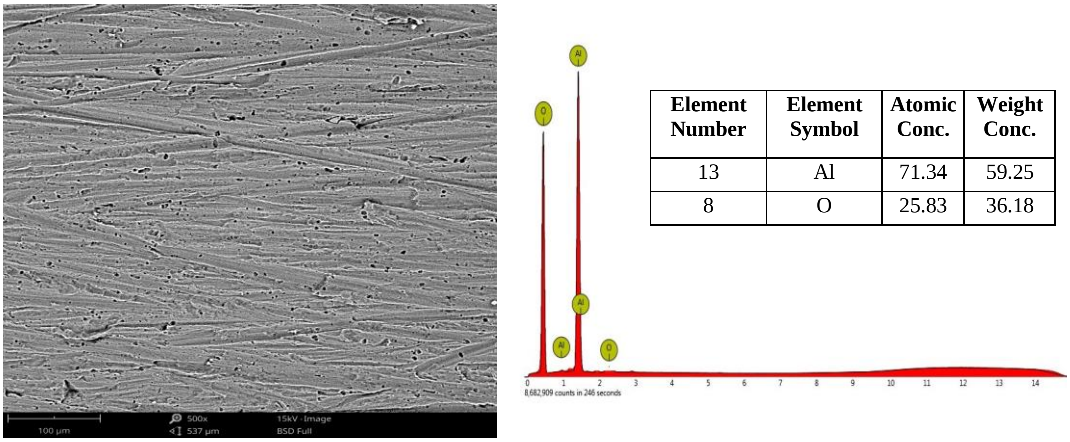


Element Number	Element Symbol	Atomic Conc.	Weight Conc.
13	Al	95.42	97.23
8	O	4.58	2.77

a) b)

Fig.4. SEM image of the Al plate before eloxation: a) SEM image; b) EDS spectra

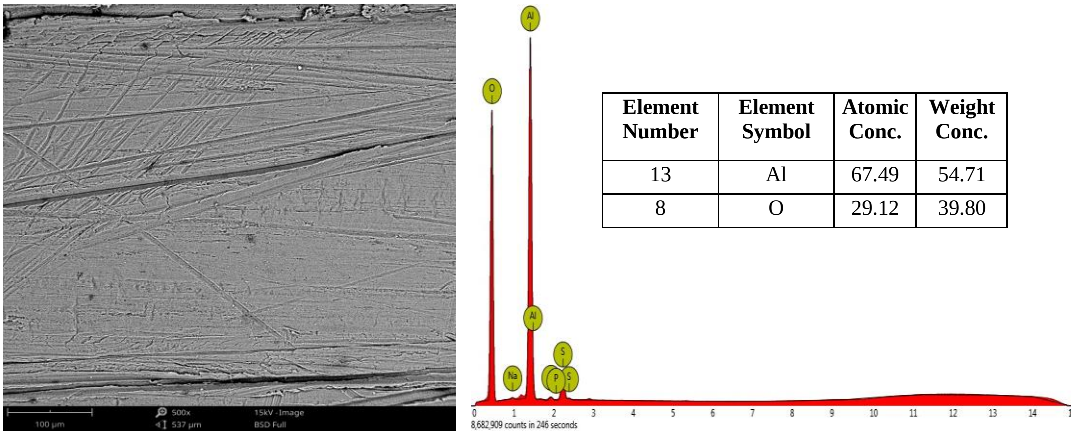
Surface analysis by element dispersive spectroscopy (EDS) spectra (Figure 4 b) shows the presence of rich aluminum phase and the small amount of oxygen, which confirm the composition of the aluminum substrate. After the anodization process the three eloxated samples in different experimental condition were subjected to quantitative and structural analysis. The distribution of the aluminum phase in the samples shows a variation of concentration according to the eloxation condition. EDS spectra (figure 5-7) confirm the existence of the aluminum oxide on the aluminum substrate. By increasing the eloxation time (figure 5 a), samples reveal a good morphological aspect of the deposited alumina layer.



Element Number	Element Symbol	Atomic Conc.	Weight Conc.
13	Al	71.34	59.25
8	O	25.83	36.18

a) b)

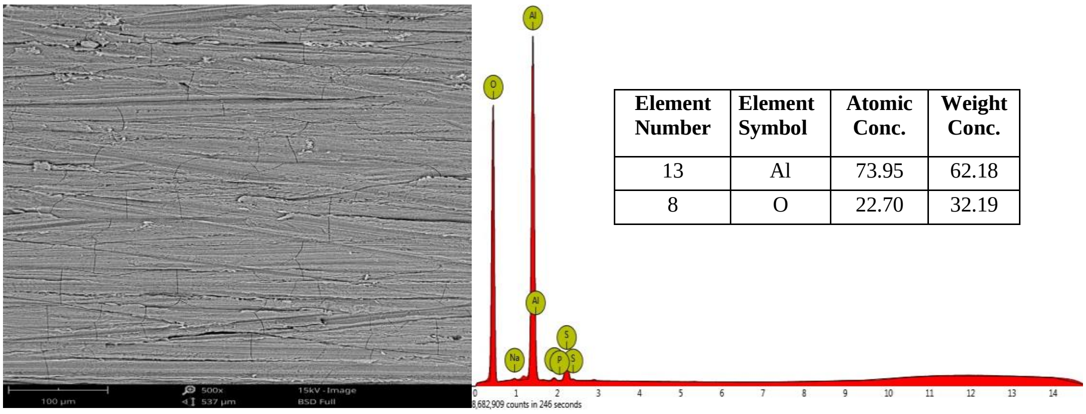
Fig.5. Sample 1 of eloxated aluminum plate: a) SEM image; b) EDS spectra



Element Number	Element Symbol	Atomic Conc.	Weight Conc.
13	Al	67.49	54.71
8	O	29.12	39.80

a) b)

Fig.6. Sample 2 of eloxated aluminum plate: a) SEM image; b) EDS spectra



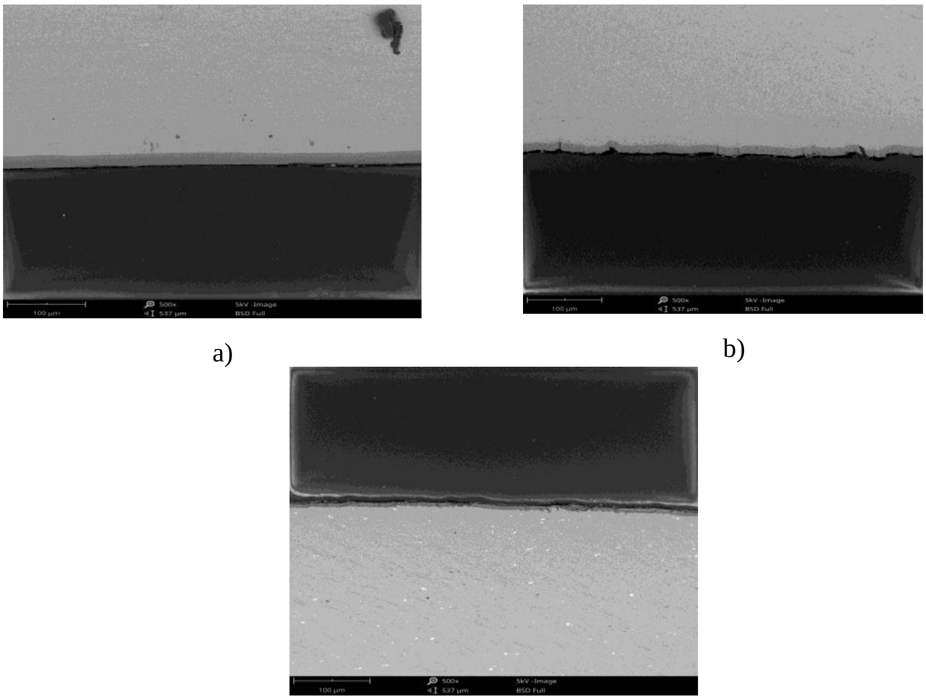
Element Number	Element Symbol	Atomic Conc.	Weight Conc.
13	Al	73.95	62.18
8	O	22.70	32.19

a) b)

Fig.7. Sample 3 of eloxated aluminum plate: a) SEM image; b) EDS spectra

Scanning electron microscopy studies were performed to obtain further information about the surface topography of the three aluminum samples covered with alumina protective layer (figure 8). Thickness of porous alumina layer is an indication of the growth rate of the oxide film on the substrate.

For each layer thickness were performed five measurements. The result (table 3) indicates the standard deviation, the minimum, maximum and mean value of the layers thicknesses. A comparable layer thickness can be observed, at the first sample where the deposited alumina layer is uniform, adherent, compact without non-uniformity interface zone (figure 8 a), and the higher degree of non-uniformity at sample three (figure 8 c).



a) b)

c)

Fig. 8. Thickness of the alumina layer deposited on the aluminum plate:
a) sample 1; b) sample 2 and c) sample 3

Table 3

Layer thickness of all samples (values are expressed in µm)

Sample	**Measurement**					**Min value**	**Max value**	**Mean**	**SD**
	1	2	3	4	5				
1	21.164	21.280	21.629	21.398	20.815	20.815	21.629	21.257	±0.301
2	15.349	15.000	14.659	14.729	14.873	14.659	15.349	14.922	±0.273
3	4.422	4.280	4.508	4.035	4.535	4.035	4.535	4.356	±0.205

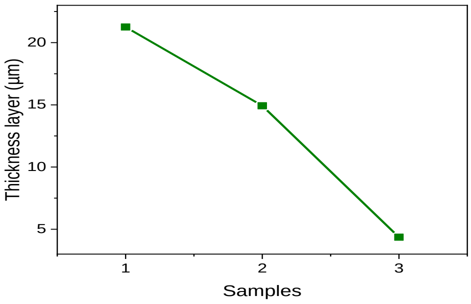


Fig. 9. Evolution of the alumina layer thickness deposited on the aluminum plate

However, the barrier type alumina layer thickness is not uniform and can observe pores zone on the surface of the film as can see in sample 2. Following the electron microscopy image for sample 3 shows a thin, porous barrier alumina layer caused by the electric field.

Based on structure investigation of the anodized layer it was possible to determine the thickness of the alumina layer. The average measurement results are: for sample 1: 21.25 μm, for sample 2: 14.92 μm and for sample 3: 4.25 μm.

According to the thickness measurement it results the sample 1 presents a good adherent layer thickness and sample 3 the most uniform layer thickness (figure 9).

4. Conclusions

One of the most common surface treatments for aluminum is made by electrochemical reaction named eloxation. The goal of this anodic oxidation deposition experiments it was to find the optimum (proper) processing conditions in order to obtain on the surface of the Al samples a good, continuous, adherent and metallic appearance layer of alumina (Al_2O_3).

The purpose of this work was to follow the evolution of the aluminum oxide layer formation resulting from the eloxation depending on the electrochemical parameters such as the eloxation time, the electrolyte temperature and the supply voltage. Throughout this work it was mentioned that the electrochemical treatment by eloxation has a protective role depending on the requirement.

Based on the scanning microscopy analysis, in sample 1 can be observed a good adhesion between the substrate and the alumina deposited area, with high layer thickness values. The thickness of alumina layer increases when the temperatures of the electrolyte decrease. For sample 2 and 3 there it is found high degree of unevenness of different layer thickness. Following the experiments, in the sample one with longer eloxation time (90 minute), higher voltage and medium electrolyte temperature it was observed a much more adherent and homogeneous layer of aluminum oxide with mean thickness of 21.257μm.

In conclusion, the anodizing time plays a very important role, being the most influential parameter for the quality of the surface treatment.

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