Influence of the Imposed Parameters on XRD Patterns of Electrochemically Top-Down Obtained Nanoporous Al₂O₃ on Al1050 Alloy

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Abstract. 1050 Aluminum alloy samples polished electrochemically in solution of 15% Na₂CO₃ and 5% Na₃PO₄ were subjected to the anodic oxidation process in an acid electrolyte, of 1 M H₂SO₄ to which 1 g / L Al₂(SO₄)₃ x 18 H₂O was added for the formation on their active surfaces of aluminum oxide nanoporous layers by top-down nanotechnology method. The applied parameters during the anodic oxidation processes were varied in order to obtain the most uniform aluminum oxide nanoporous layers. Thus the potential was varied between 1 V and 25 V, the duration of the oxidation processes was between 10 minutes and 48 minutes and the stirring rate of the electrolyte was between 0 and 700 rotations per minute. The formation of nanoporous layers of aluminum oxide was observed when the applied potential was between 15 V and 21 V, the duration of the anodic oxidation process was varied between 25 and 45 minutes and the stirring rate of the electrolyte was between 0 and 500 rpm. Too low duration and / or too low potential caused an electrochemical polishing phenomenon to occur and the imposition of too high potential caused dissolution of the alloy substrate. Also, the use of a dynamic electrolyte regime produced a homogenization of the electrolyte temperature during the anodic oxidation processes and the growth of the aluminum oxide nanoporous film is slowed down. XRD diffractogram analysis reveals an enhancement in peak intensity correspondent to aluminum oxide concomitantly with a reduction in peak intensity of metallic aluminum for aluminum nanoporous oxide layers in comparison to the surface of polished Al1050 electrochemically.

1. Introduction
Aluminum and its alloys always have a fine layer of natural oxide (alumina) on their surface. This film is topic to deterioration due to its fragility, which is due to its reduced thickness and its inhomogeneity [1-2].

The anodizing methods afford the thickness check of this oxide layer, obtaining a homogeneous and resistant layer. Using special dyes it is possible to color the anodized (eloxated) layer. Coloring of the deposited layer is an additional and optional operation. The only way to discolor the piece is to destroy the anodized layer. The completion of the anodization (eloxation) treatment is done by clogging the pores by hydrating the oxide layer formed. At once the pores are clogged; best corrosion behaviour is obtained [1-3].
The deposited aluminum oxide layer also has dielectric properties. The presence of anodized (eloxated) film on the surface of an aluminum part prevents the flow of electricity. The porosity of the anodized surfaces permits a really great attachment to the painting in electrostatic field or in the situation in which two surfaces are bonded [1, 4-6].

In the last decades, the researches in the areas of functional areas have concerned a significant number of researchers and their studies determine to obtain a diversified range of functional surfaces with unique properties. The manufacture of functional surfaces on aluminum and its alloys can be accomplished by a diversity of process, but the most commonly used is the electrochemical anodic oxidation method [7-16].

The anodic oxidation method implies the imposition of external parameters during the electrochemical process, and their variation allows a rigorous control of the morphological and functional structure of the oxide layers formed on the surface of the aluminum and its alloys. The functional surfaces obtained by anodic oxidation offer improved physical-chemical and mechanical properties to the aluminum substrate on which they are formed [10, 11, 14, 15].

Due to unique combinations of properties, aluminum and its alloys are some of the most versatile and economically attractive materials, being used in a wide range of fields. 1050 aluminum alloy is part of group 1 of aluminum alloys, which means a purity of at least 99.5%, also known as pure commercial aluminum. Pure commercial aluminum (Al1050, 99.5% purity) is malleable, ductile and the main alloying elements or impurities are iron and silicon.

This research work is dealing with anodic oxidation of 1050 Aluminum alloy in order to grown a nanoporous layer or film on its surface by top-down nanotechnology. The obtained nanoporous aluminum oxide layers are analyzed by XRD diffraction in order to evaluate the influence of applied potential and time duration of oxidizing process on structural aspects of obtained nanoporous aluminum oxide layers.

2. Experimental procedures

2.1. Materials and methods

Aluminum alloy type 1050 (Alro Slatina, Romania) was used as a substrate for the growth of nanoporous aluminum oxide layers by electrochemical methods.

**Figure 1.** Schematic drown of controlled growth of nanoporous aluminium oxide film by electrochemical oxidation: (a) electrochemical cell with anode, cathode and electrolyte, (b) schematic cross section of porous oxide film, (c) schematic view of surface porous aluminum oxide film, (d) SEM micrograph of obtained nanoporous aluminum oxide film with measured nanopores (17-38 nm).
Figure 1 shows schematically the steps taken to carry out the anodic oxidation procedure and to obtain the aluminum oxide nanoporous films.

The anodic oxidation process involves the formation of an aluminum oxide coating on the surface of the 1050 aluminum alloy used as substrate. In order to obtain nanoporous layers of aluminum oxide on the surface of aluminum alloy, different electrolytes based on sulfuric acid were tested.

The most reproducible results were obtained for 1 M H$_2$SO$_4$ electrolyte to which 1 g / L Al$_2$(SO$_4$)$_3$ x18 H$_2$O was added. Due to the fact that the anodic oxidation process causes an elimination of aluminum ions, which contaminates the electrolyte, the optimum solution identified for the electrolyte reuse was to add an aluminum salt, so that an aged electrolyte (reused) was simulated from the first use of the electrolyte in the electrochemical process.

The anodic oxidation process took place in a conventional electrochemical cell, shown in Figure 1 (a), where the electropolished Al1050 plate with an active surface of 4 cm$^2$ was used as an anode and for the cathode an Al1050 plate was used with an active surface of 12 cm$^2$.

The two Al1050 aluminum plates were immersed in 200 mL of electrolyte, at a distance of 5 cm, and then with the help of two pliers were connected to a great potential voltage source (TDK LAMBDA GEN 300-8).

Electrochemically polished Al1050 aluminum samples were subjected to an anodic oxidation process, under potentiostatic regime, in 1 M H$_2$SO$_4$ electrolyte to which 1 g / L Al$_2$(SO$_4$)$_3$ x18 H$_2$O was added, and the physical-chemical parameters of the electrolyte is indicating Table 1.

| Table 1. Physico-chemical parameters of oxidation solution. |
|---------------------------------|--------|-----------|
| pH                             | Salinity [‰] | Conductivity [mS/cm] |
|--------------------------------|-------------|----------------------|
| 0.08                           | 68.9        | 97.1                 |

| Table 2. Variation of imposed parameters to anodic oxidation process. |
|------------------------|------------------------|------------------------|------------------------|
| Substrate              | Stirring speed [rpm]   | Potential [V]          | Duration [min]          |
|------------------------|------------------------|------------------------|------------------------|
| Al1050                 | 0                       | 15                     | 25                     |
| Al1050                 | 0                       | 15                     | 35                     |
| Al1050                 | 0                       | 15                     | 45                     |
| Al1050                 | 0                       | 18                     | 25                     |
| Al1050                 | 0                       | 18                     | 35                     |
| Al1050                 | 0                       | 18                     | 45                     |
| Al1050                 | 0                       | 21                     | 25                     |
| Al1050                 | 0                       | 21                     | 35                     |
| Al1050                 | 0                       | 21                     | 45                     |
| Al1050                 | 500                     | 15                     | 25                     |
| Al1050                 | 500                     | 15                     | 35                     |
| Al1050                 | 500                     | 15                     | 45                     |
| Al1050                 | 500                     | 18                     | 25                     |
| Al1050                 | 500                     | 18                     | 35                     |
| Al1050                 | 500                     | 18                     | 45                     |
| Al1050                 | 500                     | 21                     | 25                     |
| Al1050                 | 500                     | 21                     | 35                     |
| Al1050                 | 500                     | 21                     | 45                     |
In order to obtain nanoporous layers of aluminum oxide with a uniform cell structure, the imposed parameters in the anodic oxidation procedure were varied as follows: the imposed potential in the anodic oxidation procedure was alternated between 1 and 25 V, the time of the anodic oxidation procedure was between 10 and 48 minutes, and the stirring speed of the electrolyte was between 0 and 700 rotations per minute.

After identifying the values of the optimal parameters for growing the aluminum oxide nanoporous layers, they were varied to observe their influence on the morphological, compositional and structural characteristics like the chemical, mechanical, physical properties of the aluminum oxide nanoporous layers.

Table 2 shows the variations of the values of the parameters implicated in the anodic oxidation procedure. Also, the anodic oxidation processes were repeated at least 20 times, for each set of parameters, to obtain reproducible results.

2.2. Preparation of Al alloy for oxidation process

The aluminum sheet was cut to the size of 2 x 30 x 35 mm, the obtained plates were mechanically glazed with emery paper with a granulation of #1500 and #2000, in order to remove both macroscopic defects and the native oxide layer formed on aluminum alloy.

The polished samples were rinsed with distilled water and then chemically purify by submerged in 5 M NaOH for 30 seconds, washed under running water for 60 seconds, rinsed with distilled water for 30 seconds and dried in an oven under hot air (50°C) for 60 minutes, after which they were stored in a desiccators.

Finally, they were embedded in insulating resin, with an active surface of 6.5 cm² being delimited. Before being used in the anodic oxidation procedure, the aluminum plates were subjected to electrochemical polishing treatment in a solution of 15% Na₂CO₃ and 5% Na₃PO₄ (Brytal), to obtain a surface with a small roughness and with a low number of macroscopic defects.

After the electrochemical grinding process, the surfaces of the Al1050 samples were cleaned under distilled water and after that dried in the oven under hot air (50°C) for 50 minutes.

The samples of electrochemically polished aluminum 1050 subjected to anodic oxidation treatment, at various parameters, were isolated with insulating resin in order to achieve a very properly defined surface area of 4 cm².

The anodically oxidized aluminum alloy surfaces were extracted from the resin and then prepared to be structurally characterized. Structural characterization of the aluminium oxide nanoporous layers was performed using the X-ray diffraction (XRD) method to observe the phase changes of the surfaces of the aluminum oxide nanoporous film obtained by the anodic oxidation method, depending on the parameters imposed in within the electrochemical process.

Structural characterization of aluminum oxide nanoporous films achieve by the electrochemical anodic oxidation method was performed using the ray diffraction method X (XRD) using Dron-3 equipment. XRD diffractograms were recorded using a Molybdenum anode (Mo, λKα = 0.71073 Å), and then they were analyzed using MATCH 3 software connected to Free Crystallography Open Database (COD) database.

3. Results and discussions

3.1. Structural investigations of 1050 aluminium substrate electrochemically polished

Figure 2 exhibit the XRD diffraction patterns recorded for the surface of Al1050 having the surface only electrochemically polished.

From the XRD diffractogram analysis shown in Figure 2, two peaks (maximum) of high intensity diffraction were identified corresponding to the metallic aluminum (2θ = 28.55° and 2θ = 33.65°), according to the COD pdf standard. No. 96-431-3207.
3.2. Influence of the potential applied in the anodic oxidation procedure on the structure of aluminium oxide layers

The XRD diffraction patterns register for the aluminium oxide nanoporous layers attained at anodic oxidation duration of 45 minutes and varying the imposed anodic potential are shown in Figure 3 (a-c) for the static regime of the electrolyte and respectively in Figure 4 (a-c) for its dynamic regime.

Figure 2. XRD patterns of electrochemically polished Al1050 alloy.

Figure 3. Influence of imposed oxidation potential on XRD patterns corresponding to the obtained aluminum oxide films during static regime of electrolyte: (a) 15 V, (b) 18 V and (c) 21 V.
From the analysis of the diffraction patterns presented in Figures 3 and 4 it is established that for the anodic oxidized surfaces, peaks to the metallic aluminium were identified in similar positions ($2\theta = 28.55^\circ$ and $2\theta = 33.65^\circ$) to those identified for the electrochemically polished surface of 1050 Al alloy, but the intensity of the diffraction peaks related to the amorphous aluminum oxide increased together with the value of the imposed oxidized potential during the anodic oxidation procedure while the intensity of the peaks corresponding to the metallic aluminum shows a downward trend. The obtaining of nanoporous layers of aluminum oxide with an amorphous structure has been observed by other researchers also [17-19].

![Figure 4](image.png)

**Figure 4.** Influence of imposed oxidation potential on XRD patterns corresponding to the obtained aluminum oxide films during dinamic regime of electrolyte: (a) 15 V, (b) 18 V and (c) 21 V.

Also, from the XRD diffraction patterns presented in Figures 3 and 4, it is very clear that the intensities of the peaks related to the aluminum metal show the highest intensities within the XRD diffraction patterns, regardless of the duration or potential imposed during the anodic oxidation processes. The same growth trend of the peaks related to the amorphous aluminum oxide is manifested no matters if it is a static or dynamic regime of the electrolyte during oxidation process.

R K Choudhary et al. [19] Analyzed the XRD diffraction patterns recorded for the aluminum surfaces (96% purity) anodically oxidized at 20 V and 30 V in 10% C$_2$H$_2$O$_4$, and the peaks with the highest intensity correspond also to the metallic aluminum.

### 3.3. The influence of the duration of the anodic oxidation procedure on the structure of the aluminium oxide layers

The XRD diffraction spectra recorded for the anodic oxidized surfaces at 21 V for duration of 25 minutes, 35 minutes and 45 minutes are shown in Figure 5 (a-c) for the static regime of the electrolyte and in Figure 6 (a-c) for its dynamic regime.

From the XRD patterns corresponding to the oxidized surfaces at 21 V for different durations of oxidizing process and presented in Figures 5 and 6, the corresponding peaks to the metallic aluminum
were identified in similar positions ($2\theta = 28.55^\circ$ and $2\theta = 33.65^\circ$) to those recorded for the surface of 1050 aluminum alloy electrochemically polished (Figure 2).

![Figure 5](image.png)

**Figure 5.** Effect of time period of anodic oxidation process on XRD diffraction patterns corresponding to aluminium oxide surfaces obtained in static regime of electrolyte: (a) 25 minute, (b) 35 minute and (c) 45 minute.

The intensity peaks related to metallic aluminum show a decrease in intensity as can be seen in Figures 5 and 6, and the intensity peaks related to aluminum oxide have a tendency to increase in intensity with the duration of the anodic oxidation process.

The most important factor on which the production of a nanoporous oxide film depends is the ability of the electrolyte to produce a continuous flow of Al$^{3+}$ ions from the substrate to the solution. The passage of Al$^{3+}$ ions from the substrate to the electrolyte is achieved by two mechanisms. The first mechanism is the direct rejection of the ions by the applied electric area and the second mechanism is the dissolving of the oxide film already formed [3]. The source of the pore nuclei as well as the mechanism of pore nuclei is greatly unknown; in this sense several models are proposed.

A model uses as a source for pore nucleation the electric field that assists local chemical dissolving both at the level of the solution / oxide interface and at the level of the oxide / metal interface.

Therefore the applied potential is a very important parameter in order to obtain a homogenous nanoporous aluminum oxide film.

This model explains how the metal Al$^{3+}$ ions migrate into the oxide film when using an electrolyte with a pH lower than 5. The electrolyte with a pH below 5 produces a continuous flow of Al$^{3+}$ ions, which is incorporated at the layer of oxide, thus protecting regions with an unstable oxide layer at the oxide / solution interface. These instable oxide regions cause variations in the applied electric area which manifests in increasing dissolving rate [9].

This mechanism take place at the base of metal / oxide and oxide / solution interfaces and manifests itself in a large number of hemispheric depressions / cm$^2$, a number that corresponds to the pore density. In these depressions, due to the hemispherical shapes, the electric area lead to be more
crowed, thus increasing the dissolution rate. These hemispheric depressions form the basis of the porous structure.

Figure 6. Effect of time period of anodic oxidation process on XRD diffraction patterns corresponding to aluminium oxide surfaces obtained in dynamic regime of the electrolyte at: (a) 25 minute, (b) 35 minute and (c) 45 minute.

The location of these valleys is too affected of the surface imperfections like impurities holes, scratches, grain boundaries, surface topography or treatments to which the surface was subjected prior to anodization.

In the first phases of the anodization procedure, the Al\(^{3+}\) ions migrate by the aluminium substrate through the metal / oxide interface forming an oxide film. Meantime, ions O\(^{2-}\) formed from water at the oxide / solution interface migrate to the oxide film. Through these stages, almost 70\% of the Al\(^{3+}\) and O\(^{2-}\) ions redound to the formation of an oxide film [7] while the ions remain are dissolved in the solution. Over the oxide formation, the barrier film is constantly regenerated by increasing the oxide thickness and transforming in a hemispherical oxide layer, with a constant thickness and which will form the pore base [3].

Through the formation of the nanoporous oxide film, at the anode the aluminium dissolves according to the reaction below:

\[
2Al \rightarrow 2Al^{3+} + 6e^- \tag{1}
\]

And at the cathode the following reaction occurs in which hydrogen is produced:

\[
6H^+ + 6e^- \rightarrow 3H_2 \tag{2}
\]

Reaction from anode it takes spot at the interface among metal and oxide (oxygen anions interact with aluminum):
$$2Al + 3O^{2-} \rightarrow Al_2O_3 + 6e^-$$  \hspace{1cm} (3)

The reaction from the anode it takes spot at the interface among the oxide and the electrolyte (aluminum cations react with water molecules):

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+$$  \hspace{1cm} (4)

The total reaction that takes place at the electrode (the total reaction of anodizing of aluminum):

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$$  \hspace{1cm} (5)

This depict mechanism clarifies the dependence of the size of the pore diameters on the electric field produced by the anodizing voltage. Can be remark that the power of the electric domain inside the pore walls is very poor to be able to influence the ion course in any way [2, 5]. Further investigations must be mode to correlate the applied potential for anodic oxidation process with the dimensions of pores from obtained nanoporous oxide layers.

4. Conclusions

Taking the anodic oxidation process on the surfaces of the 1050 Al alloy, a nanoporous film of aluminium oxide could be increased which would radically change the structural aspects in comparison with polished surface samples

Considering that all the parameters implicated in the anodic oxidation process can affect the compositional and structural characteristics of the aluminium oxide nanoporous film, the present work sought to highlight the influences produced by the variation of the imposed potential and the length. of the anodic oxidation process, like properly the role of the dynamic or static regime of the solution on the characteristics of the aluminium oxide nanoporous film obtained in 1 M H$_2$SO$_4$ solution to which 1 g / L Al$_2$ (SO$_4$)$_3 \times 18$ H$_2$O were added.

XRD diffraction patterns analysis reveals an enhancement in the peak intensity corresponding to aluminium oxide concomitantly with a reduction in peak intensity of metallic aluminum for nanoporous aluminum oxide layers in comparison with the surface electrochemically polished of Al1050.

The optimum parameters as applied potential and time duration of anodizing process could be revealed by analyzing the XRD diffraction patterns of obtained nanoporous aluminum oxide layers.

5. References

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