Corrosion Behavior of Aluminum Oxide Film Growth by Controlled Anodic Oxidation

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Abstract. Due to the light weight and good corrosion resistance, nowadays aluminum and its alloys are used in different industries in order to decrease the maintenance costs and also to increase the equipments lifetime cycle. When aluminum and its alloys are exposed to the extreme environments, the native aluminum oxide film lose the anticorrosive properties that lead to the damage of equipments and increasing the costs. In order to improve the anticorrosive and mechanical performances of aluminum and its alloys, different techniques are used: organic coatings, the growth of a thick aluminum oxide film through different methods, etc.. The most used method for aluminum oxide growth is anodic oxidation. Anodic oxidation is an electrochemical method that allows to growth an aluminum oxide film with controllable characteristics. The aim of present paper was to growth on 1050 aluminum alloy surface nanoporous aluminum oxide films with improved anticorrosive properties. The obtained nanoporous aluminum oxide films were characterized morphological and structural by scanning electron microscopy coupled with X-ray energy dispersive analyzer. The anticorrosive properties were evaluated by electrochemical methods such as: open circuit potential, electrochemical impedance spectroscopy and cyclic voltammetry. The results showed that anodic oxidation treatment improve the anticorrosive performances of 1050 aluminum alloy.

1. Introduction

The problems of costs received significant attention from economists, researchers and engineers in the last years. New materials were developed by the researchers, to increase the life services of equipments and also to decrease the fabrication prices, in order to reduce the costs.

Aluminum and its alloys received significant attention from the researchers because of its high technological value and its wide range of industrial applications especially in aerospace and household industries [1, 2].

The researchers tried to improve the mechanical properties of aluminum by alloying with different elements [3] but they encountered a new problem: the decreasing of corrosion resistance. The decreasing of corrosion resistance in many instances reduces the applications of aluminum alloys.

Developing successful protective coatings on aluminum and its alloys is still a challenging task even if different methods are used. Different techniques such as: conversion coatings, sol-gel deposition or anodic oxidation [1,2,4-6] are used to improve the corrosion resistance of aluminum and its alloys, but everyone method present its limitations.
Anodic oxidation is an electrochemical technique used to increase the thickness of native aluminum oxide layer and to obtain a protective coating on aluminum and its alloys, with adhesive bonding to the substrate, improved wear resistance and anti-corrosive properties [7,8].

The type of anodic oxide film that can be produced upon aluminum surface depends upon several parameters and the most important is the nature of the electrolyte. The formed anodic aluminum oxide layer could be a barrier-type layer if the aluminum oxide is insoluble in chosen electrolyte or a porous-type layer if the aluminum oxide is slightly soluble in the electrolyte [9].

Beside the electrolyte type, the involved parameters in anodic oxidation process affect the structure and the morphology of obtained aluminum oxide layer. Controlling the anodic oxidation parameters, the obtained aluminum oxide layer could be tailored for particular applications.

In order to obtain a protective aluminum oxide layer on 1050 aluminum alloy (1050AA), the anodic oxidation processes were conducted in aged sulphuric acid, at different applied potentials. In this paper we reported the effect of anodic oxide process on pores formation and improving the corrosion resistance of 1050AA. The morphological and structural analysis were investigated using a scanning electron microscope (SEM) coupled with X-ray energy dispersive analyzer. The corrosion resistance of obtained coatings were measured by electrochemical methods and compared.

2. Materials and methods

An aluminum sheet (1050AA, min 99.5% Al, 2 mm thickness) was cut in coupons with dimensions 35 mm x 30 mm. The coupons were mechanical wet-polished with SiC grinder paper (#1500 and #2000), etched in 5 M NaOH for 30 seconds at room temperature and finally washed in deionized water and alcohol under ultrasonic stirring. The samples were electropolished at 2 V, 80°C for 30 minutes in a mixture of 5% Na3PO4 and 15% Na2CO3 [10]. The electropolished aluminum pieces were placed in a two electrode cell with a parallel electrode arrangement using a large 1050AA sheet as cathode. For anodic oxidation process the electrolyte was 1 M H2SO4 in which it was added 1 gL-1 Al2(SO4)x18H2O, in order to simulate an aged electrolyte. The anodic oxidation process was performed in potentiostatic mode using a high voltage power source (TDK LAMBDA GEN 300-8) by applying constant voltages of 15 V, 18 V and 21 V at room temperature for 35 minutes.

The electrochemical assays were done in 3.5% NaCl solution using a standard electrochemical cell. The prepared samples with an exposed surface of 1.7 cm², were served as working electrode, Pt-Rh grid as counter electrode and Ag/AgCl (saturated KCl solution, E=200mV vs. NHE – normal hydrogen electrode) as reference electrode were used. The electrochemical cell was connected to a Voltalab PGZ100 potentiostat/galvanostat during the electrochemical corrosion measurements.

In order to reach the steady-state, the open circuit potential (OCP) was performed for 17 hours. The electrochemical impedance spectroscopy (EIS) tests were conducted over a frequency range of 10⁵ down to 10 Hz, with 10 points per decade, using 10 mV sin waves. The EIS results were analyzed using the fit program Zview 3.4. Before the cyclic voltammetry measurements, the analyzed samples were cathodically treated at -2100 mV for 180 seconds in 3.5% NaCl. The cyclic voltammetry measurements were initiated from -1.45 V vs. Ag/AgCl to -0.4V vs. Ag/AgCl with a potential scan rate of 1 mV/s and then reversed with the same scan rate until one complete cycle is formed.

To observe morphology and chemical composition of the 1050AA before and after anodic oxidation treatment, scanning electron microscopy (SEM, FEI QUANTA 200) coupled with X-ray energy dispersive unit was used.

3. Results and discussion

3.1. SEM and EDX analysis

In figure 1 are presented the SEM image of the top surface of 1050AA alloy taken before the anodic oxidation process. The electropolished surface of 1050AA present a cellular structure composed of randomly located depressions, bumps and small etch pits randomly distributed, which could be seeds for pore nucleation [6].
The influence of anodizing potential on the surfaces morphology formed in aged 1 M H$_2$SO$_4$ from 15 V up to 21 V in 3 V steps is shown in figure 2(a-c). It could be seen that the anodic oxidation process change the surface morphology of 1050AA samples and the nanopores are developed on anodic aluminum oxide layer. At the lowest potential (figure 2(a)), the 1050AA surface presents a disorganized structure with numerous irregularities and only a few nanopores randomly distributed could be observed. The mean diameter of nanopores is around 13 nm.

Figure 1. SEM images of electropolished 1050AA alloy surface.

Increasing the anodizing potential from 15 V to 18 V and 21 V, the surfaces morphology maintains the same irregular structure. The pattern distribution of nanopores still remains irregular, the nanopores density, as well as the nanopores diameters have increased and also, the numbers of defects have decreased. The mean diameter of nanopores increases up to 22 nm for anodizing potential at 18 V and 29 nm for anodizing potential at 21 V respectively.

Figure 2. SEM images of 1050AA alloy anodized at different potentials: (a) 15V, (b) 18V and (c) 21V.

The changing of surface morphology involves changes in chemical composition of surfaces as can be seen from table 1, where are presented the average contents of principal elements (Al, O, C and S) of analyzed samples.

From the dates presented in table 1 it could be observed that the increasing of anodizing potential lead to the decreasing of Al content and increasing of oxygen content. Also, from the EDX spectrum could be observed the presence of C and S peaks. The C presence is due to the fact that the samples
were cleaned with alcohol before SEM-EDX analyzes, and the presence of S could be attributed to SO$_4^{2-}$ ions entrapped into nanoporous aluminum oxide layer during anodic oxidation process [6, 12].

**Table 1.** The average contents of aluminum, oxygen, carbon and sulphur (wt %) as function of applied potential.

| Compound content (wt %) | Al  | O   | C   | S   |
|-------------------------|-----|-----|-----|-----|
| 0 V                     | 76.75 | 10.65 | 12.6 | 0   |
| 15 V                    | 46.74 | 46.27 | 2.19 | 4.8 |
| 18 V                    | 45.53 | 46.93 | 2.09 | 5.45|
| 21 V                    | 44.33 | 47.42 | 2.69 | 5.56|

3.2. Corrosion tests

3.2.1. Open circuit potential (OCP). In figure 3 are presented the evolution of open circuit potential with immersion time for electropolished 1050AA and anodized 1050AA samples at different applied potentials in 3.5% NaCl solution. After exposing to solution of electropolished sample, the open circuit potential oscillates around -700 mV vs. Ag/AgCl and has a slightly decreasing trend in evaluated interval. The potential fluctuations could be associated with the anodic reaction kinetics due to formation of natural oxide film and it dissolution under chloride ions presence [13].

![Figure 3](image)

**Figure 3.** The evolution of open circuit potential with immersion time for 1050AA: (1) Electropolished, (2) Anodized at 15V, (3) Anodized at 18V and (4) Anodized at 21V.

For anodized sample, the stationary steady state is attained after 9 hours of immersion in 3.5% NaCl solution. The anodized 1050AA sample at 15 V present the highest value of free potential, around -440 mV vs. Ag/AgCl, due to the small diameters and decreased number of pores. By increasing the anodization potential the potential steady state decreases to -550 mV vs. Ag/AgCl for anodized samples at 18 V and 21 V respectively due to the increases of numbers and nanopores diameters. For the both anodized at 18 V and 21 V samples, the free potential present a decreasing trend that could be associated with the dissolution of the barrier layers from the bottom of anodic oxide layers under chloride ions actions.
3.2.2. Potentiodynamic polarization (PD). In order to evaluate the electrochemical stability of prepared samples in 3.5% NaCl, the potentiodynamic polarization curves were determined and are presented in figure 4(a, b) for electropolished and anodized 1050AA samples. In order to assess the polarization domains for analyzed samples, the potentiodynamic polarization measurements were carried out.

The linear forms of potentiodynamic polarization curves showed in figure 4(a, b) present all three potential domains, namely: cathodic domain, the passive domain and the transpassive domain. The larger passive domain and the smaller value of current density in the transpassive domain show a higher corrosion resistance for the analyzed sample [14].

From figure 4(a) for electropolished 1050AA at the lower potential (15 V) could be observed all three domains, in comparison with the anodized samples at 18 V and 21 V respectively. In order to observe the passive domain for all anodized samples it was necessary to present in figure 4(b) a zoom of diagrams from figure 4(a).

![Figure 4.](image)

**Figure 4.** (a) Potentiodynamic polarization curves of 1050AA with different treatments in 3.5% NaCl. (b) Zoom of potentiodynamic polarization curves presented in figure 4(a).

For the electropolished 1050AA (figure 2(a)) it can be seen that the passive domain is more limited compared with anodized surfaces, ranging from -1.2 V to -0.66 V vs. Ag/AgCl. The lower passive domain means a poor corrosion resistance against chloride ions. Also, for electropolished 1050AA sample, the current density increase rapidly in the transpassive region which cause the dissolution of passive film and allow the chloride ions to reach metal base. Also, from figure 2(a), for anodized samples at 15 V it can be observed that the passive domain value is larger, ranging from -1.25 V to -0.59 V vs. Ag/AgCl. The larger passive domain for anodized 1050AA at 15 V in comparison with electropolished 1050AA shows that the anodic oxidation process improves the corrosion resistance of 1050AA alloy surface. The current density increase in the transpassive region and it is caused by the chloride ions penetration of nanoporous layer and dissolution of the aluminum oxide layer.

Increasing the anodizing potential, the passive domains for anodized samples at 18 V and 21 V increase to a more larger potential domains, ranging from -1.23 V to over -0.55 V vs. Ag/AgCl and -1.25 V to -0.53 V vs. Ag/AgCl, respectively. In the transpassive region for anodized samples at 18V and 21V, the current densities present lower values which mean that the electrolyte penetrate very slow the nanoporous aluminum oxide layer and the barrier layer from the bottom of aluminum oxide layer is thick enough in order to protect the metal base against the chloride ions.

3.2.3. Cyclic voltammetry (CV). The best way to analyze the pitting corrosion susceptibility for aluminum and its alloys in the presence of chloride ions is the cyclic voltammetry. The presence of the hysteresis in the transpassivation region of the recorded voltammogram curves shows that the pitting
corrosion phenomena appear. The existence of a hysteresis loop in cyclic voltammograms indicates a delay in repassivation of an existing pit when the potential is scanned toward negative direction [15].

The cyclic voltammograms of analyzed samples were recorded from -1.45 V to -0.4 V vs. Ag/AgCl, with a scan rate of 1 mV/s, and after that reversed maintained the same scan rate until a complete cycle is done.

The cyclic voltammograms (E vs. i) in linear form for electropolished and anodized 1050AA samples are presented in figure 5(a, b). The electropolished 1050AA alloy surface presents the largest hysteresis that could be associated with the pitting susceptibility and the poor repassivation performance of aluminum oxide layer.

![Figure 5. (a) Cyclic voltammograms of 1050AA alloy: (1) Electropolished, (2) Anodized at 15 V, (3) Anodized at 18 V and (4) Anodized at 21 V. (b) Zoom of cyclic voltammograms presented in figure 5(a).](image)

Anodizing the electropolished samples at 15 V, the obtained nanoporous aluminum oxide layer show a decreased surface hysteresis in comparison with electropolished sample which mean a rapid repassivation and also a better corrosion resistance. In order to obtain a better view of pitting susceptibility hysteresis for anodized samples at 18V and 21V, respectively, it was necessary to present in figure 5(b) a zoom of diagrams form figure 5(a). Increasing the anodizing potential, the pitting susceptibility decrease and the repassivation process occurred more rapidly confirming that the anodic oxidation improve the corrosion resistance of 1050AA.

The nanoporous aluminum oxide layer formed on electropolished 1050AA sample at 15 V show a decreased surface of hysteresis in comparison with the hysteresis recorded for electropolished sample and also a better corrosion resistance. By increasing the anodizing potential the corrosion resistance of 1050AA samples is increased and also the pitting susceptibility is decreased.

4. Conclusion

The surface morphology and the anti-corrosive performance of electropolished and anodized 1050AA samples were studied.

The anodic oxidation process in aged sulphuric acid at different potentials form on electropolished 1050AA samples a thick nanoporous aluminum oxide layer with improved anti-corrosive performances in comparison with electropolished samples.

By increasing the anodizing potential, the nanopores diameters have been increased and they become more regulate and also the thickness of aluminum oxide layer increase.

The electrochemical measurements show that in comparison with electropolished sample the anodic oxidation increase the passive domain and the anti-corrosive performances of 1050AA. By increasing the anodizing potential, the obtained nanoporous aluminum oxide layers show a decreasing pitting susceptibility and an improved corrosion resistance.
The electrochemical assays confirm that the anodic oxidation improve significantly the anti-corrosive performances of 1050AA alloy, being a cheap method to increase the lifecycle of aluminum alloy parts and pieces.

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