Evaluation of Sealing Process on the Surface Properties of Nanoporous Aluminum Oxide Layers Electrochemically Growth on 1050 Aluminum Alloy Surface

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Abstract. Thanks to its low density, aluminum and its alloys are extensively used in the transport and construction industries. The improving of aluminum and its alloys corrosion resistance is an extensively studied topic. Different methods are applied to improve the corrosion resistance of aluminum and its alloy: painting, waxing, zinc-chromate priming, conversion coatings and also anodic oxidation. The anodic oxidation is the most used method to fabricate nanoporous aluminum oxide layers, with controlled thickness and pores diameters, on aluminum and its alloys surfaces. The aim of this work is to evaluate the influence of the sealing process of the nanoporous aluminum oxide layers obtained by anodic oxidation on 1050 aluminum alloy surface. Scanning electron microscopy (SEM) was used to observe the morphological structure of untreated and modified surfaces. Corrosion behavior of oxidized 1050 aluminum alloy, sealed oxide layer and untreated 1050 aluminum alloy were investigated using electrochemical methods such as open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PD). The experimental results show that the anodic oxidation process improve the corrosion resistance of 1050 aluminum substrate and the sealing process improve even more the anticorrosive properties.

1. Introduction

From economical and technical point of view, light weight materials, especially aluminum and its alloys are becoming increasingly important for automotive, aerospace and construction industries [1, 2].

The corrosion performances of aluminum and its alloys are an important industrial problem. Aluminum naturally develop a thin aluminum oxide layer at material-environment interface, after the exposure to air, but the formed native aluminum oxide layer is not uniform and do not offer enough corrosion protection against aggressive factors [1, 2].

In order to fabricate corrosion resistant ceramic coatings on aluminum and its alloys, a wide range of techniques have been employed: micro-arc oxidation, physical vapor deposition, chemical vapor deposition, heat treatments, anodic oxidation, etc. [3-8]. Anodic oxidation process is used to form on aluminum and its alloys surfaces aluminum oxide layers with complex structures and improved anticorrosive and wear resistance performances [9-11].

The anodic oxide layers structures depend by the applied parameters during the anodizing processes (current, potential, electrolyte stirring rate), the electrolyte type and also by the finishing methods used for the pretreatment of aluminum substrate [9, 11].
Depending by the electrolyte type, the oxide layer could present a barrier-type structure or a duplex structure composed by an outer porous-type layer and an inner barrier-type layer. A sealing process is required to improve the corrosion resistance of aluminum oxide layers. The anodic porous aluminum oxide layers can be sealed by boiling in hot water or using different cold sealing solutions [12-15].

S. Wang et al [13] have evaluated different sealing methods on corrosion resistance of anodized Al2O3. F. Snogan et al [14] evaluate the corrosion properties of anodized aluminum sealed with 5.5 g/L Ni and Co acetate solution.

A comparison between different sealing methods was done by Y. Zuo et al [15] for different aluminum alloys anodized in 180 g/L H2SO4 solution. V. M. Dumitrascu and his co-workers [16] evaluate the influence of hot sealing process in 6% sodium molibdate for anodized Al1050 on corrosion resistance in 3.5% NaCl solution.

Electrochemical assays and especially electrochemical impedance spectroscopy are powerful methods to evaluate the corrosion resistance of nanoporous aluminum oxide layers obtained by anodic oxidation and exposed to aggressive environments [11, 15-17].

The electrochemical impedance spectroscopy data can be fitted to an appropriate equivalent circuit and allows the polarization resistance determination of porous aluminum oxide layers.

J.-P. Dasquet et al [17] evaluate the corrosion resistance of sealed aluminum oxide layers by EIS during the immersion in 0.2 M K2SO4 solution.

V.R. Capellosi and his co-workers [18] establish the corrosion resistance of sealed anodized Al2O3 by fitting the EIS specters and determine the values of polarization resistances.

Therefore, the aims of this work are to evaluate and compare the corrosion resistance of untreated Al1050, anodized Al1050 and sealed in K2Cr2O7 anodized Al1050 immersed in 3.5% NaCl solution using electrochemical assays. SEM and EDX analysis were used to investigate the structure of unsealed or sealed anodic oxide layers.

2. Experimental procedures

As received 2 mm thick Al1050 alloy sheet was cut into 35 x 30 mm size coupons. Prior to the anodizing processes, the Al1050 samples were mechanical wet-polished with 1000 and 1500 grit SiC emery paper, rinsed with distilled water, ultrasonically cleaned in alcohol and distilled water and finally dried under hot air in oven. The anodic oxidation processes were carried out in a standard two electrodes electrochemical cell in a solution of 1 M H2SO4 in which was added 1 g/L Al2(SO4)3 x 18 H2O at 300 rpm. The anodizing procedures were conducted for 15 minutes at an applied potential of 17 V at ambient conditions.

The anodized Al1050 samples were sealed by immersing in 6 g/L K2Cr2O7 at 95°C for 60 minutes, cleaned with distilled water and dried under hot air in oven for 60 minutes.

The structure of anodic oxide layers before and after sealing process was evaluated using the scanning electron microscope coupled to X-ray energy dispersive analyzer FEI QUANTA 200.

The corrosion tests were done in 3.5% NaCl solution that simulates the aggressive marine environment. The standard electrochemical cell used in the corrosion assays was composed by a Pt-Rh grid as counter electrode, an Ag/AgCl electrode (saturated KCl solution, E=+199 mV vs. NHE) as reference electrode and as prepared Al1050 samples as working electrode. The electrochemical cell was connected to a potentiostat/galvanostat PGZ100. The experimental data were recorded with VoltaMaster 4 software.

The open circuit potential (OCP) were measured for 1 hour after 17 hours of immersion, in order to attain a steady state. The electrochemical impedance spectroscopy (EIS) tests were conducted over a frequency range of 10² down to 10⁰ Hz with 10 points per decade, using 10 mV sin wave. The EIS specters were fitted using Zview 3.4f software and the quality of obtained results were evaluated using the chi-square (chi²) values, with values bellow 10⁻³. The potentiodynamic polarization (PD) curves were recorded from -1.45 vs. Ag/AgCl to -0.4 V vs. Ag/AgCl with a scan rate of 1 mV/s. Before the recording the potentiodynamic polarization curves, the analyzed Al1050 samples were cathodically treated at -2.1 V vs. Ag/AgCl for 3 minutes in 3.5% NaCl solution.
3. Results and discussions

3.1. Surface morphology and chemical composition

The SEM micrographs were recorded on Al1050 surfaces before and after the anodizing process and also, after the sealing process carried out in 6% K$_2$Cr$_2$O$_7$ at 95°C for 60 minutes.

The untreated Al1050 (Figure 1 (a)) show a rough surface, with numerous heights and valleys that present different sizes and forms. On untreated Al1050 surface can be identified nanopits with various shapes and diameters that will act further as location for nanopores developments.

![Figure 1. Top-view SEM image of (a) Untreated Al1050, (b) Anodized Al1050 and (c) Sealed anodized Al1050.](image)

The recorded SEM image exposed in Figure 1 (b) reveal that the Al1050 surface morphology was changed after the anodic oxidation process. The heights were dissolved during the anodic oxidation process and an increased numbers of nanopores were formed. Due to the short anodizing process duration, the nanopores present various shapes and diameters and their distribution is not ordered.

After the sealing process, the SEM image (Figure 1 (c)) reveal that the morphology of anodized nanoporous aluminum oxide layer was changed and the nanopores present decreased diameters.

The chemical compositions of all 3 analyzed surfaces presented in figure 1 are exposed in Table 1. For the untreated Al1050, the chemical elements identified were: aluminum (92.19 wt%), oxygen (1.94 wt%) and carbon (5.97 wt%). The presence of carbon is caused by the alcohol washing of Al1050 before the morphological and compositional analyzes.

The anodic nanoporous aluminum oxide layer present a chemical structure composed by aluminum (43.98 wt%), oxygen (48.75 wt%), carbon (2.71 wt%) and sulphur (4.56 wt%). During the anodic oxidation process, the SO$_4^{2-}$ anions were incorporated in the formed aluminum oxide layer.

After the sealing of anodized Al1050, the EDX analyzes revel that the chemical composition of aluminum oxide layers was changed. In addition to aluminum (42.57 wt%), oxygen (47.14 wt%), carbon (5.49 wt%) and sulphur (4.17 wt%) can be identified chromium (0.93 wt%). During the sealing
process in 6% K$_2$Cr$_2$O$_7$ at 95°C, the anodic aluminum oxide was hydrated and the Cr$^+$ ions were absorbed into the nanopores.

### Table 1. Chemical composition of untreated Al1050, anodized Al1050 and sealed anodized Al1050.

| Type of surface           | Element | Al [wt%] | O [wt%] | C [wt%] | S [wt%] | Cr [wt%] |
|---------------------------|---------|----------|---------|---------|---------|----------|
| Untreated Al1050          |         | 92.19    | 1.94    | 5.87    | -       | -        |
| Anodized Al1050           |         | 43.98    | 48.75   | 2.71    | 4.56    | -        |
| Anodized and sealed Al1050|         | 42.57    | 47.14   | 5.49    | 4.17    | 0.93     |

### 3.2. Electrochemical assays

#### 3.2.1. Open circuit potential (OCP).

The potential-time measurements for untreated Al1050, anodized Al1050 and sealed anodized Al1050 in 3.5% NaCl solution are shown in Figure 2. The evolution of OCP in time was monitored in order to observe the changes that occur at the electrode surface (the electrode oxidation tendency) after the immersion in the corrosive electrolyte.

From Figure 2 can be observed that after 17 hours of exposure all the samples reach a steady state. The untreated Al1050 present slightly fluctuation around -700 mV vs. Ag/AgCl due to the dissolution of native aluminum oxide layer under the aggressive action of chloride ions from the electrolyte.

For the anodized Al1050 and sealed anodized Al1050, after 17 hours of immersion, the open circuit potential values remain almost unchanged being attained equilibrium states around -770 mV vs. Ag/AgCl and -795 mV vs. Ag/AgCl, respectively.

![Figure 2](image-url)  
**Figure 2.** The evolution of open circuit potential recorded for (1) untreated Al1050, (2) anodized Al1050 and (3) sealed anodized Al1050 immersed in 3.5% NaCl.

The decreased values of steady state for anodized and sealed anodized Al1050 with immersion time could be related to the hydration of unsealed or sealed anodic aluminum oxide layers and the increasing of cathodically activity related to the partial dissolution of anodic oxide layers [19]. The stable values attained at the long exposure time might be attributed to the equilibrium between anodic and cathodic reactions that take place at electrode interface [18].

#### 3.2.2. Potentiodynamic polarization (PD).

The potentiodynamic polarization resistances curves recorded for untreated Al1050, anodized Al1050 and sealed anodized Al1050 in a linear representation are exposed in Figure 3 (a) and in a semi-logarithmic representation are exposed in Figure 3 (b). The
recorded diagrams for all three analyzed surfaces were compared in order to evaluate the passive
domains and the corrosion current of analyzed samples.

Analyzing the PD diagrams presented in Figure 3 (a) can be observed three potential domains:
cathodic domain, passive domain and transpassive domain. From all three potential domains, the
passive domain is related with the corrosion resistance of tested samples: the higher passive domain
indicate the improved anticorrosive properties of the sample.

In Figure 3 (a) are displayed the PD diagrams recorded for the all 3 analyzed surfaces. The
untreated Al1050 present the lowest passive domain, ranged between -1.25 V vs. Ag/AgCl and -0.68
V vs. Ag/AgCl. In the transpassive domain, the current density values increase exponentially,
indicating the dissolution of aluminum substrate under the aggressive action of chloride ions from the
electrolyte.

For the unsealed or sealed anodized Al1050 samples the recorded passive domains are larger, being
recorded between -1.18 V vs. Ag/AgCl and -0.63 V vs. Ag/AgCl and between -1.19 V vs. Ag/AgCl
and -0.58 V vs. Ag/AgCl. Also, the current density recorded in the transpassive domains are lower in
comparison with the values of current density recorded for untreated Al1050 sample.

The increasing of passive domains reveal that the anodizing and sealing processes improve the
corrosion resistance of Al1050 samples exposed in 3.5% NaCl solution. From Figure 3 (b) quantitative
information about the corrosion potential (E\text{corr}) and corrosion current density (\text{i corr}) can be
determined using the Stern-Geary equation [20] and are summarized in Table 2.

$$i_{corr} = \frac{B}{R_p}$$

where \(i_{corr}\) is the corrosion current density, \(R_p\) is the polarization resistance and \(B\) is a constant,
calculated using the equation:

$$B = \frac{b_a |b_c|}{2.303(b_a + b_c)}$$

where \(b_a\) and \(b_c\) are the Tafel slopes for anodic and cathodic reactions, respectively.

From Table 2 can be observed that the corrosion potential show an increasing tendency from
untreated Al1050 to anodized Al1050 followed by a slightly decrease from anodized Al1050 to sealed
anodized Al1050. Also, the anodizing and sealing processes decrease the corrosion current densities in comparison with the untreated Al1050.

### Table 2. The corrosion potential and the corrosion current determined for the analyzed samples immersed in 3.5% NaCl solution.

| Type of surface           | $E_{i=0}$ [mV vs. Ag/AgCl] | $i_{corr}$ [$\mu$A/cm$^2$] |
|---------------------------|-----------------------------|-----------------------------|
| Untreated Al1050          | -1251.9                     | 16.1862                     |
| Anodized Al1050           | -1186.2                     | 6.2711                      |
| Anodized and Sealed Al1050| -1191.5                     | 3.9103                      |

The results confirm that the anodic oxidation process improves the anticorrosive performances of Al1050 and the sealing process improves even more the corrosion resistance of aluminum substrate.

#### 3.2.3. Electrochemical impedance spectroscopy (EIS).

Figure 4 shows the Nyquist representation of electrochemical impedance spectroscopy specters and their fitted results for untreated Al1050, anodized Al1050 and sealed anodized Al1050 immersed in 3.5% NaCl solution for 18 hours.

From Figure 4 (a) it is clear that the diameter of capacitive arc is higher for anodized Al1050 and sealed anodized Al1050, so, in Figure 4 (b) it is presented a zoom of Figure 4 (a) to observe the EIS specter of untreated Al1050.

For the untreated Al1050 the recorded EIS specter (Figure 4 (b)) present a single capacitive loop that corresponds to the native aluminum oxide layer formed on Al1050 substrate. For anodized Al1050 and sealed anodized Al1050, from Figure 4 (a), 2 time constants can be identified, that corresponds to the complex structure of anodic aluminum oxide. The first time constant, recorded at high frequency is attributed to the porous aluminum oxide layer from the anodic oxide–electrolyte interface and the second time constant is attributed to the inner barrier-type aluminum oxide layer from the aluminum substrate–anodic oxide interface (barrier aluminum oxide layer from the bottom of nanopores).

Figure 5 presents the equivalent circuits used in the fitting of EIS experimental results recorded for untreated Al1050, anodized Al1050 and sealed anodized Al1050.
For the untreated Al1050, a simple equivalent circuit (Figure 5 (a)) was used to fit the EIS data and was composed by: R_e – electrolyte resistance, R_n – the native aluminum oxide layer resistance and CPE_n – the constant phase element.

Based on the complex structure of anodic aluminum oxide layer, the EIS specters of anodized Al1050 and sealed anodized Al1050 presented in Figure 4 (a) were fitted with the equivalent circuit shown in Figure 5 (b) made from 2 simple circuits connected in parallel, one for each component of anodic aluminum oxide layer. The R_e is the electrolyte resistance, the R_p and CPE_p are the polarization resistance and the constant phase element of porous aluminum oxide layer and the R_b and CPE_b are the polarization resistance and the constant phase element of the barrier aluminum oxide layer from the bottom of pores.

The CPE element was used to account for a non-ideal frequency response in equivalent circuits instead of capacitance elements, in order to explain the depression of capacitance semicircles caused by the surface heterogeneity, roughness, porosity, impurities, etc. [20].

The impedance of the constant phase element (CPE) was expressed accordingly with A. Lasia equation [21]:

$$Z_{CPE} = \left[ Q \omega^\alpha \right]^{-1}$$  \hspace{1cm} (3)

where: Q is a frequency independent parameter, j is the imaginary number ($j = \sqrt{-1}$), \(\omega\) is the angular frequency and \(\alpha\) is an exponential factor ranged between -1 and 1. The CPE response correspond to those of a capacitor, a resistor or an inductor when the \(\alpha=1\), \(\alpha=0\) or \(\alpha=-1\), respectively.

Fitting the EIS experimental data using the proposed equivalent circuits, the specific polarization resistances of analyzed samples were determined. For the untreated Al1050, the specific polarization resistance has the lowest value, around 0.163 Mohm cm\(^2\) and for the anodized and sealed anodized Al1050, it were determined values of polarization resistance of 1.697 Mohm cm\(^2\) and 9.356 Mohm cm\(^2\), respectively.

Analyzing the specific polarization resistances values can be observed that the anodic oxidation process increase the corrosion resistance with more 10 grade of magnitude and the sealing procedure if anodic aluminum oxide layer increase even more the anticorrosive performances of Al1050 substrate.

The specific polarization resistances determined by fitting the electrochemical impedance spectroscopy specters are in good agreement with the results of potentiodynamic polarization diagrams and the evolution of open circuit potential.

4. Conclusions

The untreated Al1050, anodized Al1050 and sealed anodized Al1050 were characterized morphologically by SEM-EDX and electrochemically by open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy.
The anodic oxidation process changes the morphological structure of the untreated Al1050, the anodic oxide layer being strongly porous and disorganized. After the sealing procedure, the anodic aluminum oxide layer is still heterogeneous.

The corrosion behavior of analyzed samples was evaluated using electrochemical assays, after the immersion in 3.5% NaCl solution.

The anodized and sealed anodized aluminum oxide layers show higher reactivity after the immersion into electrolyte, the anodic layers become hydrated and the anticorrosive performances increase.

The potentiodynamic polarization measurements reveal that the passive domains increase for the anodized Al1050 and sealed anodized Al1050 in comparison with the passive domain of untreated Al1050. Also the recorded corrosion currents present a decreasing tendency concomitant with the increasing of treatment steps.

The electrochemical impedance spectroscopy diagrams indicate that the specific polarization resistance increase with 10 grade of magnitude for anodized Al1050 in comparison with the untreated Al1050 and the specific polarization resistance is increased with almost 8 grade of magnitude after the hot sealing process in K2Cr2O7 solution.

The anodic oxidation process followed by the sealing procedure increase the corrosion resistance of Al1050 exposed to corrosive environments.

5. References
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