Effect of the layer of anodized 7075-T6 aluminium corrosion properties

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Abstract. Aluminium alloys are widely used in various sectors of industry. The 7075-T6 alloy corresponding to an Al-Zn T6, is mostly used as structural component in the aviation industry, due to the good relationship between weight and mechanical properties. However, the negative point of this alloys is the resistance to corrosion, which is why they need to be coated with an anodic film. Different surface treatments, such as anodizing, are used to improve corrosion resistance. Anodizing is an electrolytic process by which a protective layer of "alumina" is formed, this is formed by the passage of an electric current in an acidic electrolyte. This investigation presents a study of the effect of the thickness of layers of alumina deposited by anodized method, in the corrosion resistance of 7075-T6 aluminium. This study was performed by using in a solution of tartaric acid - sulfuric acid and an inorganic salt. To evaluate the influence alumina layer thickness on the corrosion properties some tests were carried out by using the electrochemical spectroscopy impedances (EIS) technique and Tafel polarization curves. It was found that the grown of the thickness of film favourably influences in the corrosion resistance.

1. Introduction
Aluminium alloys are widely used in different industry sectors [5-10]. The negative point of these alloys is the corrosion resistance, whereby they need to be coated with an anodic film. Different types of surface treatments, such as anodized, are used to improve corrosion resistance [1-11]. The anodized is an electrolytic process, in which a protective layer of "alumina", it is generated on the surface of the aluminium through current flow, gives the aluminium excellent anticorrosive properties.

Despite the high corrosion protection obtained by the anodizing technique, one of the main current concerns is the great environmental effect resulting from the use of chromic acid [6,7], commonly used as electrolyte in the realization of these coatings [2-4]. It has been known that chromium (VI) compounds (also known as chromates) have been used for the last 60 years and are toxic and dangerous to the ecosystem [5], in addition to causing carcinogenic problems to people who are exposed and in contact with chromates.

For this reason, one of the challenges facing the coating industry is the production of cleaner and less harmful products for the environment. This regard, some electrolytic baths of lower toxicity have been investigated and capable of even improving the mechanical and corrosive properties of anodizing coatings of aluminium alloys [8-9]. In this work, the anodized were made using a solution of tartaric acid - sulfuric acid and a molybdic sodium salt as the electrolytic bath and studied the effect of the thickness of the alumina layer in corrosion resistance of the 7075-T6 aluminium alloy.
2. Experimental development

2.1. Anodized process

A. The specimens of 7075-T6 aluminium alloy (chemical composition showed in Table 1), with dimensions of 40mm, 50mm and 5mm of width, long and high respectively, were subjected to a conventional cleaning treatment, consisting of degreased with NaOH 5% to 50°C for about 3 minutes. Subsequently, the specimens were rinse in distilled water for 2 minutes, and were pickled for 5 seconds with a solution of HCl 5% to 25°C. Then this was rinse in distilled water for 2 minutes.

In the step of anodized, the specimen was completely immersed in an electrolytic cell containing an aqueous acidic solution composed of 0.40M sulfuric acid, 0.53M of tartaric acid and 0.25M sodium molybdate a Temperature of 20 °C and pH between 1 and 1.2 [11]. The aluminium parts played the role of anode, while the cathode was composed of AISI 304 stainless steel plates.

A potential difference of 14V was used and immersion times of 40, 60 and 90 minutes. After this time the pieces were extracted and were rinse in deionized water for 3 minutes. Subsequently, were sealed with boiling deionized water for 40 minutes and dried with a hot air stream.

2.2. Characterization of specimens

The thickness of the alumina layer was determined by scanning electron microscopy (SEM) with a EVO MA 10 equip operated at 20kV.

Tests of electrochemical impedance spectroscopy and potentiodynamic polarization were performed with a Gamry potentiostat model PC4. All tests were at room temperature, using a glass cell in where located working electrode (aluminium alloy) with an area of 0.079 cm² a reference electrode of Ag/AgCl and a platinum wire as counter electrode, immersed in a solution of NaCl 3.5%. This solution was chosen because of simulates a marine solution, which corrodes active materials, forming chlorides over the metal [4].

Table 1. Chemical Composition of Alloy 7075-T6.

| Alloy   | Al  | Zn  | Cu  | Mg  | Mn  |
|---------|-----|-----|-----|-----|-----|
| 7075-T6 | bal | 5.1 | 1.152 | 2.163 | 0.037 |

Impedance spectroscopy test and potentiodynamic polarization were performed. An AC voltage of 10mV was use in the first case, with initial and final frequencies of 100,000Hz and 0.1Hz respectively. On the potentiodynamic polarization test were used potentials between -250mV to 250mV with respect to corrosion potential, scan rate of 2mV/min in anodic direction.

3. Results and discussion

3.1. Thickness of the anodized layer

The thickness of the anodized layer was measured from the micrographs shown in Figure 1. It is noted that the thickness of the alumina layer in specimen AA7075-T6 varies directly with the anodizing time. A 40 minutes immersion time produces a thickness of 6.14μm, while times of 60 and 90 minutes produce an increase of the oxide film of 8.4μm and 14.9μm respectively. The images of the left side of Figure 1 correspond to the results of X-ray energy scattering spectroscopy microanalysis, EDS made to the coating. It is observed that the layers are composed mainly of oxygen and aluminium, this corroborates the existence of a layer of deposited alumina.
Figure 1. SEM of anodized AA7075-TSA (a) 40 minutes, (b) 60 minutes and (c) 90 minutes.
3.2. Electrochemical Impedance Spectroscopy (EIS)

The results obtained in the Nyquist diagrams (Figure 2) show an increase of the diameter of the semicircles with the increase in the thickness of the anodized layer, for thicknesses lower than 14.9 μm. It is observed that the less resistive behaviour is obtained with the aluminium free of superficial treatment, this phenomenon is attributed to that the anodized samples contemplate a layer of alumina that prevents the transfer of reducible species to the base metal. The behaviour of the curve of EIS for the aluminium with an anodized thickness of 14.9 μm shows a diffusion phenomenon that indicates a gradient of the concentration of ionic charges in the interface metal-solution, which evidences the protection or barrier of the coating to the corrosion.

The obtained values of the resistance to the polarization of the electrode with the thickness of the layer were of 1,610 Mohms for a coating of 14.9 μm microns and values of 1.25 Mohms, 38.05 Kohms for 8.34 μm and 6.14 μm respectively.

![Figure 2. Nyquist for anodic layers 6.14 μm, 8.34 μm, 14.9 μm and for the Specimen pattern.](image)

3.3. Potentiodynamic polarization curves (Tafel)

Figure 3 shows the potentiodynamic polarization curves (Tafel) of the aluminium 7075-T6 with and without anodized exposed to a saline environment of 3.5% by weight of NaCl. It is observed that the increase in the thickness of the anodized layer causes displacement of the cathodic zones towards the smaller values of current, leading to the decrease of the speed of corrosion of the material. The current major of the corrosion is reached when the aluminium is found without anodized, while when coated with a layer of Al2O3 of 14.9 μm decreases considerably. The change the corrosion potential to the highest values indicates that aluminium tends to behave as noble with respect to the other samples.

![Figure 3. Polarization curves for the anodic layers 6.14 μm, 8.34 μm, 14.9 μm and for the specimen pattern.](image)
The Figure 4 shows the behaviour of the corrosion rate versus the thickness of the layer of anodized.

![Graph showing corrosion rate vs. thickness of the layer of anodized.](image)

**Figure 4.** Corrosion rate vs. thickness of the layer of anodized.

### 3.4. Equivalent circuits

Equivalent circuits are used to describe the electrochemical behaviour and to calculate the parameters of interest such as electrolyte resistance (Rs), charge transfer resistance (Rct) and electrochemical double layer capacitance (Cdl). In real cells the double layer capacitor, with behaves with frequency as a constant phase element (constant phase element: CPE) and not as an ideal capacitor. The CPE element is use in the model in place of the capacitor to compensate for non-homogeneity in the system. The impedance of this element (ZCPE) is determined by the following equation:

\[
Z_{CPE} = Y_0 - 1(iw)^n
\]  

(1)

Where \(Y_0\) is the constant CPE, \(w\) is the angular frequency and \(n\) is an exponent used to indicate the heterogeneity of the roughness surface, usually is the value of the slope and is in the range of 0.5 to 1.

In order to analyse the metal/electrolyte interface in anodic layers with thickness lower than 14.9µm, a modified Randless circuit with a constant phase element was chosen, which allowed to obtain a good fit with the experimental data. Figure 5 represents the proposed equivalent circuit.

![Diagram of the proposed equivalent circuit.](image)

**Figure 5.** Equivalent Circuit for impedance diagrams obtained for low thicknesses to 14.9µm of the specimen of Al7075-T6.

For a thickness of 14.9µm, was chosen the equivalent circuit of Figure 6. In this the Randles circuit is included an impedance of Warburg (W) that represents the diffusion phenomena that take place.
4. Conclusions
It was determined that the thickness of the oxide film increases the corrosion resistance of the aluminium. Higher thicknesses generate lower corrosion rates. The best results were obtained with a 14.9μm layer.

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