FORMATION OF CERAMIC NANOSTRUCTURED COATINGS ON ALUMINIUM FOR ENHANCED CORROSION RESISTANCE

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Abstract:
Double anodisation has been considered as a novel technique to form ceramic nanostructured coatings on aluminium alloys for corrosion protection. In this study, the anodic alumina was produced by two type anodising process (conventional anodisation and double anodisation) in 1 M sulphuric acid at constant cell potential of 25 V. The temperature was kept constant at 5°C during both anodising processes. Anodised samples exposed to 0.2 M K₂SO₄ solution for up to 24 h have been studied by means of electrochemical impedance spectroscopy (EIS). The results reveal that the EIS technique is a good tool for obtaining detailed information on the influence of the ageing process on anodised aluminium. Potentiodynamic polarization tests were conducted to assess the corrosion resistance of the coatings. Measurements of polarization resistance show that a double anodising process confers on material a clear improvement with corrosion in very aggressive medium. The analysis was completed with the aid of the SEM. It was found that the modified anodising, an environmentally friendly coating method, could produce an oxide coating with good corrosion protection for the Al–Mg alloy.

Keywords: Aluminium, Anodisation, Corrosion protection, electrochemical impedance spectroscopy, nanostructured coating.

1 Introduction

Alumina (Al₂O₃) ceramics is the most important technical oxide ceramic material and has the widest range of applications. It is characterized by high strength and hardness, low density, temperature stability, and high wear and corrosion resistance [1]. Aluminium and its alloys exposed to air are naturally protected by an oxide film. However, this layer is heterogeneous and does not provide adequate corrosion resistance in many environments. Aluminium alloys often undergo a treatment, mainly to improve corrosion resistance [2].

This important treatment used for the protective, decorative or adhesive surface treatment of aluminium is anodic oxidation (anodisation). Anodisation consists of the controlled electrochemical growth of an aluminium oxide film by the anodic polarization of the aluminium substrate in a particular electrolyte solution [3, 4].

Since the application of two steps procedure (of anodisation) results in self organized porous structures on anodised aluminium [5], this technique become promising for preparing such ordered porous structures due to its low cost and relative easy use. The procedure involves two separate anodisation processes. The first
anodisation process consists of a long period of anodisation forming disorderly porous structure. After the removal of this porous structure, an array of highly ordered dimples is formed on aluminum. These dimples act as initiation sites for growing highly ordered porous structure. Characteristic parameters of porous anodic alumina including pore diameter, interpore distance, porosity, pore density and thickness of the oxide layer can be easily controlled by adjusting anodising conditions such as type of electrolyte, anodising potential (in potentiostatic regime), current density (in galvanostatic regime), temperature and duration of the process. Nowadays, it is possible to obtain by anodisation porous alumina structures with pore diameters ranging from several to several hundred nanometers and depth of pores exceeding hundreds of microns [6].

The oxide layer formed in this process has a duplex structure consisting of the inner barrier layer and the outer porous layer. The outer layer is characterized as a close-packed array of columnar hexagonal cells, each containing a central pore that is normal to the substrate surface, and between the outer layer and the substrate there is a barrier-type film layer. The barrier layer is very thin and dense. The outer porous layer is a much thicker, porous oxide that has a close-packed hexagonal cells structure. Due to their porous structure, anodic films are sensitive to aggressive environments.

Generally, the corrosion resistance provided by anodic films depends on the properties, integrity and thickness of the films and sealing quality is one of the factors affecting the film properties [7, 8]. However, previous work showed that the total resistance of anodic aluminium is governed by the barrier layer because of its compactness and tightness vis-à-vis the harsh environment outside [9].

In this work, the electrochemical behaviour of anodised Mg-Al alloy in neutral NaCl (3.5%) solution was investigated using electrochemical methods and SEM. The aim of this research is to estimate corrosion resistance of aluminium anodised in the sulfuric acid by the two techniques (anodisation traditional and double anodisation). The aging behaviour of films, carried out according to these two techniques, was studied using the electrochemical impedance method under neutral K₂SO₄ (O. 2 M).

2 Experimental

Rectangular coupons (50 × 30 × 3mm) of a cast Al–Mg alloy were used as the substrate for anodic coating deposition. The composition of this alloy (wt %) was 2.75 % Mg, 0.1 % Mn, 0.4 % Si, 0.1% Cu, 0.4% Fe, 0.25% Zn, 0.25% Cr)) other, and Al balance.

2.1 Traditional anodising

Prior to anodising, the specimens were treated as follows:

(a) chemical polishing in a solution containing HNO₃ and H₃PO₄ in a respective rate of 15% and 85% (V/V) at 85 °C for 2min, (b) cold water rinsing, (c) etching in 1M NaOH solution at room temperature for 1 min, (d) cold water rinsing, (e) chemical pickling in with 30% in volume HNO₃ solution at room temperature for 30 s (f) deionised water rinsing and drying. Afterwards, the specimens (exposed area 2x2 cm²) were anodised in vigorously stirred 1 M sulphuric acid electrolyte maintained 5 °C for 6 hours. The voltage applied across the electrodes is 25 V, and then the specimens washed in deionised water and dried.
2.2 Double anodising

Prior to anodising, aluminium sheet was degreased in acetone, and electropolished at a constant current of 500 mA cm$^{-2}$ for 1 min at 10°C in an electrolyte containing perchloric acid and ethanol in a ratio of 1:4 by volume and anodised at 5 °C in 1M sulfuric acid solution at a constant potential of 25V for 10minutes. Then the anodic oxide layer, part of which was disordered, was removed in a phosphoric acid. Next, the plate was anodised again for 6 h under the conditions identical to those for the first anodising step. The SEM image of alumina films is shown in figure 1.

3 Results and discussion

The surface structures of alumina layers obtained after anodising are shown in figure. 1.

![Figure 1: Top view SEM image of porous alumina. Anodising was conducted in 1 M sulfuric acid solution at 5°C at 25 V for 6 h (a) Conventional anodising process. (b) Double anodising processes.](image-url)
The porous structure of the anodic layer formed by double anodising is much more orderly and regular than that obtained by conventional anodising (Figure 1.b). The surface of the anodic layer giving by the conventional anodising presents many cavities a few microns in length. These cavities probably correspond to the Al₂Mg-M particles (M are the other elements which contains like traces in aluminium) dissolved during acid scouring. Consequently, it appears that the formation of the oxide layer during anodising follows the initial roughness of surface.

After anodising, the specimens were coated with resin, leaving an area of 1 mm² exposed for electrochemical testing. The potentiodynamic polarization tests were carried out using a Potentiostat-Galvanostat (PGZ 301) the anodic polarization curves were measured in 3.5% NaCl solution at 25°C with a scanning rate of 1 mV/s. The potential applied to the sample vary continuously -1500 mV to+1500 mV/SCE. A saturated calomel electrode (SCE) was used as reference electrode and the counter electrode was platinum.

3.1 Corrosion tests

Potentiodynamic polarization results for the anodised samples of Al–Mg alloy in a 3.5% NaCl solution are shown in Fig. 2. There is a considerable decrease in the anodic current of the anodised samples compared to the uncoated alloy substrate. The corrosion current density of the anodised samples was significantly lower than that of the uncoated alloy. The corrosion potentials of the two anodised samples were around -680.00 mV, which is higher than that for the substrate (about –698.9 mV). The corrosion protection efficiency of the anodic coatings is evident from both the increase in corrosion potential as well as the reduction in the corrosion current density. The polarization resistance (Rp) values were determined using the relation-ship [10] [11]:

\[
R_P = \frac{\beta_a \beta_c}{2.3I_{corr}(\beta_a + \beta_c)}
\]

Where \(I_{corr}\) is the corrosion current density

A summary of the results of the potentiodynamic corrosion tests is given in Table 1. The data clearly show the enhanced corrosion protection afforded by the coatings. The two coated samples showed a higher corrosion resistance than the Al–Mg alloy substrate. The double anodising coating had the best corrosion resistance. The corrosion potential \(E_{corr}\) and the corrosion resistance \(R_P\), respectively, increased from -698.9 mV and 57.32 KΩ.cm², for the substrate, to -682.5 mV and 80.22 KΩ .cm², for the double anodising coating. The corrosion current density obtained by double anodising processes is much lower because the layer is more uniform and free from defects such as pits and intermetallic areas located in the layer obtained by conventional anodising.
Figure 2: Potentiodynamic polarization curves of the anodic layer in a 3.5% NaCl test solution.

Table 1- The results of the potentiodynamic corrosion tests in a 3.5% NaCl solution.

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<th>Substrat</th>
<th>Conventional anodisation</th>
<th>Double anodisation</th>
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<tr>
<td>$E_{corr}$ (mV)</td>
<td>-698.9</td>
<td>-684.3</td>
<td>-682.5</td>
</tr>
<tr>
<td>$R_p$ (KΩ.cm$^2$)</td>
<td>57.32</td>
<td>74.74</td>
<td>80.22</td>
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<tr>
<td>$i_{corr}$ (µA.cm$^{-2}$)</td>
<td>2.07</td>
<td>1.57</td>
<td>1.18</td>
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3.2 Electrochemical impedance spectroscopy (EIS)

The electrochemical characteristics of the film were investigated by electrochemical impedance spectroscopy (EIS) in 0.2M $K_2SO_4$ solution, without stirring and at 25 °C. The latter solution has the advantage of not being aggressive and thus allows providing a comparison of holding exclusively to aging of the films produced by the two methods of anodising. The results obtained in NaCl 3.5% and 0.2 M $K_2SO_4$ are complementary.
Figure 3: EIS analysis of Al-Mg alloy anodised at different immersion times (black) 30 min; (red) 2 h; (green) 4h; (blue) 24h in 0.2 M K$_2$SO$_4$ solution at 25 °C. (a) Conventional anodising, (b) double anodising.

EIS analysis Nyquist plots of Al-Mg alloy anodised for different immersion times in 0.2 M K$_2$SO$_4$ solution are shown in (figure 3). The Nyquist diagram is characterized by a single capacitive loop representing the electrochemical behaviour of the barrier layer. Extrapolating this capacitive loop on the real axis determines the polarization resistance $R_p$ whose value provides a relative assessment and comparison of the corrosion resistance of samples treated according to the aforementioned operating conditions.
The $(R_{bf})$ resistance values present a private interest for this comparative study (intersection of the capacitive loop with the axis of realities). The larger $(R_{bf})$ is the more the anodic layer is of better quality because more resistant to the hydration $(\text{Al(OH)}_3)$ and to the swelling which are the facts even ageing. The variations of the resistances $(R_{bf})$ deduced from the diagrams of Nyquist for the samples are gathered in (figure 4).

![Graph showing the variation of $R_{bf}$ resistance over time](image)

**Figure 4**: $R_{bf}$ Resistance evolution in 0.2 M $K_2SO_4$ solution at 25 °C for different immersion times.

The films impedance spectra obtained in 0.2 M $K_2SO_4$ solution at 25 °C for different immersion times showed:

A decrease in $R_{bf}$ resistance over time (figure 4). The $R_{bf}$ resistance is greater in the case of double anodising and this confirms the results obtained by the polarization curves shows that the values of polarization resistance higher in the case of double anodising.

The interpretation of $R_{bf}$ resistance variation over time can be explained by: the beginning of immersion, the solution of $K_2SO_4$ has not yet reached the barrier layer at the base of the pores; it is still consisting of alumina more or less contaminated by the anions of anodising electrolyte. There by increase the $K_2SO_4$ solution through the pores until the barrier layer is to diminish rapidly $R_{bf}$ by hydration of this layer.

4 Conclusion

A comparative study between two techniques conventional and double anodisation, it allows obtaining a highly ordered structure.
(1) Electrochemical characterization of alumina films in the electrolyte NaCl 3.5% by weight clarified regarding the corrosion occurring on the surface of the sample. It was observed that the presence of chloride ions causes corrosion more pronounced. The films prepared by double anodising have a polarization resistance $80.22 \text{ K}\Omega \cdot \text{cm}^2$ higher than that obtained by conventional anodising $74.74 \text{ K}\Omega \cdot \text{cm}^2$.

(2) The EIS technique offers the possibility of studying carefully the ageing process in anodised aluminium. This technique allows you to monitor changes in the intermediate (barrier and porous layers) during the ageing process. The evolution of spectra with immersion time also showed that the oxide layers obtained by both techniques are sensitive to ageing. Analysis of impedance spectra revealed that the resistance "low frequency" is higher in the case of double anodising thus highlighting the beneficial role of an oxide film regular and uniform; this confirms the results obtained by the polarization curves shows that the values of polarization resistance higher in the case of double anodising.

References