

Electrochemical Synthesis and Surface Characterization of Anodic Non-Porous Alumina Coatings (ANPAC) by Anodization

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ABSTRACT

Anodic non-porous alumina coatings (ANPAC) were fabricated by anodizing treatment in a mixed electrolyte containing 0.3 M sulphuric acid with various concentrations of ammonium oxalate (AO). The fabricated ANPAC coatings were characterized by SEM and EDS. The corrosion resistance of bare and anodized coatings has been investigated in 3.5% NaCl solution by Tafel polarization technique. The anodizing treatment of aluminum alloy in mixed electrolyte provides better thickness with maximum anticorrosion properties in comparison with the anodizing treatment in H₂SO₄ alone and bare aluminium. The present findings provide a promising route to fabricate ANPAC coatings with the highest corrosion resistance.

KEY WORDS: ANPAC, Anodizing, Mixed electrolyte, Ammonium oxalate, Corrosion.

1. INTRODUCTION

Aluminum and its alloys have a huge number of applications. These range from all sorts of packaging, through the aeroplanes, cars and train carriages. Aluminum is also vital in aircraft domains, building, construction industry and common place household objects. Although aluminum has a huge advantage when compared to other metals, an untreated aluminium surface will spontaneously react with water or moist air to form an aluminium oxide layer. But unfortunately these natural oxide layers are not uniform and does not offer sufficient protection against corrosion. Application of aluminum alloys in many fields depends on their corrosion properties. In this respect, protection of this material against corrosion, has been a critical problem. Countless research has been done on this issue. Chromate conversion coatings (CCCs) have been commonly applied as corrosion protection technology of Al alloys for a long time. CCCs significantly improve the corrosion stability and provide good adhesion strength between organic coatings and metal surfaces. However, due to toxicity and carcinogenic properties of Cr (VI) severe restrictions have been imposed on its use by international environmental standards (Forsyth, 2008; Decroly, 2005). So, it is in high demand to develop highly effective and selective method to counter this phenomenon.

Several techniques have been applied to produce protective coatings on aluminium components, such as micro arc discharge oxidation (MDO), gas flame spray, plasma thermal spray, physical vapour deposition, high temperature glass enameling methods, chemical passivation coating and polymer coating. Among these various synthesis methods, electrochemical anodization is one of the quite popular methods that replaces the thin natural oxide layer with a structured, highly resistant anodic layer, which provides an excellent protection against these local corrosion attacks. It is superior over other techniques due to the following advantages: (i) single step process, (ii) relatively short process time, (iii) effective control of the size and shape of the grains, (iv) less cost consumption and (v) easy to anchor firmly on the substrate.

Sulphuric acid, though a universal electrolyte, the oxide surface being porous, acid may entrapped into the pores which may ooze out with time and leads to corrosion. Hence, various proportions of suitable additives are added to the constant concentration of sulphuric acid bath which changes the porous surface morphology to the non-porous one. This study proposed a mixed bath containing sulphuric–ammonium oxalate for the anodizing of aluminum alloy and reveals their anticorrosion properties.

2. MATERIALS AND METHODS

2.1. Fabrication of ANPAC coatings: High purity (99.999% pure) aluminum plates with a thickness of 0.1 mm were used as the starting material with an exposed area of 1 cm² and the rest of the surface was covered with insulation tape. Firstly, all samples were degreased in acetone and then annealed at 450°C for 30 min to remove mechanical stresses on the aluminum. The natural oxide film on the aluminum plate was electropolished in a mixed solution of perchloric acid and ethanol (1:4) under a constant voltage of 15 V for 3 min at 10°C to obtain a smooth-surfaced samples for anodization. The pretreated specimen was weighed (W₁) using analytical balance (AL104, Mettler–Toledo International Inc) and it was subjected to anodization. Finally, the samples were rinsed with ethanol and dried. The anodization was performed in a two-electrode configuration connected to a direct current power supply where the aluminum plate was used as anode and graphite sheet as cathode. In order to investigate the influence of electrolyte concentration on the properties of ANPAC coating, the process was conducted in various concentrations of ammonium oxalate (0.1 M–0.5 M). After anodization, the specimen was rinsed with deionised water and weighed (W₂). The coating properties like thickness and growth rate of the ANPAC coatings were obtained by the following formulas.

$$\text{Thickness} = \frac{W_2 - W_1}{\text{Density of Aluminium} \times \text{Specimen area}}$$

$$\text{Growth rate} = \frac{\text{Thickness}}{\text{Reaction time (min)}}$$

Where W_1 and W_2 are the weights of the specimen before and after anodization.

3. RESULTS AND DISCUSSION

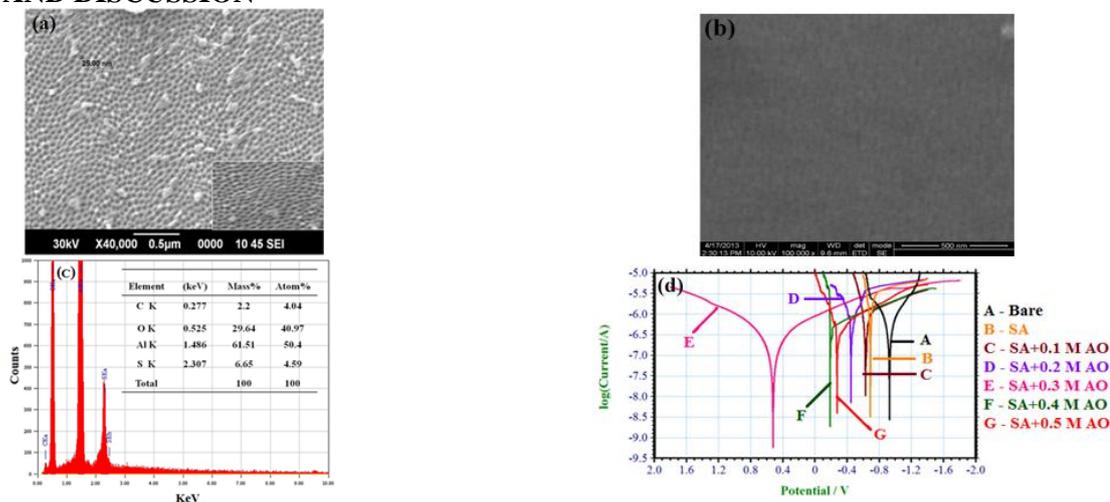


Fig.1.(a,b) SEM images of anodic coatings on aluminium (a) 0.3 M sulphuric acid, 20 V, 90 min, 10°C (b) 0.3 M sulphuric acid + 0.3 M ammonium oxalate, 30 V, 90 min (c) EDAX spectra of ANPAC coating obtained from optimized condition. (d) Comparative Potentiodynamic polarization curves of ANPAC coatings (SA – sulphuric acid; AO – ammonium oxalate)

3.1. Effect of ammonium oxalate concentration on ANPAC coatings: Effect of concentration of ammonium oxalate on the formation and properties of ANPAC coating was studied by varying the concentration between 0.1 M and 0.5 M at constant concentration of H_2SO_4 (0.3 M) at room temperature ($29 \pm 1^\circ\text{C}$) for 90 min. In this bath, the coating with maximum thickness ($22 \mu\text{m}$) and growth rate ($0.24 \mu\text{m}/\text{min}$) was obtained from mixture of 0.3 M sulphuric acid and 0.3 M ammonium oxalate. The conceivable reason behind this is, when the concentration of the bath is increased, the availability and the inward migration of the oxygen ions (O^{2-}) or hydroxide ions (OH^-) towards the Al/oxide interface in the bath increases which react with the Al^{3+} ions that are migrated outwards from the Al surface. This leads to increase in the growth rate of anodic coating and the oxide layer covers the entire surface of the specimen. When the concentration of ammonium oxalate is greater than 0.3 M, more amount of hydrogen ions is produced in the bath which acidified the electrolyte near the anodic area. Based on these results, the anodization process carried out at room temperature using a mixture of 0.3 M sulphuric acid and 0.3 M ammonium oxalate at 30V for 90 min has been chosen as the optimum condition.

3.2. Morphological Analysis: Scanning Electron Microscopy: The Surface morphology of the ANPAC coating formed in mixed electrolyte and sulphuric acid alone were analysed by SEM. Fig. 1 a and b shows the SEM image of alumina coating fabricated from 0.3 M sulphuric acid alone and with the addition of ammonium oxalate at optimized conditions. From the Figs we can see that the surface morphology of anodic coatings produced in a mixture of electrolyte and sulphuric acid alone are completely different. From Fig. 1a, the coating formed in sulphuric acid has ordered and uniform nano pores with almost equal diameter and size. The diameter of the nanopores was found to be 22 nm. So in order to produce thickest nonporous alumina coatings with highest corrosion resistance anodization of aluminium was carried out in a mixture of ammonium oxalate and sulphuric acid. Thus the coating formed from mixed electrolyte is non-porous and compact as shown in fig 1 b. Hence, ammonium oxalate added to the constant concentration of sulphuric acid bath which changes the porous surface morphology to the non-porous one (ANPAC).

3.3. EDS analysis: The composition of the elements present in anodic coatings formed in sulphuric with the addition of ammonium oxalate at optimized conditions, was done by EDS analysis the EDS spectra are shown in Fig. 1 c. From the Fig. the major elements composing the coatings are: Al, O, C and S at 1.486keV, 0.525 keV, 0.277keV and 2.307 keV respectively. The existence of sulfur indicates the presence of sulfate ions in oxide films incorporated (diffusion) during the film growth. The sulfur and carbon come from sulphuric and oxalate bath. Due to the presence of Al and O as the major elements in the coatings formed from sulphuric acid with the addition of ammonium oxalate, it can be confirmed that the coatings are mainly composed of alumina.

3.4. Corrosion behaviour of the ANPAC coatings:

Tafel polarization: The comparative polarization curves of anodic coatings formed from sulphuric acid and mixed electrolytes, at various concentrations along with the substrate are shown in Fig.d. Corrosion potential (E_{corr}),

corrosion current density (I_{corr}), cathodic/anodic Tafel constants (b_c and b_a) and polarization resistance (R_p) values were determined from Stern-Geary equation.

$$R_p = b_a b_c / 2.303 i_{\text{corr}} (b_a + b_c)$$

Due to the higher coating thickness obtained at the optimized conditions, the corrosion resistance is also high compared to coatings obtained below and above the optimized conditions. The E_{corr} and R_p values are found to increase with increase in concentration of ammonium oxalate upto 0.3 M, which indicates that the corrosion resistance of the ANPAC coating is enhanced by the addition of ammonium oxalate in the bath and best corrosion resistances is achieved for the ANPAC coating formed from the bath containing 0.3 M sulphuric acid containing 0.3 M ammonium oxalate (lower corrosion current and higher polarization resistance than other coatings). The polarization curve of ANPAC coating obtained from the 0.3 M sulphuric acid containing 0.3 M ammonium oxalate bath has relatively higher Tafel slope, which could be attributed to the coating with larger thickness, uniform structure and compact inner barrier layer formed in the bath. The corrosion potential (0.521V) of the coating obtained from the optimized condition is more positive compared to that of the coating formed from sulphuric acid alone (-0.690 V) and bare aluminium which is shown in Fig.d. Thus, the occurrence of pitting corrosion might be delayed.

4. CONCLUSIONS

Anodic non-porous alumina coatings (ANPAC) were produced electrochemically by anodization method from 0.3 M sulphuric acid containing various concentrations of ammonium oxalate (0.1-0.5M). The maximum thickness and growth rate were obtained using 0.3 M sulphuric acid containing 0.3 M ammonium oxalate by applying 30 V for 90 min at RT. From the SEM analysis, it has been found that the coating formed at optimized conditions has non-porous, thick, compact and dense coatings. EDX spectrum also confirmed the formation of alumina. Corrosion studies show that the ANPAC coatings on aluminium obtained from optimized conditions offered highest corrosion resistance compared to coating formed from sulphuric acid and bare aluminium. These results demonstrate that the addition of ammonium oxalate into the sulphuric acid electrolyte have an impact on the anodic coating with highest corrosion resistance because of the formation of non-porous coatings.

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