



Comparative study of formation and corrosion performance of porous alumina and ceramic nanorods formed in different electrolytes by anodization



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ABSTRACT

Fabrication of Al₂O₃–TiO₂ nanoceramic coatings on aluminium was carried out in a single step using cost effective sulphuric acid electrolyte with the addition of potassium titanium oxalate (PTO) by anodization method. For comparison, the anodization was also carried out in sulphuric acid electrolyte alone. The effect of composition of the electrolyte, current density and electrolyte concentration on formation and surface characteristics of anodic alumina and ceramic coatings produced from different electrolytes have been investigated. The growth process, surface morphology, nanostructure, distribution of chemical elements, phase constitutions and corrosion resistance of the coatings formed in two different electrolytes were investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Tafel polarization technique and electrochemical impedance spectroscopy (EIS). As the concentration of electrolyte and current density increased, the surface properties of the coating increased up to certain content and beyond that they decreased. Dense, uniform nanoceramic coatings with less surface defects were obtained from sulphuric acid + PTO electrolyte. The corrosion studies reveal that ceramic coating formed in sulphuric acid + PTO electrolyte offers better corrosion resistance compared to the alumina coating formed in sulphuric acid electrolyte.

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1. Introduction

Aluminium is one of the important materials of research because of its high technological value, electrical capacity and wide range of industrial applications [1–5] especially in aerospace and household industries. However, Al is highly reactive metal and prone to corrosion in sea water [6]. The corrosion of aluminium has long been a problem in society and hence it is an important area of research [7]. Developing successful protective coatings on aluminium and its alloys, is still a challenging task due to the restrictions imposed by the Environmental Protection Agency (EPA) on the use of environmentally hostile chemicals. The alumina coatings formed by anodization have good corrosion resistance but in some aggressive environments, the efficiency of this oxide layer gets depleted. There is an immense need for novel environmentally benign coatings on aluminium in the ever growing materials industry. Ceramic coating is a promising means to combine advantages of the metal substrate and the ceramic materials, which can simultaneously meet mechanical properties and environmental service demands. Many

researchers have tried to improve their performance by developing nanoceramic coatings through embedding other tougher components such as SiO₂, TiO₂ and ZrO₂ [8,9] together with alumina. Nanoceramic coatings offered an attractive combination of wear resistance, corrosion resistance, mechanical strength, interfacial adhesion and thermal property [10–13]. The most recent trend is to prepare Al₂O₃–TiO₂ coatings which can retain the beneficial features of both TiO₂ and Al₂O₃. The addition of titania improves the fracture toughness of alumina. Many techniques like physical vapour deposition (PVD) [14], plasma spraying [15,16], ball milling [17], chemical vapour deposition (CVD) [18,19], high temperature oxidation [20,21] and gas-flame spraying [22] have been put forward to prepare those excellent candidates. The coatings produced by PVD and CVD techniques are harder and have more corrosion resistance but these techniques have some disadvantages like they need high vacuum and complicated equipment. The coatings produced by the plasma spraying and other techniques have insufficient adhesion to the base material and they require high substrate temperature. Among various synthesis methods, electrochemical anodization has been demonstrated a facile and excellent approach to increase the life time of aluminium by fabricating ceramic coating on Al foil. It is superior over other techniques due to the following advantages: (i) single step process at room temperature, (ii) relatively short process time, (iii) effective control

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of the size and shape of the grains, (iv) less cost consumption and (v) easy to anchor firmly on the substrate.

Sulphuric acid is a universal anodizing electrolyte and to this, many additives are added to get coatings with improved surface properties. An attempt was made in the present work to fabricate denser $\text{Al}_2\text{O}_3\text{-TiO}_2$ coatings on aluminium from sulphuric acid electrolyte containing PTO as additive by anodization at room temperature so that, the cost of production of such potentially important materials can be minimized. This study aims at the investigation on effect of anodizing parameters (concentration of the electrolytes and current density) on surface morphology and corrosion resistance of the coatings one at a time while keeping the others constant. The corrosion behaviour was analyzed by potentiodynamic polarization and EIS methods in 3.5 wt% NaCl solution.

2. Experimental

2.1. Materials

Commercially available Al foil (99% pure), nitric acid, sodium hydroxide, sulphuric acid, phosphoric acid, chromic acid, potassium titanium oxalate were purchased from Aldrich chemicals (Aldrich, India). All the chemicals were of analytical grade and used as such without further purification.

2.2. Fabrication of ceramic coating

Annealed Al foils were used as starting materials. A preliminary treatment was performed in which Al foils were degreased with acetone, alkali cleaned with 5% NaOH at 30 °C for 2 min followed by desmutting in 25% HNO_3 at 30 °C for 1 min. The pretreated specimen was weighed (W_1) using analytical balance (AL104, Mettler – Toledo International Inc) and it was subjected to anodization. All the electrolytes were prepared from triply distilled deionized water. The anodization was performed in a two-electrode configuration connected to a direct current power supply with Al foil as anode having the working area of about 1 cm^2 and lead sheet as cathode in a thermostatically controlled set up following the recipe reported in literatures [23,24]. In order to investigate the influence of electrolytes on anodic coating, anodization was conducted in two different electrolytes; (i) various concentrations of H_2SO_4 (10–60 g/l). (ii) 50 g/l H_2SO_4 with different concentrations of PTO ranging from 10 to 50 g/l. The applied current density was varied between 0.01 A/cm^2 and 0.06 A/cm^2 for anodization in H_2SO_4 electrolyte and 0.01–0.09 A/cm^2 for anodization in H_2SO_4 +PTO electrolyte. The anodic coatings were fabricated from both electrolytes with stirring at room temperature (29 ± 1 °C) for 45 min. The anodic coating was stripped off by immersing in a mixture of 0.4 M H_3PO_4 and 0.2 M CrO_3 for 15 min at 60 °C and weighed to find the exact amount of coating formed and Al dissolved. Thickness of the coating was evaluated using Dermitron thickness tester. The thickness values were measured in three places in the specimen and the average value was taken. The thickness value was divided by the anodic treatment time in minutes to get the growth rate. The unit of the growth rate is $\mu\text{m}/\text{min}$. The coating ratio [25,26] was obtained by the following formula

$$\text{Coating ratio} = \frac{\text{weight of the coating}(W_2 - W_3)}{\text{weight of Al dissolved}(W_1 - W_3)} \quad (1)$$

where W_1 and W_2 are the weights of the specimen before and after anodization and W_3 is the weight of the specimen after stripping off the coating. The amorphous, as-anodized samples were crystallized by oxygen annealing at 500 °C for 5 h.

2.3. Characterization of the fabricated coatings

The surface morphology of the alumina and nanoceramic coatings was analyzed by Scanning Electron Microscope (SEM, Hitachi X-650, Japan). All the samples were sputtered with thin gold film before SEM analysis to prevent surface charging effects. Subsequently the elemental composition of the coatings was analyzed by energy dispersive X-ray spectroscopy (EDX). The crystallographic characteristics of the coatings were investigated at different time periods with X-ray diffractometer (XRD, X-pert Graphics, Brooker, Germany) working on $\text{CuK}\alpha$ radiation. The corrosion resistance of the alumina and ceramic coating was evaluated by Electrochemical impedance spectroscopy and Tafel polarization studies. The corrosion studies were carried out in 3.5 wt% NaCl at 30 °C using Electrochemical workstation (CHI instruments, 760 model). A three electrode cell with alumina or ceramic coated aluminium as working electrode, Ag/AgCl/saturated KCl as reference electrode and a platinum wire as counter electrode was used. All the experiments were conducted in aerated and non stirred conditions. In order to obtain reliable results, the experiments were repeated in triplicate.

3. Results and discussion

3.1. Influence of concentration and current density on coating properties

3.1.1. Sulphuric acid electrolyte

The concentration of sulphuric acid and current density were varied between 10–60 g/l and 0.01–0.06 A/cm^2 respectively at room temperature (29 ± 1 °C) for 45 min. In this bath, the coating with maximum thickness (29 μm), growth rate (0.65 $\mu\text{m}/\text{min}$) and coating ratio (1.62) was obtained from 50 g/l concentration of sulphuric acid at 0.05 A/cm^2 . At low concentration and current density, a small amount of oxide formation takes place. As the concentration of sulphuric acid and current density were augmented from 10 g/l and 0.01 A/cm^2 respectively, the properties (thickness, growth rate and coating ratio) of the anodic coating increase to a certain level i.e. up to concentration of 50 g/l and current density of 0.05 A/cm^2 . Beyond that, the properties decrease as shown in Figs. 1a and b and 2a and b. The conceivable reason behind this is, when the concentration of the bath and the current density 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 sulphuric acid is greater than 50 g/l, more amount of hydrogen ions are produced in the bath which acidified the electrolyte near the anodic area. Owing to this, oxide dissolution predominates the oxide formation. Here, the hydrogen ions play an egregious role. Meanwhile, on increasing the current density beyond 0.05 A/cm^2 , the local joule heat effect occurs which weakens the junction strength between the cells, leads to oxide dissolution.

3.1.2. Sulphuric acid + PTO electrolyte

In this bath, the concentration of sulphuric acid was maintained as constant after making a series of optimization processes (at various concentrations and current densities) as given in the above section. Based on the surface properties of anodic coatings (thickness, growth rate, coating ratio), the best conditions were chosen. The anodization was carried out in the optimized bath (50 g/l H_2SO_4) with the addition of PTO at room temperature (29 ± 1 °C) for 45 min. Anodization parameters such as the concentration of

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