



## Synthesis of anodic films in the presence of aniline and TiO<sub>2</sub> nanoparticles on AA2024-T3 aluminium alloy

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### ABSTRACT

Coatings, comprising an inner porous anodic alumina film and an outer polyaniline/TiO<sub>2</sub> nanoparticle layer, were electrochemically synthesised on an AA2024-T3 aluminium alloy by single-step, anodic polarisation in an oxalic acid-based electrolyte. The morphology and composition of the coatings were examined by TEM, SEM and XPS, with the size and zeta-potential of the TiO<sub>2</sub> nanoparticles in the oxalic acid solution also measured. Observation of the growth of the coating during of anodic polarisation revealed that a distinct, two-layered coating is formed from the early stages of polarisation, with the anodic film forming at a constant rate and the outer layer developing at a rate that decreases markedly with times beyond about 30 min. Nanoparticles, agglomerated in the electrolyte, migrate to the anode due to the negative zeta-potential and form the nanoparticle-containing layer at the surface of anodic film. Such particles are not incorporated in the pores due to agglomeration and disordered film porosity at the outer layer of the anodic film.

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### 1. Introduction

The high strength AA2024T3 aluminium alloy is commonly used in aerospace applications after appropriate corrosion control measures. The corrosion mechanisms of this alloy and protection treatments have been extensively studied [1–6]. For example, anodising, with subsequent priming and top coating, is widely employed for effective performance under service conditions. In the aerospace industry, anodising in chromic acid has been used to provide superior corrosion resistance and adhesion performance compared with anodising in other electrolytes. Further, dichromate sealing of anodic films has been shown to be highly effective for corrosion protection of this alloy [7–9].

Due to the carcinogenic nature and toxicity of hexavalent chromium species, various alternatives have been developed in recent years to replace conventional anodising in chromic acid. An approach to provide chromate-free corrosion protection treatments is the use of electroconducting polymers that may be electropolymerised on aluminium substrates by anodic oxidation. Electrosynthesis of polyaniline and polypyrrole on aluminium and its alloys has been reported [10–12]. For example, Naoi et al. [10] proposed a mechanism for the simultaneous formation of a barrier alumina film and polypyrrole over the aluminium surface. It was suggested that the initially formed alumina film contains cracks where hydrophilic groups of the

surfactant electrolyte are attached, and hydrophobic groups form a micelle that hosts the pyrrole molecules. The electropolymerisation of pyrrole on the micelles forms electronically conducting paths of polypyrrole that extend from the aluminium electrode to the surface of the alumina film. Tsai et al. [11] proposed a mechanism similar to that of Naoi and co-workers. Huerta-Vilca et al. [12] also concluded that primary polymerization of aniline on aluminium proceeds at defects in the anodised alloy substrate.

The incorporation of inorganic fillers into conducting polymer matrices by electrochemical polymerisation processes has also been studied [13,14]. Zhu and Iroh [13] electrosynthesised polyaniline in the presence of TiO<sub>2</sub>, ZrO<sub>2</sub> and SiO<sub>2</sub> nanoparticles on AA2024 aluminium alloy. The potentiodynamic polarisation behaviour suggested a beneficial effect of the fillers on the corrosion resistance provided by polyaniline coatings, although no mechanistic information was provided. Lenz et al. [14] electrosynthesised polypyrrole on mild steel in the presence of TiO<sub>2</sub> particles. The polypyrrole/TiO<sub>2</sub> composite films showed improved performance compared with the polypyrrole films that was attributed to the reduced porosity of the polymer through filling by TiO<sub>2</sub> particles. In contrast, Kamada et al. [15,16] studied the incorporation of oxide nanoparticles into alumina films, with anodic oxidation of the aluminium and electrophoretic deposition of nanoparticles performed in a single step. The surface charge and size of the nanoparticles were considered to be significant in enabling their migration to the substrate during anodising, with subsequent incorporation into the pores of the anodic alumina films.

Here, an anodic polarisation process leading to formation of a porous anodic alumina film, with an outer layer of polyaniline with

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incorporated TiO<sub>2</sub> nanoparticles, in an oxalic acid-containing electrolyte is examined. The evolution of the anodic film and the nanoparticle/polyaniline-containing layer with time are of particular interest.

## 2. Experimental details

### 2.1. Materials and preparation of the specimens

An AA2024T3 aluminium alloy, of nominal composition given in Table 1, was used as the substrate. Specimens, of dimensions 50 × 100 mm and 0.5 mm thickness, were cut from the as-received sheets. Prior to anodic polarisation, the specimens were degreased with acetone, followed by alkaline etching in *Turco 4215NCLT* for 10 min at 50 °C and desmutting in *Turco Smut Go* for 5 min at room temperature. Anodic polarisation was undertaken at a constant voltage of 8 V in 0.5 M oxalic acid and 0.1 M aniline electrolyte, with 1 g/l of dispersed TiO<sub>2</sub> (anatase) nanoparticles for 1, 5, 15, 30, 60, 90 and 120 min. The size range of the TiO<sub>2</sub> nanoparticles was 5–10 nm. The cell was maintained under a nitrogen atmosphere, with continuous stirring of the electrolyte during anodic polarisation. Specimens were also formed under similar conditions for 120 min in the oxalic acid-based electrolyte without nanoparticles or aniline, with nanoparticles and without aniline, and with aniline and without nanoparticles.

### 2.2. Characterisation of morphology and composition

Sections of the anodically polarised substrates were examined by transmission electron microscopy (TEM). For TEM examination, electron transparent sections were prepared using a Leica Ultracut UCT ultramicrotome. Final sections, of 15 nm nominal thickness, were generated with a diamond knife (Microstar) from the coated alloy that had been encapsulated previously in cured resin and observed in a JEOL 2000FX II transmission electron microscope. Cross-sections were also examined by scanning electron microscopy operating in the backscattered electron mode at 1.5 kV, using a Zeiss Ultra 55 instrument. For scanning electron microscopy, the specimen was prepared by ultramicrotomy, with a diamond knife finish, and examined immediately to minimise possible contamination from the laboratory atmosphere.

The composition of the final films obtained after 120 min in electrolytes with and without aniline were further analysed by X-ray photoelectron spectroscopy (XPS) using a PHI 5500 Multitechnique System. Analysis was undertaken over an area of 0.8 mm diameter, with depth profiles generated by sputtering with a 4 keV energy argon ion source.

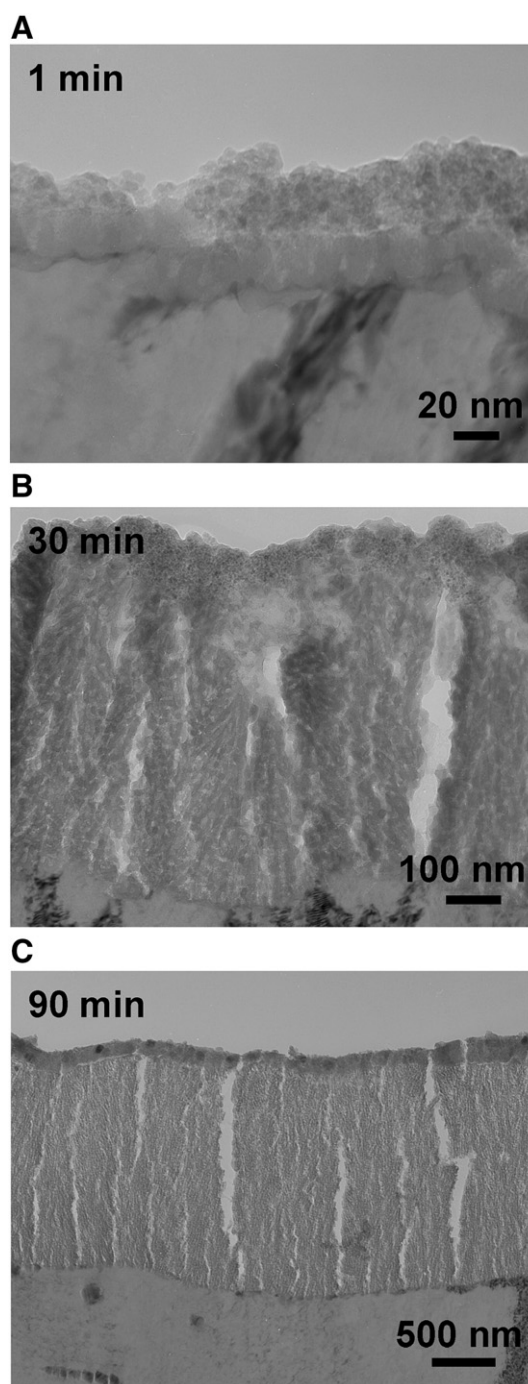
### 2.3. Zeta-potential and particles size measurements

The zeta potential and size measurements of the TiO<sub>2</sub> nanoparticles were determined using an AcoustoSizer II from Colloidal Dynamics. Three different dispersions, with a TiO<sub>2</sub> nanoparticle content of 5 g/l, were analysed. One of the dispersions contained 0.1 M aniline and the required amount of oxalic acid to achieve pH 2. The second dispersion, also of pH 2 and based on oxalic acid, did not contain aniline. The third dispersion, with 0.1 M aniline, was adjusted to pH 2 by addition of nitric acid. For these measurements, the aqueous solutions of oxalic acid, with aniline in the first case and without aniline in the latter, were used as the background electrolyte. Values of 3.9 g/cm<sup>3</sup> and 40 were used respectively for the density and

**Table 1**

Nominal chemical composition of the aluminium alloy 2024T3 [1].

Element	Al	Si	Fe	Cu	Mn	Mg	Zn	Ti	Cr
(wt.%)	90–93	0.50	0.50	3.8–4.9	0.3–0.9	1.2–1.8	0.25	0.15	0.10



**Fig. 1.** Transmission electron micrographs of the AA2024-T3 aluminium alloy after anodic polarisation in oxalic media with aniline and TiO<sub>2</sub> nanoparticles for different times: (A) 1 min; (B) 30 min and (C) 90 min.

the dielectric constant of titanium oxide nanoparticles. The concentration of the nanoparticles and the pH values were higher than those used in the anodic polarisation process because of the analytical limits of the instrumentation.

## 3. Results and discussion

### 3.1. Morphology of the coatings

The variation of the coating morphology with duration of anodic polarisation from 1 to 90 min is displayed in the transmission electron micrographs of the ultramicrotomed sections of Fig. 1. Independent of

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