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Corrosion performance of anodic films containing polyaniline and TiO_2 nanoparticles on AA3105 aluminium alloy

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ABSTRACT

The corrosion protection afforded to an AA3105 aluminium alloy supporting an anodic film with incorporated polyaniline and TiO_2 nanoparticles has been examined. The films were synthesised by simultaneous anodizing and electropolymerisation of aniline in the presence of nanoparticles. The morphology and composition of the films were probed by TEM, SEM, rf-GDOES and XPS. The resultant coatings comprised a thin porous anodic film of 2–3 μm thickness, with an outer hybrid polyaniline/TiO_2 layer of several tens nanometres thickness, with the dimensions of TiO_2 nanoparticles being below 10 nm. Electrochemical impedance spectroscopy analysis and salt spray testing revealed that TiO_2 containing films provide improved corrosion protection to the AA3105 aluminium alloy compared with the film without nanoparticles. The improved protection provided by the coatings containing TiO_2 nanoparticles is attributed to the TiO_2 particle-rich thin film layer formed on the outer part of the coating that acts as a blocking barrier layer for the anodic porous aluminium oxide film.

1. Introduction

The widespread use of aluminium alloys in applications ranging from transport to architecture demands surface treatments for their corrosion protection [1,2]. Anodizing of aluminium is a widely studied and accepted method that consists in electrochemically forming a protective anodic aluminium oxide layer [2]. The growth, composition and morphology together with performance of the anodized substrates anodic films are described in the literature, for both pure aluminium and aluminium alloys [2–7]. In addition, sealing mechanisms of porous anodic oxide films have also been reported [6–10].

Various alternatives have been proposed in recent years to replace anodic films formed in chromic acid to protect aluminium alloys from corrosion. For example, Mourtalier et al. [11–13] studied the incorporation of cerium (IV) and molybdate ions as inhibitors in the anodic films obtained in sulphuric acid media. An improvement of corrosion protection was reported for AA2024-T3 aluminium alloy compared with anodizing in the absence of such ions. Further, Kamada et al. [14,15] reported the incorporation of oxide nanoparticles into alumina films, with anodic oxidation of the aluminium and electrophoretic deposition of nanoparticles proceeding in a single step. Alumina films containing SiO_2 nanoparticles showed an increase in the capacitance and improved corrosion protection of the substrate. The incorporation of SiO_2 nanoparticles into the nanosized pores of anodic alumina films was also examined, with the surface charge and size of the nanoparticles considered to be significant in enabling nanoparticles to migrate to the substrate during anodizing with subsequent incorporation into the anodic film.

A further approach to provision of chromate-free corrosion protection solutions is the use of the conducting polymers that may be electropolymerised on aluminium substrates by anodic oxidation. However, porous anodic alumina films may grow in the acidic solutions commonly used for the electrosynthesis of conducting polymers, thereby acting as a barrier for electron transfer and, thus, inhibiting the polymerisation process. However, successful electrosynthesis of polyaniline and polypyrrole on aluminium and its alloys has been reported. Husler and Beck [16] showed that the pores of the anodic alumina layer play an important role as nucleation centres in the electropolymerisation of pyrrole on aluminium. Huerta-Vilca et al. [17] also concluded that primary polymerisation of aniline on aluminium surfaces proceeds in the defects present of the anodized surface. Naoi et al. [18] proposed a mechanism for the simultaneous formation of a barrier alumina film and polypyrrole over the alumina surface, where the initially formed alumina film contained cracks in which the hydrophilic groups of the surfactant electrolyte are attached and the hydrophobic groups form a micelle that hosts the polypyrrole molecules. The electropolymerisation of pyrrole in the micelles forms

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electronically conducting paths of polypyrrole that extend from the aluminium electrode to the surface of the alumina film. Such conducting paths allow current flow and formation of polypyrrole layers on the surface of the alumina film. Tsai et al. [19] proposed a three-stage mechanism, similar to that of Naoi et al.; the first stage consisted of the formation of porous anodic alumina and the nucleation of polypyrrole within the pores, that was followed by the propagation of the polymer over the alumina layer and, in the last, the over-oxidation of polypyrrole located within the pores occurred.

Incorporation of inorganic fillers into conducting polymer matrices has also been studied, utilising both chemical [20–24] and electrochemical [20,25–28] polymerisation processes. For example, TiO_2 [23,25–28], ZrO_2 [22,24,27] and SiO_2 [27] particles have been incorporated in polyaniline and polypyrrole matrices. Zhu et al. [26] electrosynthesised polyaniline in the presence of such nanoparticles on an AA2024 aluminium alloy. The potentiodynamic polarisation behaviour suggested a positive effect of the fillers on the corrosion resistance provided by polyaniline coatings, although no information on the mechanism was provided. Lenz et al. [27] electrosynthesised polypyrrole on mild steel in the presence of TiO_2 particles and the corrosion resistance was examined by measuring the release of iron to 3.5% NaCl solution and the weight loss of the specimen. The polypyrrole/TiO_2 composite films showed improved performance compared with the polypyrrole films, which was attributed to the low porosity of polypyrrole/TiO_2 films due to the filling of the pores in the polymer by TiO_2 particles.

Given the potential of incorporating nanoparticles into porous anodic films and conducting polymer matrices, with the latter forming within the pores, the incorporation of both TiO_2 nanoparticles and polyaniline in single step anodizing, is considered here. The corrosion performance of the coated aluminium alloy has then been examined by salt spray exposure and by electrochemical impedance spectroscopy.

2. Experimental

2.1. Materials and treatment

An AA3105 aluminium alloy of 0.5 mm thickness was used as the substrate, with the alloy composition given in Table 1. Specimens of dimensions 50×100 mm^2 were cut from as-received sheets.

Prior to anodizing, the specimens were degreased with acetone, followed by alkaline etching in *Turco 4215NCLT* for 10 min at 50 °C and, finally, desmutting in *Turco Smut Go* for 5 min at room temperature. Anodizing was undertaken at a constant voltage of 8 V in 0.5 M oxalic acid with 0.1 M aniline and 1 g/l of dispersed TiO_2 nanoparticles of 5–10 nm size; the cell was maintained under a nitrogen atmosphere with continuous stirring of the pH 1 electrolyte. Specimens were also anodized in a similar electrolyte without nanoparticles, for comparison.

2.2. Coating morphology and composition characterization

The morphology and composition of the coatings were examined by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), using a JEOL JSM 5910LV microscope fitted with an INCA 300 spectrometer. Additionally, cross-sections of the coated substrates were examined by SEM and transmission electron microscopy (TEM). For TEM examination, electron transparent sections were prepared using a Leica Ultracut UCT ultramicrotome. Final sections, of nominal thickness 15 nm, were generated with a diamond knife from the coated alloy that had been encapsulated previously in cured resin and observed in a JEOL 200FX II transmission electron microscope.

Elemental depth distribution profiles were generated by rf glow discharge optical emission spectroscopy (rf-GDOES), using a GD-Profiler 2 (Horiba Jobin Yvon) operating at 13.56 MHz. A 4-mm copper anode and argon gas were used for generation of the plasma; the response from the sputtered elements was detected with a polychromator of focal length of 500 mm. Sputtering was carried out at an argon pressure of 640 Pa and power of 35 W.

The coating composition was analysed by X-ray photoelectron spectroscopy (XPS) using a PHI 5500 Multitechnique System. Analysis was undertaken in an area of 0.8 mm diameter, with depth profiles generated by sputtering the surface with an argon ion source of 4 keV energy.

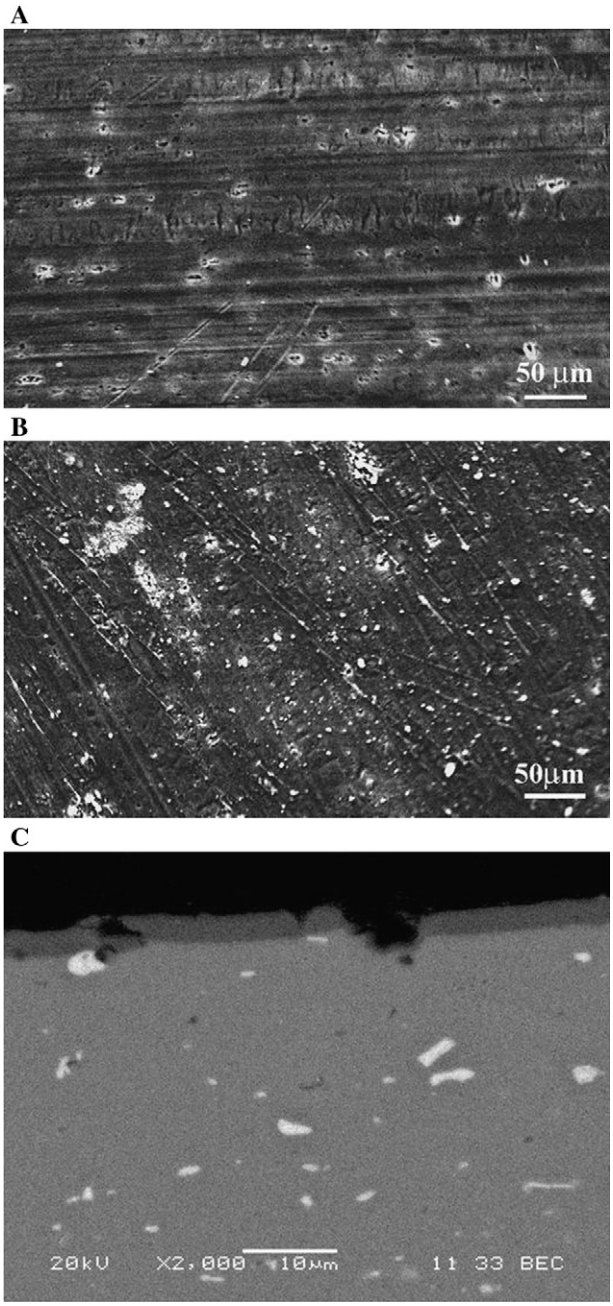

Fig. 1. Scanning electron micrographs of the surface of the AA3105 aluminium alloy anodised in oxalic media with (A) polyaniline and (B) polyaniline and TiO_2 nanoparticles; (C)—cross-sectional view of the film formed in the presence of nanoparticles.

Table 1
Chemical composition of the AA3105 aluminium alloy

Element	Si	Fe	Cu	Mn	Mg	Zn	Ti	Cr	Ni	Al
(wt.%)	0.298	0.629	0.044	0.437	0.350	0.025	0.018	0.022	0.013	98.160