Sol–gel sealing characteristics for corrosion resistance of anodised aluminium

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ABSTRACT

Conventional anodising electrolytes based on sulphuric acid, oxalic acid and phosphoric acid have been used to form nanoporous layers on AA3003-H14 and sealed with silane based sol–gel sealers. It is shown that the sol–gel chemistries have varying levels of pore penetration depending on the synthesis conditions. The extent of sol–gel penetration and pore sealing is analysed by electron microscopy and energy dispersive X-ray spectroscopy. To describe the sealing phenomena observed a sol–gel penetration and sealing rating has been proposed to explain the interactions of the sol–gels with the pores of the anodised layers. The corrosion resistance of the sol–gel sealed anodised aluminium surfaces was evaluated using neutral salt spray testing and electrochemical impedance spectroscopy.

1. Introduction

Aluminium is used extensively for lightweight structures such as automotive and aerospace components where the combination of strength and corrosion resistance is essential. Aluminium owes its inherent corrosion resistance to a naturally occurring passive oxide which forms on the metal when exposed to the atmosphere [1]. This oxide has a nanoscale thickness which limits the metals performance against extreme mechanical and chemical attacks [2].

Anodising is a process which increases the thickness of the aluminium oxide through an electrochemical reaction in acidic electrolytes such as sulphuric, phosphoric or oxalic acids. The features and properties of the anodic oxides produced are dependent on many parameters including the aluminium alloy used, electrolyte type and anodising conditions (e.g. temperature and current density). The process is commonly used to increase corrosion resistance and adhesion properties of the aluminium surface for a variety of applications.

The anodised aluminium oxide layer is nanoporous in structure with a self assembled, hexagonal array of pores extending from the surface of the oxide to a thin barrier layer at the metal oxide interface. The oxide growth and nanopore formation mechanism has been recently proven to result from a flow of anodic alumina in the barrier layer region due to the combination of growth stresses and field assisted plasticity [3–5]. The stresses that drive the flow of material are due to electrostriction of the oxide layer which is plasticised under the electric field [4–6]. The flow of material proceeds from the barrier layer into the pore walls forming Al_2O_3 columns in a self assembled structure.

In order to fully protect the underlying aluminium metal the porous oxide layer requires a sealing treatment to prevent penetration of aggressive corrosion inducing ions or chemicals to the base metal. Historically the most effective sealing has been achieved using Cr^{6+} compounds which impart excellent corrosion resistance to the metal due to the self healing ability of the Cr^{6+} ions [7]. These compounds however are known carcinogens and restrictions are enforced in many industries forcing alternative chemistries to be adopted [8]. A recent review of sealing processes benchmarked replacement sealing technologies for sodium dichromate sealing such as hydrothermal, sodium silicate and nickel based sealers [9]. The sealing mechanisms reviewed include chemically altering the surface of the anodised layers to close the pores by forming aluminium hydroxide, alumino-silicates or nickel hydroxides to block the pore mouths. Though these sealers have been shown to be promising replacements for Cr based sealers some concerns still exist regarding high production costs, long term exposure performance and environmental issues.

Sol–gel materials have been extensively studied for corrosion control replacements for Cr(VI) based conversion coatings. The sol–gel process can be used to form nanostructured inorganic films (typically 200 nm to 10 μm in overall thickness) that can be tailored to be more resistant than metals to oxidation, corrosion, erosion and wear while also possessing good thermal and electrical properties [10–12]. The chemistry of the sol–gel process is well known [13–16] with excellent reviews [17–19] and books [20] available. The most common sol–gel materials used as coatings are based on organically modified silicates (ormosils), which are formed by the hydrolysis and condensation of alkoxide precursors [21].

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Despite the breadth of research conducted in the area of sol–gel corrosion control, little research has been published in the use of sol–gel sealing of anodised layers to enhance corrosion resistance. A previous study reported that zirconium oxide sol–gel films dip coated on phosphoric acid anodised aluminium films enhanced alkaline corrosion resistance [22]. The sols were applied by several dip coating cycles and the use of a boiling water treatment increased the alkaline resistance of the surfaces. The results suggested that some reaction by products of the boiling water treatment in the coating layer enhances the corrosion resistance. Subsequent research found that UV irradiation curing of the sol–gel produced a further improvement in alkaline corrosion resistant compared to thermally cured coatings [23]. A PTFE/silane system for anodised aluminium substrates with SiO_2/TiO_2 nano-fillers and a dispersion of various PTFE based fillers has also been reported [24]. The system combined the non-stick, low surface energy properties of PTFE with high scratch resistance and durability of the silane sol–gel. Vacuum dip coating of a TiO_2 based sol–gel coating was also conducted on oxalic acid anodised aluminium substrates [25]. It was shown that due to the air pressure inside the porous alumina the TiO_2 colloidal solution cannot penetrate the pores and vacuum dip coating is required to dispel the air pressure. Interestingly the authors showed that the addition of the crystalline anatase form of TiO_2 inside the pores of the anodised layers effectively inhibits the corrosion of the aluminium substrate when compared to unsealed anodised films.

It is unlikely that there is any chemical change in the bulk anodised aluminium layers due to sol–gel deposition, if the process is carried out at temperatures below 80° (temperature for boehmite conversion [1]). The penetration of sol–gel material in porous anodised structures may be considered to be key to obtaining corrosion resistance comparable to existing commercially used mechanisms. Current studies provide little evidence that sol–gel materials can be fully incorporated into anodised layers for corrosion protection, and findings to date have utilised the assistance of a vacuum deposition technique [25] or an electromotive force [26,27] to influence sol–gel impregnation. It has been reported that the charge on the surface of the anodic layers can play a role in the possible penetration of silica particles in the pores of anodic alumina [28] though current literature provides little clarification on the important parameters required for pore penetration of sol–gel materials, in anodic films, for corrosion control.

This study will analyse the interactions between silane based sol–gel chemistries and anodised layers including the pore penetration and compare corrosion performance on different anodised aluminium layers. Sol–gel films based on Tetraethylorthosilicate (TEOS) and Phenyltriethoxysilane (PhTEOS) have been used as sealing chemistries for anodic layers formed in sulphuric, oxalic and phosphoric acid electrolytes. The effect of pore sizes produced from each electrolyte on the sol–gel penetration has been investigated by FESEM and EDX. Sol–gel sealers prepared by both acid and base hydrolysis have been used to determine the effect of pH on penetration of sol–gel in the pores of the anodic layers. Corrosion evaluation has been conducted using neutral salt spray testing and electrochemical impedance spectroscopy.

2. Experimental

2.1. Sol–gel preparation

The silane precursors Tetraethylorthosilicate (TEOS) (98%) and Phenyltriethoxysilane (PhTEOS) (98%) were purchased from VWR International Ltd. (Irl), and hydrolysed separately under both acidic and alkaline conditions using 0.04 M HNO_3 and 0.1 M NH_4OH respectively. Absolute ethanol was immediately added to each mixture and left to stir for 45 min. De-ionised water was then added dropwise and the final solution was left to stir for 24 h before use. The final molar ratios for the acid catalysed (AC) and base catalysed (BC) formulations (silane:ethanol:water) were 1:2.5:3.5 and 1:3:4 respectively.

2.2. Particle size analysis

The particle size of the colloidal sol–gel dispersions was measured by a dynamic light scattering method using a Malvern Zetasizer ZS. Dynamic light scattering records the hydrodynamic diameter of the colloidal sol–gel particles undergoing Brownian motion in a dispersant of known viscosity and refractive index. By measuring the scattered light fluctuations with detectors at 90° or 173° from the sample the hydrodynamic diameter can be determined. The system was calibrated before analysis using a standard polystyrene latex material with particle size of 300 nm. The sol–gel was filtered though a 0.2 μm syringe filter to remove large contaminants from the sol–gel. A disposable cuvette cell was used for the measurement which was pre-cleaned using 0.2 μm filtered high purity ethanol.

2.3. Anodisation

AA3003-H14 (Si 0.6%, Fe 0.7%, Cu 0.05–0.25, Mn 1–1.15%, Zn 0.1%, other 0.15%, Al remainder) aluminium panels (150mm × 100mm × 0.6mm) were sourced from Q-Lab Europe Ltd. All pretreatment and anodising chemicals were purchased from Sigma Aldrich (IRL). The panels were degreased in acetone, etched in 10% NaOH at 40 °C for 50 s and rinsed in de-ionised water. The panels were then treated in 50% HNO_3 at room temperature for 90 s to remove any intermetallics from the surface prior to anodising. Anodising solutions were prepared using H_2SO_4 (98%), $C_2O_4H_2 \cdot 2H_2O$ and H_3PO_4 (85%) in de-ionised water. A 25% w/v and a 3% w/v solution of sulphuric acid and oxalic acid respectively were used for anodising at a constant current of 1.5 A/dm^2. For both acids the anodising times was 20 min. Phosphoric acid was prepared at 10% w/v and anodised at a constant of 40 V for 60 min. The anodising cell consisted of a counter electrode made of lead and the power was supplied by a Hewlett Packard DC power supply. Following anodisation the panels were rinsed for 20 min in an agitated de-ionised water bath to remove residual electrolyte from the pores. The panels were then force dried with hot air.

2.4. Sol–gel deposition

The aluminium oxide naturally hydrates in the atmosphere reducing the pore diameter. In the case of sulphuric and oxalic acid anodising the pores can fully close due to natural hydration. The anodic layers were therefore dip coated in the sol–gel formulations immediately after anodising, rinsing and drying using a KSV DC dip coater. The dip cycle consisted of a 20 minute immersion step in the sol–gel solution following withdrawal at a rate of 10 mm.min^{-1}. The panels were then cured in an oven at 110 °C for 16 h. The three anodic finishes were dip coated in the four formulations (AC TEOS, BC TEOS, AC PhTEOS and BC PhTEOS). Unsealed anodised panels were used as reference controls and were left unexposed for 1 week prior to testing.

2.5. Electron microscopy characterization and rating

The pore dimensions and penetration of the sol–gel sealers into the anodic layers were determined by electron microscopy using a Hitachi SU 70 Field Emission Scanning Electron Microscope (FESEM). Anodic film cross sections were prepared by bending the aluminium sample over 180° to induce micro-cracks in the oxide layer. The cross section of the crack face exhibits the pore structure of the anodic alumina for imaging at 1.5–3 keV. For imaging purposes the samples were sputter coated with a 4 nm layer of Pt/Pd using a Cressington 208HR sputter coater.

Dot Map energy dispersive X-ray spectroscopy was conducted using an Oxford Instruments INCA X-MAX Energy Dispersive X-ray Spectrometer. Cross sections were prepared by mounting samples in an epoxy resin before grinding using progressive grades of carbide paper and polished to a mirror finish with diamond solutions. The