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Corrosion protection of clad 2024 aluminum alloy anodized in tartaric-sulfuric acid bath and protected with hybrid sol–gel coating

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ABSTRACT

Clad AA2024 T3 specimens were anodized in a tartaric-sulfuric acid bath (TSA) and subsequently protected either by classical Cr-free water sealing treatment or by application of a hybrid sol–gel coating. The sol–gel coating was prepared using a solution with high water content (58 %v/v) and obtained by the hydrolysis and condensation of tetraethoxysilane (TEOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS). The morphology of the sealed anodic films and their thicknesses were evaluated by scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM) and glow discharge optical emission spectrometry (GDOES). The corrosion resistance of the samples was evaluated by electrochemical impedance spectroscopy (EIS) and salt-spray test. The results showed that the treatment with the hybrid sol–gel increased the resistive properties of the pores compared to the classical water sealing, delaying the access of aggressive species to the barrier layer.

1. Introduction

The 2xxx aluminum alloys are frequently used in the aircraft industry due to their high specific strength and light weight [1]. These alloys contain elements, as copper, used to improve their mechanical properties. However, copper rich intermetallics form microscopic galvanic couples which make these materials very sensitive to corrosion. To prevent the onset of localized corrosion processes that could impair the mechanical performance of the built structures the most common practice is to avoid the direct contact of the electrochemically active matrix with the surrounding environment by applying a protective coating system. In order to extend the service life of the parts, in the aircraft industry, prior to painting application, the basis matrix is frequently cladded or anodized.

The corrosion protection afforded by Alclad products relies in two basic principles. Initially the cladding material must be anodic in comparison with the base metal [2], providing cathodic protection to this latter in case of severe corrosion damage. In addition the microstructure of the cladding material must exhibit a lower number of intermetallic particles [3], providing superior localized corrosion resistance to the whole system, as proved in several published scientific works [3–5].

Anodization is based on the growth of an Al oxide layer by applying anodic potentials. This treatment gives rise to a duplex structure composed of a porous layer, comprising a close-packed array of hexagonal columnar cells perpendicular to the substrate, and a thin compact barrier layer in contact with the substrate [6]. The chromic acid anodizing process is the most widely used to produce these layers providing excellent corrosion protection [7]. This treatment can be used before painting without sealing post-treatment thanks to Cr(VI) self-healing ability. Furthermore, the roughness of the unsealed layer favors paint adhesion. Nevertheless, due to toxicological and environmental problems associated with hexavalent chromium, a range of developments on the production of Cr(VI)-free anodization baths has emerged in recent years. Researchers have mainly focused on the replacement of chromic acid anodizing by sulfuric acid anodizing (SAA) without [8–10] or with [5,11–15] the addition of modifiers. One of such modifier is tartaric acid [5,12–14,16,17], which, like other organic acids [18–21], seems to be able to produce anodic aluminum films with self-ordered porosity [17,22].

In the aircraft industry, whenever anodized Al alloys are used in service, the layer must be either painted or sealed. This latter process is frequently carried out by immersion in hot aqueous potassium dichromate solution. In order to completely remove Cr(VI) from the process, anodic films produced from

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tartaric-sulfuric anodizing (TSA) baths have been frequently sealed by immersion in boiling water [12]. Several works have shown that hydrothermally sealed anodic films produced on 2xxx Al alloys from TSA baths have superior corrosion resistance when compared with their counterparts produced from sulfuric acid baths [12,23]. It has been suggested that residual tartaric acid left inside the pores after the anodizing process [24] may form chelates complexes with Cu(II) cations present in the anodic film reducing the heterogeneities of this latter [23]. Boisier et al. [12] have concluded that sealed TSA anodized layers produced on AA2024-T3 substrate presents superior corrosion resistance than those produced in dilute sulfuric acid due to the higher compactness of the porous layer and higher resistance of the barrier layer. On the other hand, Garcia-Rubio et al. [5] have shown that hydrothermally sealed TSA clad Al 2024-T3 alloy has similar corrosion resistance to that exhibited by similar samples sealed in hot dichromate solution.

In this study, a post-treatment process based on the use of a hybrid sol–gel film applied on clad AA 2024-T3 anodized in a TSA bath is proposed. These films are reported to be environmentally friendly alternatives to replace chromate conversion coatings. Their synthesis is based on the sol–gel process which consists in hydrolysis and condensation of metal or silicon-alkoxides precursors, forming thin, dense and chemically inert films on substrates. In the case of hybrid organic–inorganic sol–gel coatings, precursors containing non-hydrolysable groups are used to incorporate an organic part in the coating. This organic contribution provides flexibility, reduces defects and improves compatibility with polymer coatings while the inorganic constituent provides superior adhesion to the metal surface and improves scratch resistance [25–30].

This work focuses on the comparison of the corrosion resistance of TSA anodized clad AA2024-T3 protected with this new system with that exhibited by samples sealed in boiling water. The cladding allows avoiding in this first approach the interference of the copper intermetallics on the anodic layer morphology and properties [31]. The morphology of the anodic films and their thicknesses were evaluated by scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM) and glow discharge optical emission spectrometry (GDOES). In addition, corrosion properties of the barrier, porous and sealed layers were determined by electrochemical impedance spectroscopy (EIS), which is a quick, non-destructive method providing reliable results about corrosion protection behavior. EIS data were interpreted on the basis of electrical equivalent circuits consisting of a combination of resistances and capacitances associated in series or in parallel providing the same electrical response as the studied electrochemical interface [7,10,32–35].

The novelty of the proposed system relies on the fact that, to the best of the authors' knowledge, no study is available in the literature where cladded or uncladded anodized Al alloys have been protected with hybrid films. In addition the compatibility of the organic precursor used in the present study (3-glycidyloxypropyl)trimethoxysilane (GPTMS)) with epoxy-based painting systems may constitute a major achievement for the aerospace industry as, at present, paintings are only applied to non-sealed anodized layers, which, recognizably, present inferior corrosion resistance than the sealed ones [5,12].

2. Experimental

The clad aluminum alloy AA2024-T3 was supplied by SONACA S.A (Gosselies, Belgium). The nominal composition of clad layer is 0.7 wt.% Si + Fe, 0.1 wt.% Cu, 0.05 wt.% Mn, 0.05 wt.% Mg, 0.1 wt.% Zn, 0.03 wt.% Ti and 0.03 wt.% others. The specimens of size 5 cm × 10 cm × 0.126 cm were degreased by sonication in acetone for 10 min and immersed in a commercial alkaline degreasing bath (Turco 4215 NCLT) at 50 °C for 10 min. Before anodizing, the samples were dipped in an alkaline etching bath (NaOH solution, 40 g L^{-1}) at 40 °C for 30 s and in a chromate-free commercial acid dismutting bath (Turco Smuttgo) at room temperature for 15 s. Between each step, the specimens were rinsed in deionized water.

The anodizing process was performed in a tartaric-sulfuric acid bath (TSA). It was carried out in a solution of 40 g L^{-1} H_2SO_4 + 80 g L^{-1} $C_4H_6O_6$ at a constant voltage of 14 V (current density between 0.32 and 0.35 A/dm^2) for 20 min at 37 °C. After anodizing, the samples were rinsed with deionized water and then either sealed in boiling deionized water for 25 min or protected with a hybrid organic–inorganic coating applied by the sol–gel route for 2 min.

Sol–gel films were prepared as follows: tetraethoxysilane (TEOS) (20 %v/v) and (3-glycidyloxypropyl)trimethoxysilane (GPTMS) (10 %v/v) were added in a mixture of ethanol (10 %v/v) and distilled water (58 %v/v). The pH was adjusted by acetic acid in the range of 2.3–2.5. The solution was stirred at room temperature for 2 h in order to allow hydrolysis of the alkoxy groups. The anodized samples were immersed in the hydrolyzed solution and maintained for 2 min by a dip-coating process. The withdrawal rate was fixed at 100 mm/min. The samples were then cured at 150 °C for 1 h in an oven. All the reagents were purchased at Aldrich and used as received without further purification.

The morphological characterization of the samples was determined using a Philips XL-20 and an Oxford WDX 600 scanning electron microscope (SEM) coupled to an energy dispersive X-ray spectrometer analyzer (EDX). The FE-SEM (field emission scanning electron microscopy) surface characterization was carried out using a FEI Inspect F50. Composition profiles were recorded in depth by GDOES using a Horiba Jobin Yvon profiler instrument operated at Ar pressure of 650 Pa and power of 25 W. The atomic percentage accuracy is around 50 ppm for the element signals such as O, H, S, P, N and higher for the others.

The corrosion protection provided by the different treatments was evaluated by means of electrochemical impedance spectroscopy (EIS). Electrochemical tests were performed using a Princeton Applied Research Parstat 2273 (Ametek) potentiostat-frequency analyzer controlled using Power Suite software. A classical three electrodes arrangement was used. An Ag/AgCl (+0.207 V vs. SHE) electrode and a platinum plate were used as reference and counter electrode, respectively. EIS measurements were performed using signal amplitude of 20 mV (rms) and the frequency was ranged from 10^5 to 10^{-2} Hz. The contact immersed area was 7.0 cm^2. The impedance measurements were performed after different immersion times in a 0.5 M NaCl naturally aerated solution at room temperature. Accelerated corrosion tests were carried out in a salt spray chamber Q-FOG Cyclic Corrosion tests (Labomat). The samples were exposed for 1008 h (42 days) using 5 wt.% NaCl solution ($6.5 < pH < 7.2$) with a spray flow rate of 40 mL h^{-1}, according to standard ASTM B117-07a [36]. During the test the chamber was kept at 35 ± 1 °C. The samples were periodically removed from the chamber for visual evaluation of the extent of corrosion. The coating efficiency was visually assessed by comparing the size of the corroded area before and after the test.

3. Results and discussion

3.1. Morphological characterization

Fig. 1 presents the FE-SEM micrographs of the surface of anodic layers unsealed, hydrothermally sealed (after 25 min of sealing in boiling water) and coated with the hybrid sol–gel. As shown in Fig. 1(a), the porous structure of the anodic layer is clearly observable before sealing. The pore distribution is regular with an average