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Silane and epoxy coatings: A bilayer system to protect AA2024 alloy

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ABSTRACT

This work has proved that a good combination of a simple and fast metal pre-treatment, followed by the deposition of a thin layer of an organic–inorganic silane coating and further layer of epoxy coatings, are able to protect the aluminium alloy AA2024-T3 against corrosion in high concentrations of NaCl solution. The alloy AA2024 is one of the most employed aluminium alloy in structural applications due to its good mechanical properties. However, AA2024 alloy series commonly presents galvanic corrosion due to the rich content of copper element. The influence of different surface pre-treatments, the presence of a silane layer as pre-coating treatment and the influence of phosphonic acids combined with the silane layer on the corrosion protection and adhesion to the aluminium alloy have been examined using accelerated corrosion tests. High roughness and the presence of a pre-coating film between the metal surface and the organic coating were essential for a good protection and resistance to blistering appearance in the surface of AA2024-T3.

1. Introduction

Aluminium alloy AA2024-T3 is a high strength material usually obtained by a rolling based transformation process. Its hardness, improved by means of precipitation process during the cooling, provides an alloy with very interesting applications as structural materials (e.g. fuselage skin in aerospace industry). However, its excellent mechanical properties, which are mainly due to copper content (about 4–5%), are in contrast with a poor resistance against corrosion. This drawback is consequence of the galvanic coupling between copper and aluminium, which results in microstructural changes based on the segregation of intermetallic compounds into grain boundaries producing intergranular corrosion [1].

Chromic anodizing has been widely used to protect the AA2024-T3 alloy, several inhibitors being incorporated to increase the performance of anodic film formed [2]. However, the use of Cr(VI) is becoming very problematic due to its classification as carcinogenic to human health and also its contribution to environmental pollution as a toxic residue. Alternative inhibitors are being currently investigated to substitute the Cr(VI), such as vanadates, molibdates and permanganates based solutions and triazol or thiazol derivatives [3–5].

The development of non-chromate environmentally friendly coatings has been promoted in the last decade. In particular, a considerable effort has been devoted to investigate aluminium surface modification with silane films, which can be applied coupled with organic coatings. Usually, silane coatings are the first layer of the hybrid organic–inorganic barrier in contact with the metal surface, whereas the second layer is an organic resin (e.g. epoxy commercial primers) applied onto the silane coating. Alternatively, silane compounds can also be pre-hydrolyzed to obtain stable polysiloxanes miscible with primers based in polymer resins [6–10]. Surface modification of metals by phosphonic acids and derivatives (e.g. aminotrimethyllenephosphonic acid) is another strategy to replace chromium based pre-treatments by formation of self-assembled monolayers through spontaneous or induced adsorption in metal surface [11–13]. Sol–gel technologies commonly use liquid sample deposition combined with curing processes. Furthermore, sol–gel matrices may result in a particular technology that offers many possibilities by, for example, incorporating nanoparticles of ceramic substances (e.g. zirconium dioxide or cerium nitrates) to protect metal surfaces [14,15], as well as to control the viscosity of the hydrolysed silane solution before deposition.

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Among silanes for sol–gel depositions, TEOS (tetraethylorthosilicate), VTMS (vinyltrimethoxysilane), VTES (vinyltriethoxysilane), and GPTMS (3-glycidoxypropyltrimethoxysilane) have been frequently used in several previous works [16–19]. An interesting review has been published by Wang and Bierwagen [20] regarding sol–gel technology and corrosion protection. The effect of the surface treatment with these silanes in combination with phosphonic acid compounds, such as 1,2-diaminoethanetetrakismethylenephosphonic acid (EDTPO) or aminotrimethylenephosphonic acid (ATMP), has been studied for the protection against corrosion of AA2024 aluminium alloy [21–23]. Authors were particularly interested in the influence of different parameters, such as hydrolysis time, temperature and acid concentration, in the silane coating formation and further protective effect. Characterization of these compounds was carried out by means of FTIR and Raman spectroscopies and electrochemical impedance spectroscopy (EIS). Morphological aspects related with the characteristics of films were controlled by means of optical and electron microscopies. The corrosion protection was evaluated through accelerated assays using sodium chloride solutions (0.05 mol L^{-1}) and polarization techniques.

The present work attempts to constitute the nexus with these preceding works. Thus, the same sol–gel technology has been used for the deposition of VTMS and TEOS in a solution medium with a very low concentration of an organic phoshonic acid derivative, diethylenetriaminepentakis-methylphosphonic acid (DETAPO). Phosphonic molecules have a positive synergic effect on the formation of thicker silane films, as proved in previous work [23]. Therefore, one of our aims is to test a phosphonic derivative with higher concentration of O=P—OH groups as compared to ATMP or EDTPO molecules. Another important objective is the evaluation of two different pre-treatments to obtain a suitable metal surface, which are intended to guarantee a good adhesion of the silane coating. Thus, the mechanical dealing with ceramic abrasive has been compared with a chemical etching typically applied in anodising technology. The surface state is controlled in both cases by tracing the roughness after the different pre-treatments. Physicochemical, thermal and morphological characterization have been carried out using techniques like FTIR spectroscopy, DSC, TGA, optical and scanning electron microscopy (SEM). Finally, protective properties of the bilayered system, composed by the new silane films and a commercial epoxy primer, have been studied using accelerated corrosion assays. Results have been contrasted with a monolayered system composed by the epoxy coating directly adhered to the aluminium surface.

2. Experimental

2.1. Materials

All reagents used were of analytical grade and supplied by Sigma–Aldrich. The chemical structure of the two silane derivatives, VTMS ($C_5H_{12}O_3Si$) and TEOS ($Si(OC_2H_5)_4$)), and the phosphonic acid, diethylenetriaminepentakis(methylphosphonic acid) (DETAPO, $C_9H_{28}N_3O_{15}SiP_5$), employed in this work are shown in Scheme 1.

2.2. Surface pre-treatment

Disc specimens of aluminium AA2024-T3, with diameter 40 mm and length 10 mm, were used for the corrosion assays. They were obtained from a rolled bar, which was turned in a conventional lathe in order to obtain the required diameter. Later, the discs were cut in a band saw. Discs were faced in a conventional lathe up to required thickness. Before the silane deposition, two different pre-treatments were applied on the aluminium surface to remove dirt and fat residues and to improve the adhesion of the hybrid material on the metal surface. In the first pre-treatment, some specimens were mechanically polished with corundum 800 [24] as abrasive grain, in an automatic polishing machine Presi Mecapol 230 at a speed of 50 min^{-1} and with work-piece force on the disc of 1.5 daN. This was followed by a wash with distilled water. Hereafter, such specimens have been labelled as “C”. The second pre-treatment consisted on a chemical etching with an industrial acid degreaser used in anodising and painting technology to prepare aluminium surfaces (Novaclean® AL 86LF from Henkel Ibérica S.A.). For this purpose, specimens were previously sanded with silicon carbide of different grain size (320, 600 and 1200) [24], cleaning with water and acetone being performed after change each sand paper and also before and after the immersion in Novaclean® AL 86LF. These specimens have been named “N”. Finally, all AA2024 specimens were dried with a hot air flow before the silane deposition.

2.3. Silane film preparation and deposition

A mixture containing 50 mL of ethanol, 46 mL of deionized water, 3 mL of VTMS and 1 mL of TEOS was prepared. Then, 2.3 mg of DETAPO, corresponding to a concentration of 3.75×10^{-5} mol L^{-1}, was incorporated, the mixture being stirred mechanically for 1 h at room temperature and subsequently stored for 3 days prior to use. Immediately after the pre-treatment, AA2024 samples were immersed in the sol–gel bath for 30 min and cured in an oven at 110 °C for 1 h. The silane film was applied to several specimens previously pretreated with mechanical decaling and chemical etching, as detailed before.

2.4. Epoxy paint preparation and application

The primer used as a second coating layer to the protection of the AA2024 surface is a two components epoxy-polyamide material commercialized by Pinturas Hempel S.A. (Hempadur 15570 and curing agent 95570). This primer is characterized by a high performance in protection against corrosion and the dry film paint has good mechanical properties as hardness, toughness and good adherence. The resin–hardener ratio (v/v) used was 4/1 according to the manufacturer recommendations. The mixture was prepared in a polyethylene reservoir at room temperature (25 °C) by stirring for about 30 min. The discoid specimens were immersed into the reservoir containing the liquid paint suspended by a nylon thread. This process should be reproducible as much as possible in order to obtain a homogeneous distribution of paint across the surface and comparable thickness in all specimens tested.

The painted specimens were allowed to cure for 7 days at room temperature. Finally, commercial paint Hempadur 15300/15302 was applied to the edges and holes to avoid corrosion preferential beginning. Once the paint was completely dried, thickness was measured by using the meter Mega-Check Pocket of Neurtek S.A. The apparatus was previously calibrated to non-ferrous basis by using the gauges supplied.

2.5. Characterization techniques

2.5.1. Roughness measurements

In order to obtain required roughness parameters of chemically and mechanically polished samples, a contact roughness meter Taylor-Hobson Talysurf series 2 was used. In order to discard a preferred direction of the polishing or etching marks on the sample's surface, both longitudinal and transversal measurements were performed. Roughness parameters that were taken into account are detailed below [25].