



Influence of the alloy microstructure and surface state on the protective properties of trivalent chromium coatings grown on a 2024 aluminium alloy



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ABSTRACT

The protective properties of trivalent chromium process (TCP) coatings grown on a 2024-T3 aluminium alloy were studied on the basis of electrochemical measurements performed both in sulphate and chloride solutions and neutral salt spray tests. The influence of the alloy microstructure and surface state was studied: two batches, each one characterized by its own coarse intermetallic particle distribution, and two surface states, i.e. laminated and polished, were considered. Results showed that in 0.1 M Na₂SO₄, the protective properties of the TCP coatings decreased when the roughness of the initial surface increased. Furthermore, improved protective properties were observed for a TCP coating grown on a surface containing a lower amount of Al-Cu-Mg IMCs in the initial microstructure. The most plausible explanation is that a fast kinetics of coating growth, either associated to strong initial roughness or a great surface copper coverage, was detrimental for the protective properties of the coatings. In more aggressive solutions, i.e. 0.5 M NaCl solution or for neutral salt spray tests, the differences are not significant. The findings are highly relevant for industrial applications: the results showed that variations in batches, for a same type of alloy, or in initial surface state should not be detrimental for the corrosion resistance of the TCP coated samples. However, the conversion process had to be adapted for different types of alloys, characterized by their own microstructure.

1. Introduction

Aluminium alloys are widely used in the aeronautical industry due to their high specific modulus E/ρ (E , Young modulus and ρ , density) that allows the mass of the structures to be reduced [1]. Their good mechanical properties are mainly related to the addition of different alloying elements that, unfortunately, lead to a decrease of the corrosion resistance of the alloys when compared to pure aluminium [2,3]. Chromate conversion coatings were largely used to improve the corrosion resistance of aluminium alloys. However, European regulation REACH, that bans the use of hexavalent chromium, will become effective in 2024 [4]. Therefore, new chemical conversion treatments are developed. Trivalent chromium processes (TCP) constitute one of the most promising substitution solutions [5–9].

Contrary to chromate coatings, anti-corrosion properties of trivalent chromium coatings are known to depend significantly on the surface preparation, i.e. pre-treatments performed before TCP [2,7,10–17]. Before chemical conversion, the alloy surface is cleaned in a degreasing

solution to remove fats and oils. Then, a desmutting solution dissolves the native oxide and allows the formation of a new oxide with controlled thickness and composition [2]. Li et al. have shown that a long desmutting step reduces the anti-corrosion performance of a commercial trivalent chromium coating (Alodine 5900 RTU coating, Henkel group) [17]. They attributed the decrease of the anticorrosion properties to the roughness generated by the desmutting process, and more precisely, to the nucleation and growth of pits with increasing depth over the time of desmutting in Turco Liquid Smut-Go NC. Toh et al. have studied different desmutting solutions on aluminium alloy 7475-T7651; they have shown important differences in the morphology and oxide roughness at the alloy surface [18]. Others works have shown a huge influence of the substrate microstructure on the surface reactivity during the pre-treatments and as a consequence on the anti-corrosion properties of the coatings [19–22]. Considering the complex microstructure of industrial aluminium alloys, it seems difficult to establish a clear relationship between the effects of the pre-treatments on the surface morphology, the kinetics of TCP coating growth and the

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subsequent protective properties of the TCP coatings. All of this gave rise to new challenges at the industrial scale. The first one concerns the ability to generalize the conversion process to different alloys; the second one is related to the need to get away from the influence of the surface state of the substrate before the pre-treatments on the growth of the TCP coatings and their subsequent anticorrosion properties.

In the present work, the surface morphology, chemistry and reactivity after different steps of pre-treatment (degreasing and desmutting) were studied for three samples of AA 2024-T3: two polished samples from two batches of AA 2024-T3 to study the influence of the microstructure and a laminated sample of one of the two batches to determine, by comparison with the polished sample of the same batch, the effect of the surface state before pre-treatment. Then, the growth rate of the TCP coatings was analysed and their protective properties were evaluated by means of OCP measurements, potentiodynamic polarisation, electrochemical impedance spectroscopy measurements and neutral salt spray tests.

2. Materials and methods

2.1. Materials and sample preparation

The material used was a cold rolled AA 2024-T3 provided as sheets of different thicknesses with similar chemical compositions (Table 1). Two batches were studied and called as alloy A for the 1 mm thick sheet and alloy B for the 3 mm thick sheet respectively. All samples corresponded to $125 \times 80 \times 3 \text{ mm}^3$ parallelepipeds removed from the sheets. Alloy A was studied as received, i.e. after rolling: the samples were called as laminated samples in the following. Other samples of alloys A and B were abraded using SiC paper down to 1200 and then mechanically-polished to a $1 \mu\text{m}$ colloidal diamond finish prior to the pre-treatment. They constituted a reference surface state and are called as polished samples in the following. The samples were protected using a silicone one-component (CAF1, Bluestar Silicones) in order to expose only one side to the different solutions with a 4 (or 10) cm^2 surface area. They were rinsed with acetone prior to the pre-treatments in order to remove inks and other surface pollutants. Then, they were degreased in an alkaline bath ($40 \text{ g}\cdot\text{L}^{-1}$ sodium tripolyphosphate, $40 \text{ g}\cdot\text{L}^{-1}$ borax and $5 \text{ mL}\cdot\text{L}^{-1}$ Turco 4215 additive, $\text{pH} = 9$) for 1200 s at 60°C . Finally, they were immersed in the desmutting bath, i.e. a sulfo-nitro-ferric solution ($\text{pH} = 1$) for 300 s at room temperature. All the pre-treatment steps were followed by a rinsing in deionised water. All reactants used are of industrial quality.

For the formation of the TCP coating, the degreased and desmutted samples were first immersed for 600 s in the conversion solution (32% v/v Socosurf TCS (Socomore, France), pH between 3.8 and 4) at 40°C to form the conversion layer. The coated samples were then immersed in the post-treatment solution (10% v/v Socosurf PACS (Socomore, France), 5% v/v H_2O_2 at 35% v/v in water, pH between 4.2 and 5.3) at room temperature for 300 s. All treatments were followed by rinsing in deionised water. Finally, the samples were dried at 60°C during 600 s.

2.2. Characterisation of the surface morphology and microstructure. Morphology of the TCP coatings

Scanning Electron Microscopy – Field Emission Gun (SEM-FEG) observations were performed with a JEOL JSM 7800F Prime (platform of Micro-characterisation Raimond Castaing, Toulouse) operating at

Table 1
Composition of 2024-T3 aluminium alloys.

Wt%	Al	Cu	Mg	Mn	Fe	Si	Cr	Zn	Ti	V	Zr	Other
A	Balance	4.5	1.4	0.57	0.21	0.08	0.01	0.13	0.02	0.01	0.01	0.05
B	Balance	4.4	1.4	0.51	0.15	0.08	0.01	0.17	0.02		0.01	0.05

Table 2
Classification criteria used for the identification of IMCs ($\phi > 2 \mu\text{m}$) where \bar{X} corresponds to the results of measurements performed for the matrix.

Type	Al-Cu-Mn-Fe-Si	Al-Cu-Mg	Al-Cu
Classification criteria	$\text{Fe} > \bar{Fe} + 0.2$ $\text{Cu} > \bar{Cu}$	$\text{Mg} > \bar{Mg} + 0.5$ $\text{Fe} \approx \bar{Fe}$	$\text{Mg} \approx \bar{Mg}$ $\text{Fe} \approx \bar{Fe}$ $\text{Cu} > \bar{Cu} + 1$

5 kV (secondary electrons) and 10 kV (backscattered electrons) to characterize both the surface morphology and microstructure of the alloys. Concerning the microstructure, attention was paid to coarse intermetallic particles (IMC); energy dispersive spectroscopy (EDS) measurements performed by means of a EDS SDD X-Max 80 mm^2 Oxford Instruments AZtecEnergy allowed three types of IMC ($\phi > 2 \mu\text{m}$) to be distinguished on the basis of the classification criteria described in Table 2. Transmission electron microscopy (TEM) observations were performed with a JEOL JEM 2100F (platform of Micro-characterisation Raimond Castaing, Toulouse) operating at 200 kV to characterize the structure of the TCP coatings. TEM samples were prepared with a Scanning Electron Microscopy – Focused Ion Beam FEI HELIOS 600i (platform of Micro-characterisation Raimond Castaing, Toulouse) equipped with a Gallium Ionic Canon. Samples were covered by an electronic carbon coating ($0.5 \mu\text{m}$, operating at 5 kV and 2.5 nA, precursor: Naphtalene (C_{10}H_8)) and an ionic platinum coating ($3 \mu\text{m}$, operating at 30 kV and 0.43 nA, precursor: Methylcyclopentadieny(trimethyl)platinum ($\text{C}_5\text{H}_4\text{CH}_3\text{Pt}(\text{CH}_3)_3$)) before cutting operating at 30 kV and 47 nA to 80 pA.

2.3. Characterisation of the electrochemical behaviour and protective properties

The reactivity of the alloy surface before and after the two pre-treatment steps, related mainly to the corrosion behaviour of the IMCs present on the sample surface, was evaluated by performing anodic polarisation in a 0.1 M Na_2SO_4 solution [23]. A three-electrode cell connected to a Bio-Logic VSP potentiostat was used with a saturated calomel electrode (SCE) as reference electrode and a graphite rod as counter electrode. The working electrode was placed vertically with a surface exposed to the electrolyte of 4 cm^2 . Polarisation was performed from open circuit potential (OCP) minus 0.05 V to 0.5 V/SCE at $500 \text{ mV}\cdot\text{h}^{-1}$ after 1 h of immersion at OCP.

The relative electroactive copper content on the sample surface (4 cm^2 exposed to the solution) was determined by cyclic voltammetry (CV) experiments performed in deaerated borate buffer solution ($8.17 \text{ g}\cdot\text{L}^{-1}$ $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$, $7.07 \text{ g}\cdot\text{L}^{-1}$ H_3BO_3 , $\text{pH} = 8.4$) at room temperature [16,24]. The solution was deaerated for 15 min with nitrogen bubbling before CV experiments. The procedure consisted of (a) a 5 min polarisation at $-0.7 \text{ V}_{\text{SCE}}$; (b) scan from $-0.7 \text{ V}_{\text{SCE}}$ to $0.3 \text{ V}_{\text{SCE}}$ then back to $-1.2 \text{ V}_{\text{SCE}}$ at $1 \text{ mV}\cdot\text{s}^{-1}$; (c) hold at $-0.7 \text{ V}_{\text{SCE}}$ during 10 min; (d) repeat step (b); (e) hold at $-0.7 \text{ V}_{\text{SCE}}$ during 20 min; (f) repeat step (b). The area under $\text{Cu}(0) \rightarrow \text{Cu}(I)$ peak in the last scan was used to determine the relative electroactive copper content as largely detailed in Scully's work [25,26].

Electrochemical impedance spectroscopy (EIS) measurements were performed in naturally aerated 0.1 M Na_2SO_4 solution at room temperature to evaluate the protective properties of the coatings using the

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