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## Corrosion Science

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# Influence of the microstructure on the corrosion behaviour of 2024 aluminium alloy coated with a trivalent chromium conversion layer

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## ARTICLE INFO

## Keywords:

A. Aluminium  
A. Copper  
A. Intermetallics  
A. Metal coatings  
B. Cyclic voltammetry  
B. EIS

## ABSTRACT

The influence of 2024 aluminium alloy microstructure on the protective properties of trivalent chromium process (TCP) coatings was studied: samples aged at 190 °C were analysed by comparison to a T3 state. The surface Cu coverage after deoxidation was higher for long-aged samples because nanometer scale Cu-rich precipitates formed during ageing behaved as distinct electrochemical entities and contributed to the formation of copper deposits. The growth mechanisms and kinetics of TCP coatings were directly related to the surface Cu coverage: thicker but more defective TCP coatings formed on long-aged samples leading to the lowest anti-corrosion properties.

## 1. Introduction

Aluminium alloys are largely used in the aeronautical field because of their low density close to  $2.7 \text{ g cm}^{-3}$  and their high mechanical properties due to the addition of some alloying elements such as copper, zinc or lithium [1]. However, these alloying elements lead to a heterogeneous microstructure and increase the alloy susceptibility to localised corrosion [2–6].

2024 aluminium alloy (AA 2024) is one of the most used alloys for aircraft manufacturing. Copper and magnesium are the major alloying elements in this alloy; they are involved in the formation of intermetallic coarse particles (IMCs), the composition of which is widely discussed in the literature [7–10]. When the alloy is exposed to an aqueous solution, these particles can act as anodic sites or cathodic sites compared to the aluminium matrix, and even evolve, due to composition changes, from anodic to cathodic sites [4,5,11,12]. Such differences in electrochemical reactivity lead to galvanic coupling processes between matrix and IMCs associated with pitting corrosion [4,13,14].

To protect the alloy against corrosion, surface treatments are used, such as conversion processes for parts that require electrical conductivity. For more than 50 years, chromate treatments based on hexavalent chromium have been used for their outstanding anti-corrosion properties: they show good barrier properties, are less susceptible to chloride adsorption and correspond to self-healing coatings [15–18]. Nevertheless, hexavalent chromium is harmful for the health and the environment and is destined to disappear to comply with the REACH

regulation (Registration, Evaluation and Authorisation of CHemicals) [18,19]. In this framework, manufacturers in the aeronautics field have developed new conversion processes based on trivalent chromium and referred as TCP (Trivalent Chromium Process).

Actually, TCP coatings are considered as promising solutions to replace hexavalent chromium-rich coatings. However, their anti-corrosion properties strongly depend on the underlying microstructure. Qi et al. studied the growth mechanism of a TCP coating on AA 2024-T351 focusing on the difference between the coating developed on the matrix and that grown on IMCs [20]. They observed a thicker TCP coating on S-phase particles, the formation of the conversion layer being controlled by the local increase of pH [21,22]. After dealloying, S-phase particles constituted cathodic sites where protons and oxygen reduction occurred. Due to the local increase of pH they produced, those reactions promoted the precipitation of TCP coating, i.e. chromium- and zirconium-rich layer [11]. Moreover, Meng et al. studied the effect of copper content in a 7xxx aluminium alloy on the protective properties of chromate conversion coatings [23]. With copper content in the range [0.013–2.0 wt. %], they observed better corrosion resistance for samples with low copper content. The authors attributed the detrimental effect of copper to the copper enrichment of the sample surface after pre-treatments for samples containing a high copper amount. However, depending on the initial copper amount of the alloy, copper does not exist in the same chemical form. In the AA 2024, copper is involved in IMCs (Al-Cu-Mg or Al-Cu-Mn-Fe types); it is present in supersaturated solid solution ( $\alpha$ -Al) but can be present also,

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<https://doi.org/10.1016/j.corsci.2018.07.007>

Received 24 April 2018; Received in revised form 3 July 2018; Accepted 5 July 2018

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depending on the metallurgical state, in the form of hardening precipitates (clusters of solute elements, GP zones and  $S'/S$ - $Al_2CuMg$  or  $\theta'/\theta$ - $Al_2Cu$  phases). Considering the ability to define a critical feature sizes in the context of corrosion of Al-alloys as shown by Ralston et al. [14], an analysis of the effect of copper on the anticorrosion properties of the TCP coatings depending on its chemical form would be clearly of both scientific and industrial interest.

Therefore, this study attempts to provide some new insights about the role of the alloy microstructure on the anticorrosion properties of TCP coatings and focussed on AA 2024 and its major alloying element, i.e. copper. Different samples corresponding to ageing treatments from a T3 state at 190 °C for durations between 0 to 72 h were considered in order to have a set of samples with copper in different chemical forms. Clearly, such ageing treatments will lead to a decrease of the mechanical properties of the alloy and do not have an industrial interest from this point of view. However, the aim here is to increase the knowledge concerning the influence of copper on the protective properties of the TCP coatings, as requested by the industrial partners of the NEPAL project in which this work was involved. Therefore, the different microstructures were studied by Scanning Electron Microscopy with a Field Emission Gun (FEG-SEM) and Transmission Electron Microscopy with a Field Emission Gun (FEG-TEM). Their corrosion behaviour was studied by open circuit potential and potentiodynamic polarisation measurements. Then, the copper enrichment of the sample surface after pre-treatments was measured by cyclic voltammetry. Finally, the growth kinetics and morphology of the TCP coatings on both T3 and aged AA 2024 samples were studied and the corrosion behaviour of the coated samples was evaluated by open circuit potential and electrochemical impedance spectroscopy measurements.

## 2. Materials and methods

### 2.1. Materials

The material studied was AA 2024 cold rolled 3 mm thin sheet with the chemical composition given in Table 1. The alloy was provided in the T3 metallurgical state, i.e. hot rolled, cold rolled, solution heat treated, water quenched, stress relieved and naturally aged at room temperature. Samples in T3 state were referred as T3-reference samples. Then, in order to induce copper precipitation, heat treatments were performed for some T3 samples. The heat treatments consisted in an ageing at 190 °C for 1 h, 12 h or 72 h from the T3 metallurgical state; the samples were referred as 190-1, 190-12 and 190-72 aged samples respectively. Before the experiments, all samples were ground with abrasive paper SiC 1200, 2400 and 4000 then polished with diamond paste down to 1  $\mu$ m. Then, they were ultrasonically cleaned in demineralised water for 30 s.

### 2.2. Preparation of the TCP coated samples

The whole TCP included a first step of pre-treatment followed by a second step of conversion layer growth. Regarding the pre-treatment step, the samples were first degreased with acetone. Then, they were degreased for 20 min at 60 °C in a pH = 9 alkaline solution with the following composition: 40 g L<sup>-1</sup> of sodium tripolyphosphate, 40 g L<sup>-1</sup> of borax and 5 mL L<sup>-1</sup> of Turco 4215 additive. Afterwards they were deoxidised in the Socosurf A1858/A1806 bath (Socomore, France), i.e. a pH = 1 sulfo-nitro-ferric solution, for 5 min at 50 °C. After degreasing and deoxidation, the pre-treated samples were first immersed for

10 min in the TCS conversion solution (32% v/v Socosurf TCS provided by Socomore, France, pH between 3.8 and 4) without bath agitation at 40 °C; during this step, the open circuit potential was measured for all samples to study the growth kinetics of the TCP coatings. This step was followed by an immersion of the coated samples in the post-treatment PACS solution (10% v/v Socosurf PACS provided by Socomore, France, 5% v/v H<sub>2</sub>O<sub>2</sub> at 35% v/v in water, pH between 4.2 and 5.3) at room temperature for 5 min. All the conversion steps were followed by a rinsing step under reverse osmosis water. All reactants used are of industrial quality. Finally, samples were dried at 60 °C during 10 min. For coated samples, all tests were performed at least 48 h after the conversion treatment.

### 2.3. Experimental methods and techniques

#### 2.3.1. Analysis of the microstructure and characterisation of the TCP coatings

An optical microscope (OM, MA200 by Nikon) was used to observe the samples after electrochemical etching with a Flick reagent (3.5 ml of HBF<sub>4</sub> in 96.5 ml of deionised water) to determine the grain size. OM observations also allowed different types of IMCs to be observed but, for a more accurate analysis, IMCs were characterised by using a Scanning Electron Microscope (SEM VEGA 3 by TESCAN) coupled with Energy Dispersive X-ray spectroscopy (EDS BRUKER). All analyses were performed at an accelerating voltage of 15 kV. Observation of finer precipitates required the use of a Scanning Electron Microscope with a Field Emission Gun (FEG-SEM FEI HELIOS 600i) for intergranular precipitates and a Transmission Electron Microscope with a Field Emission Gun operated at 200 kV (FEG-TEM JEOL JEM 2100F) for intragranular hardening precipitates. For the TEM observations, the samples were ground with abrasive paper SiC 1200, 2400 and 4000 down to 100  $\mu$ m, cut in discs of 3 mm diameter and electropolished at -15 °C in TenuPol-5 with 900 ml of CH<sub>3</sub>OH and 300 ml of HNO<sub>3</sub>. Both FEG-SEM and FEG-TEM observations were performed using apparatus available in the Raimond Castaing Microanalysis Center (Toulouse, France). Hardness measurements performed with a micro-hardness instrument (Omnimet-2100 by BUEHLER) with a Vickers indenter and a 500 g load completed the characterisation of the specimens.

Concerning the TCP coatings, samples were prepared with a Scanning Electron Microscope – Focused Ion Beam (FEI HELIOS 600i) using a Gallium Ionic Canon. In a first step, they were covered by a gold deposit then an electronic carbon coating (thickness of 0.5  $\mu$ m) using Naphtalene (C<sub>10</sub>H<sub>8</sub>) as a precursor (experimental conditions: 5 kV and 2.5 nA). Then, a 3  $\mu$ m thick ionic platinum coating was deposited using Methylcyclopentadieny(tri-methyl)platinum (C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>Pt(CH<sub>3</sub>)<sub>3</sub>) as a precursor (experimental conditions: 30 kV and 0.43 nA). Cutting was operated at 30 kV and 47 nA to 80 pA.

#### 2.3.2. Electrochemical measurements

All the electrochemical measurements were performed with a three electrodes cell (with a platinum electrode as counter electrode and a saturated calomel electrode as reference) by using a VSP-128 Biologic potentiostat. The corrosion behaviour was analysed for uncoated and coated samples in a 10<sup>-1</sup> M Na<sub>2</sub>SO<sub>4</sub> + 10<sup>-3</sup> M NaCl solution and in a 0.5 M NaCl solution respectively. The NaCl solution was considered as representative of the electrolyte used for industrial tests performed for coated samples but was too aggressive for uncoated samples. For uncoated samples, open circuit potential (OCP) measurements were performed by recording values with a 1 s interval for 90 min.

**Table 1**  
Chemical composition of the 2024 aluminium alloy (weight percent).

Elements	Al	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Zr
wt. %	Bal.	0.08	0.15	4.4	0.51	1.4	0.01	54 ppm	0.17	0.02	0.01

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