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Trivalent chromium conversion coating formation on aluminium

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ABSTRACT

The formation of a trivalent conversion coating on aluminium has been investigated using analytical electron microscopy, atomic force microscopy, ion beam analysis, glow discharge optical emission spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. The coating is shown to comprise a chromium- and zirconium-rich outer layer and an aluminium-rich inner layer. Zirconium and chromium are present in chemical states consistent with ZrO_2, ZrF_4, $Cr(OH)_3$, $Cr_2(SO_4)_3$, CrF_3 and CrO_3 or CrO_4^{2-}. However, negligible amounts of Cr(VI) species occurred in coatings formed in de-aerated solution. Electrochemical impedance spectroscopy revealed that the inner layer provides the main corrosion protection during short-term tests in 0.1 M sodium sulphate solution at room temperature.

1. Introduction

Chromate conversion coatings are widely used as protective coatings for high-strength aluminium alloys, such as AA 2024-T3, which are susceptible to pitting corrosion [1,2]. However, due to the toxicity and high disposal costs of Cr(VI) compounds, alternative treatments are being sought, amongst which trivalent chromium conversion (TCC) coatings are considered promising [2–4]. A TCC coating bath generally contains ZrF_6^{2-}, Cr^{3+} and SO_4^{2-} constituents in an aqueous solution with a pH of 3.8–4.0 and coating is undertaken at a temperature of 40 °C [3,5]. The bath is similar to those used for the formation of zirconium-based conversion coatings, but with an addition of a trivalent chromium salt [6]. The resultant coatings on aluminium alloys have been reported to provide corrosion protection similar to that of chromate-based conversion treatments [7].

The coatings are considered to form by precipitation of an outer chromium- and zirconium-rich layer due to an increase of pH at sites of the usual cathodic reactions:

$$2H^+ + 2e \rightarrow H_2 \quad (1)$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-. \quad (2)$$

The pH at the coating surface can increase from 3.9 to 8.5 according to measurements using a tungsten microelectrode [8]. At the same time, aluminium is oxidized, forming an inner alumina film across the aluminium surface:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e. \quad (3)$$

The alumina film dissolves by reaction with hydrofluoric acid [9]:

$$Al_2O_3 + xF^- + 6H^+ \rightarrow 2AlF_x^{(3-x)} + 3H_2O. \quad (4)$$

The dissolution is balanced by formation of fresh alumina at the aluminium/alumina interface. A high electric field is maintained across the alumina layer, which enables the outward migration of Al^{3+} and inward migration of O^{2-} ions within the alumina and continued oxidation of the aluminium [10]. The relatively thin residual alumina film thickness permits electron tunnelling to support the cathodic reactions [11]. The coatings have been reported to contain hydrated chromium and zirconium oxides [12,13], which may play a role as a hydroxide ion conductor with ligand exchange with fluorine [14].

Despite the absence of Cr(VI) species in the TCC coating bath, recent research has reported that Cr(VI) species are present in the coatings after ageing in air or following a corrosion test in sodium chloride solution at ambient temperature [5,13,15,16]. The Cr(VI) species in coatings formed on zinc were suggested to result from oxidation of Cr(III) species by oxygen [15]. Other work considered the possibility of oxidation of Cr(III) species by hydrogen peroxide generated by the reduction of oxygen at copper-rich particles in an AA 2024 alloy in a sodium chloride solution [16].

In the present work, the formation of a TCC coating on high purity aluminium is investigated. The substrate was selected as a relatively simple system compared with the AA 2024 aluminium alloy that has

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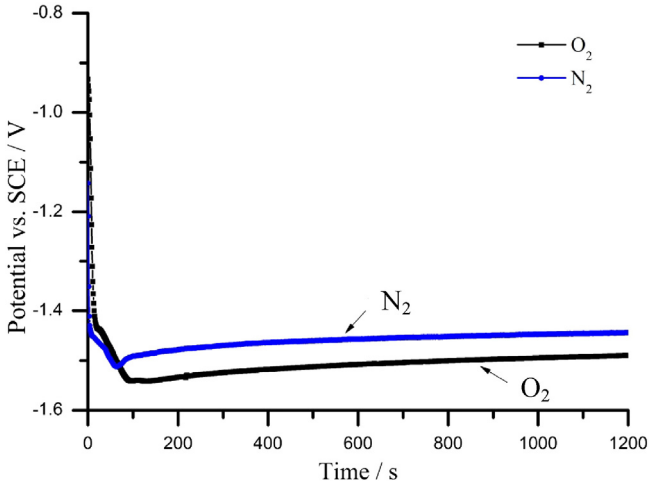

Fig. 1. The dependence of the open circuit potential of electropolished aluminium on the time of immersion in a dilute SurTec 650 bath at 40 °C under the usual naturally-aerated condition (labelled O_2) and under the de-oxygenated condition (labelled N_2).

usually been used in the previous studies. High-resolution analytical electron microscopy is combined with glow-discharge optical emission spectroscopy (GDOES), atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS), nuclear reaction analysis (NRA), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The study focuses on the composition and morphology of the resultant coatings, and provides evidence for the formation of Cr(VI) species in the absence of copper-rich, second phase particles in the substrate. The corrosion protection afforded by the coating is investigated by electrochemical impedance spectroscopy.

2. Materials and methods

2.1. Materials and reagents

Specimens, with dimensions of either 30 × 24 mm or 30 × 12 mm, were cut from 99.99% aluminium sheet of ≈0.3 mm thickness and rinsed with acetone, ethanol and deionized water, each for 5 s. Individual specimens were then electropolished for 240 s in a 20% (v/v) perchloric acid (60 wt.%) and 80%(v/v) ethanol mixture below 10 °C, using a potential of 20 V applied between the specimen and an aluminium counter electrode, followed by rinsing in deionized water and drying in a stream of cool air. They were then immersed in naturally-aerated SurTec 650 solution (1:4 v/v deionized water, pH = 3.9 (adjusted with 1% NaOH or 5% H_2SO_4)) at 40 °C for times from 15 to 1200 s. The solution includes both Cr(III) and zirconium species. After removal from the coating bath, the specimens were immersed in deionized water at 40 °C for 120 s and then rinsed in deionized water at room temperature, dried in a cool air stream, and finally aged in the ambient laboratory atmosphere at about 20 °C, typically for 24 h, before being subjected to analysis or corrosion testing. The exposure to the ambient atmosphere is expected to result in further drying of the coating. Coatings were also formed in a solution that was de-oxygenated, by bubbling nitrogen for 1 h, in order to determine the influence of dissolved oxygen on the formation of Cr(VI) species.

2.2. Examination techniques

The open circuit potential (OCP) of the aluminium was measured during coating formation for 1200 s using a Solarton electrochemical workstation with a Modulab software controller. The exposed area of the coated surface was ≈2 cm^2. Electrochemical impedance measurements were carried out on specimens coated for 60, 300

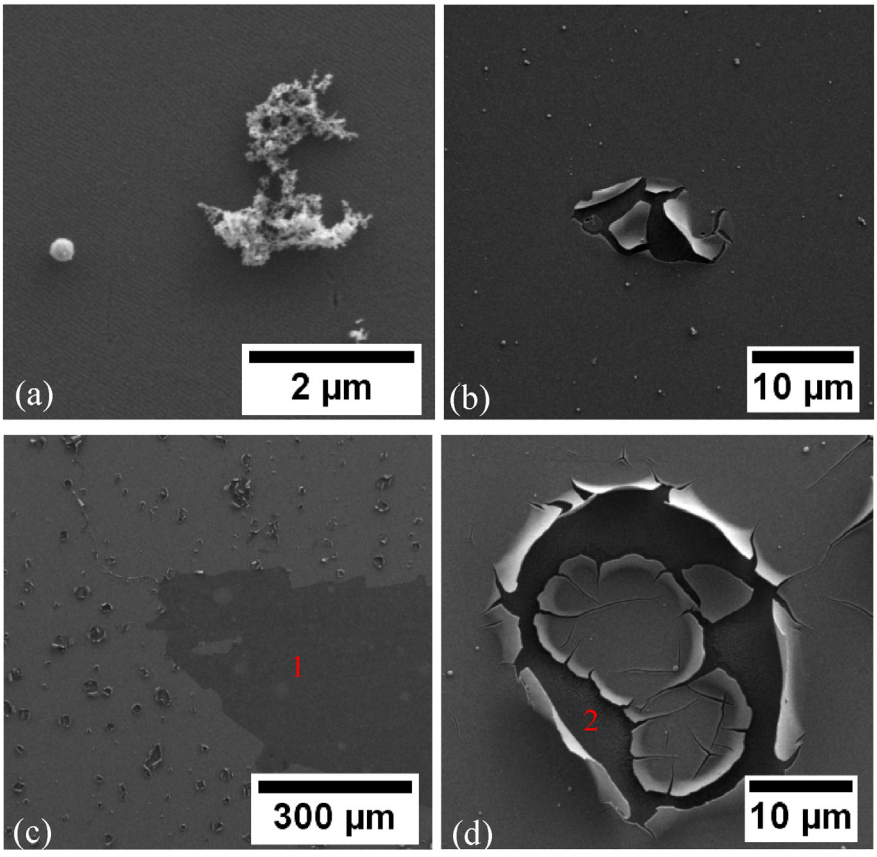

Fig. 2. Scanning electron micrographs (3 kV SE2 signal) of TCC coatings formed on electropolished aluminium in a dilute SurTec 650 bath at 40 °C for different times: (a) 15 s; (b) 120 s; (c) and (d) 600 s.