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Impedance study of the influence of chromates on the properties of waterborne coatings deposited on 2024 aluminium alloy

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ABSTRACT

Coatings formulated with either $SrCrO_4$ or a mixture of Cr(VI)-free pigments were compared in an impedance study. In addition to classical EIS measurements carried out in the metal/coating/electrolyte configuration, the study involved measurement of the impedance of the coatings in the dry state, both before exposure to the electrolyte (0.5 M NaCl solution) and after a 1-month exposure followed by a 12-month drying. The results were analysed with reference to models that assumed resistivity variations along the coating thickness. The resistivity-position dependence was close to a power law for dry coatings and close to exponential for wet coatings. In the latter, and for short immersion times, the exponential variation was located in the outer coating region, at shorter distances from the coating/solution interface, and then, for longer immersion times (>1 week), extended to the whole coating thickness. The effect of $SrCrO_4$ leaching on the properties of the coating is discussed. For both coatings, the barrier effect remained high for a 1-month exposure.

1. Introduction

In the aeronautic industry, an important challenge today is to develop new efficient coatings with the replacement of hexavalent chromium, as inhibitive pigment, due to future environment legislation. The corrosion protection performance of chromate-free coatings has to be compared to chromated systems, which constitute the "reference". In the present paper, a comparison is provided for the impedance behaviour of two waterborne coatings with different pigments in their formulation. One of them (henceforth denoted CC) contained $SrCrO_4$. Most results obtained with CC were already described in reference [1], and are recalled in the present work only for the sake of comparison. The other coating (henceforth denoted NCC) contained a mixture of pigments, replacing $SrCrO_4$, and is described here for the first time. Following the same methodology described in [1], the impedance of each coating was measured first under dry conditions, *i.e.* by contacting the outer coating face with mercury, obtaining an AA2024/coating/Hg system, to assess permittivity and resistivity of the as-prepared coating. Then, the impedance was measured under the ordinary wet conditions, *i.e.* in the AA2024/coating/solution configuration, as a function of the immersion time in 0.5 M NaCl solution, for a duration up to 1 month. Finally, after leaving the previously exposed samples to dry during ca.12 months in air, the coating impedance was measured again in the AA2024/coating/Hg configuration, to assess possible permanent changes in the coating properties, induced by the prolonged exposure to the NaCl solution. The results relevant to these dried samples, henceforth called "aged", are originally presented in this paper for both NCC and CC coatings.

This study was focussed on the use of different models for analysing the impedance data. The analyses highlighted major differences in the time dependence of the barrier properties of CC and NCC, which were ascribed to chromate leaching. Therefore, the amount of chromate released from the CC was determined by UV–vis spectroscopy for various exposure times to 0.5 M NaCl solution.

2. Experimental

The coating samples used and the impedance measurement protocol are presented in this section.

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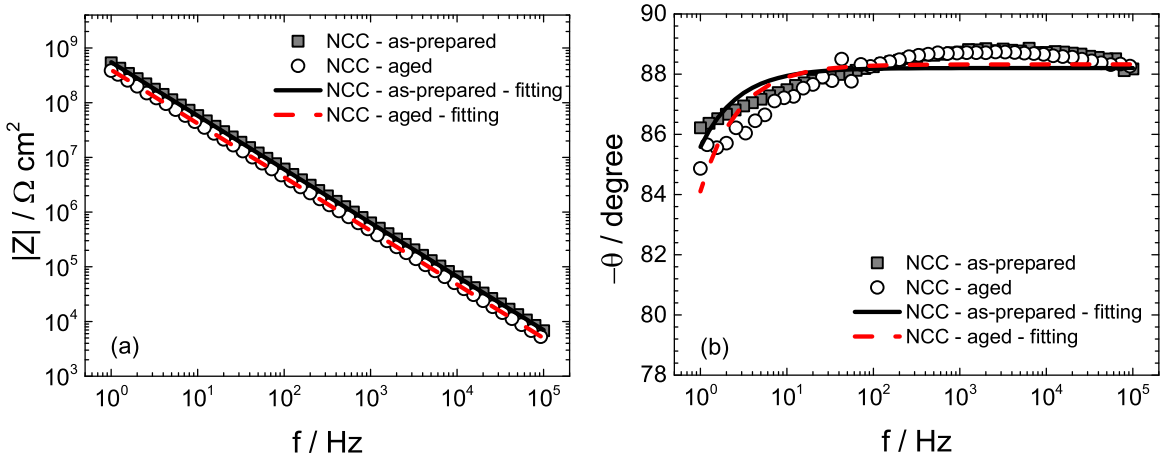

Fig. 1. The impedance modulus (a) and phase angle (b) obtained for the dry as-prepared and aged NCC coating (18 μm thick). The experimental data are compared with the regression result with the power-law model according to Eq. (1).

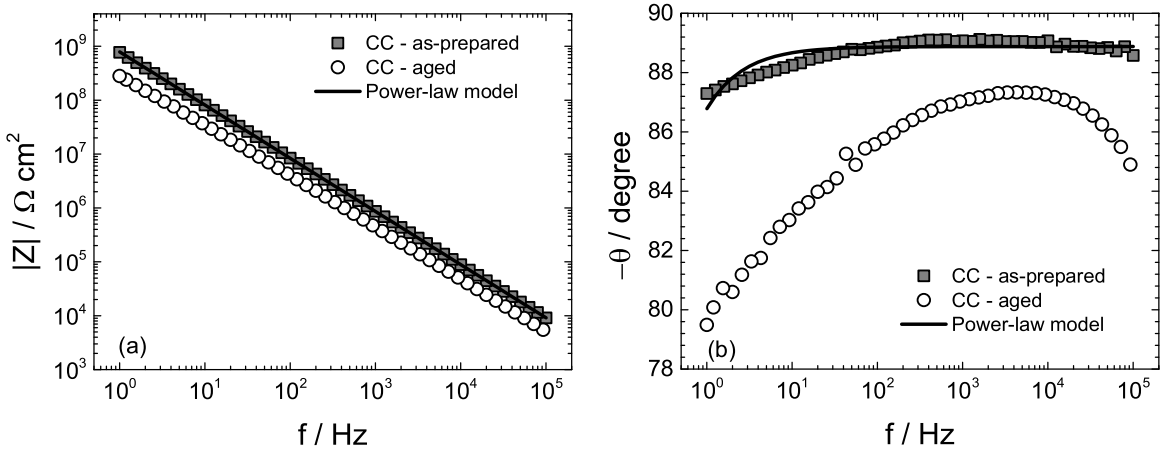

Fig. 2. The impedance modulus (a) and phase angle (b) obtained for the dry as-prepared and aged CC coating (21 μm thick). The experimental data for the as-prepared sample (■) are compared with the regression result with the power-law model according to Eq. (1).

2.1. The coating samples

Both CC and NCC consisted of a two-component water-based paint, manufactured by Mapaero SAS, Pamiers, France, using a polyaminoamide (Versamid® type) as base and a bisphenol A epoxy polymer as hardener, titanium oxide (12 wt.%), talc (11 wt.%) and silica (1 wt.%). In the CC, $SrCrO_4$ (16 wt.%) was added as inhibitive pigment, whereas in the NCC, $SrCrO_4$ was replaced by a mixture of zinc oxide and a phosphosilicate (10 wt.%). The coatings were deposited onto 2024 T3 aluminium alloy plates. The chemical composition in weight percent of the alloy was: Cu: 4.90; Mg: 1.31; Mn: 0.56; Si: 0.08; Fe: 0.26; Zn: 0.10; Ti: 0.01 and Al to balance. The specimens consisted of 125 mm × 80 mm × 1 mm plates machined from a rolled plate. Before painting, the samples were degreased at 60 °C (pH = 9) for 15 min, rinsed twice with distilled water, then etched in an acid bath at 52 °C for 10 min, and rinsed again with distilled water. The liquid paints were applied by air spraying. After curing at 60 °C, the coatings were 18–22 μm thick.

2.2. Electrochemical impedance measurements

A two-electrode configuration was used in the measurement of the impedance of dry coatings. A cylindrical Plexiglass tube was fixed on top of the coated sample, exposing a surface area of 5.94 cm^2, and filled with Hg into which a Cu wire was dipped to create electrical contact. Impedance measurements, carried out using a Solartron 1255 Frequency Response Analyzer and a 1296 Dielectric Interface, were obtained with a 0 V dc bias and a 100 mV peak-to-peak sinusoidal perturbation. Frequency was swept downwards from 10^5 Hz to 1 Hz, recording 10 points per decade. For this dielectric measurement (AA2024/coating/Hg configuration), the signal to noise ratio worsened below 1 Hz due to the high impedance to be measured (> 1 GΩ). Therefore, frequencies lower than 1 Hz were not investigated in the experiments.

Impedance measurements in the conventional metal/coating/electrolyte configuration were performed in a classical three-electrode cell, realized by fixing a cylindrical Plexiglas tube on top of the coated sample, and filled with a 0.5 M NaCl solution. The working electrode was a 24 cm^2 portion of the sample. An SCE and a Pt sheet were used as reference and counter electrode, respectively. A Biologic VSP apparatus was used to measure the impedance of the coated samples, for exposure times ranging from 2 h to ca. 1 month. Measurements were performed under potentiostatic conditions, at the open-circuit potential, with a 30 mV peak-to-peak sinusoidal perturbation. Frequency was swept downwards from 10^5 Hz to 0.1 Hz, recording 8 points per decade. All data were found to satisfy the Kramers-Kronig relations.

A non-commercial software developed at the LISE CNRS, Paris, was used for analysing the impedance data relevant to both dry and wet coatings. The LISE CNRS software allows the use of models consisting of combinations of passive circuit elements and analyti-