Electrochimica Acta xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Impedance analysis of the distributed resistivity of coatings in dry and wet conditions

Anh Son Nguyen [a], Marco Musiani [b], Mark E. Orazem [c], Nadine Pébère [a,*], Bernard Tribollet [d], Vincent Vivier [d]

[a] Université de Toulouse, CIRIMAT, UPS/INPT/CNRS, ENSIACET, 31030 Toulouse cedex 4, France
[b] Istituto per l'Energetica e le Interfasi, CNR, Corso Stati Uniti 4, 35127 Padova, Italy
[c] Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611, USA
[d] LISE CNRS, Université Pierre et Marie Curie, 75252, Paris cedex 05, France

ARTICLE INFO

Article history:
Received 5 December 2014
Received in revised form 10 February 2015
Accepted 12 February 2015
Available online xxx

Keywords:
aluminium alloy
corrosion protection
constant phase element (CPE)
Young impedance permittivity
water uptake

ABSTRACT

A commercial coating (epoxy-polyaminoamide waterborne paint) deposited on a 2024 aluminium alloy was characterized by impedance measurements, first in dry conditions and then as a function of the immersion time in NaCl solutions (wet conditions). The behaviour of the dry coating was close to that of an ideal capacitor and could be accurately modelled with the power-law model corresponding to a constant phase element (CPE) behaviour. Upon immersion in NaCl solutions, the behaviour of the wet coating became progressively less ideal, i.e. farther from a capacitive behaviour. This result provided support to the hypothesis that an inhomogeneous uptake of the electrolyte solution was the cause of the often observed non-ideal responses of wet coatings. The experimental EIS data recorded for immersion times up to 504 hours were compared with models assuming either a power-law or an exponential variation of the coating resistivity along its thickness, respectively implying a phase angle independent of frequency or slightly dependent on it.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

In two recent papers [1,2] our group has proposed that the CPE behaviour observed in the impedance of metal/coating/electrolyte systems was the result of power-law dependences of the coating resistivity (ρ) and permittivity (ε) along their thickness. In turn, the resistivity and permittivity variations were attributed to an inhomogeneous uptake of electrolytic solution into the coating, stronger in proximity of the coating/electrolyte interface and progressively weaker along the coating thickness as the metal/coating interface was approached. Accordingly, local resistivity and permittivity were calculated as a function of the local electrolyte volume fraction, using effective-medium formulas corresponding to parallel combinations of coating material and electrolyte. The proposed model, henceforth called "power-law model", took into account both through pores, directly connecting the metal/coating and coating/electrolyte interfaces via low-resistivity paths, and pores less deep than the coating thickness. In related previous work [3,4], it had been shown that the variation of the local permittivity, by a factor of 10 to 100 at most, had a negligible effect, and so the CPE behaviour could be entirely ascribed to a power-law resistivity profile. The power-law model was used to analyse experimental data obtained with hybrid sol–gel coatings deposited onto a 2024 aluminium alloy and exposed to electrolytic solutions [1]. It was shown that an inaccurate knowledge of the resistivity of the coating material ρ_c did not affect the quality of the agreement between model and experimental data, nor the values of the regressed parameters, as long as ρ_c was large [2]. Instead, the lack of an accurate knowledge of the resistivity of the electrolyte (ρ_w) within the coating pores, which could not be assumed to be identical to that of the bulk electrolyte, prevented the calculation of accurate water uptake values from the resistivity profiles [2].

A strong implicit assumption underlying the use of the power-law model, previously developed [3,4] and applied to films of various chemical natures [5,6], in the analysis of the impedance of anti-corrosion coatings was that the non-ideally capacitive behaviour was the result of the uptake of the electrolytic solution, not of a pre-existing variation of resistivity along the film thickness. Heterogeneities in the pristine coating morphology, e.g. some nano-scale porosity, were not excluded. However, as long as the coating was not exposed to a solution, the air-filled pores had no effect on the conductivity. Only the ingress of an electrolytic

* Corresponding author. Tel. : +33 5 34 32 34 23; fax: +33 5 34 32 34 99.
E-mail address: Nadine.Pebere@ensiacet.fr (N. Pébère).

http://dx.doi.org/10.1016/j.electacta.2015.02.109
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

Please cite this article in press as: A.S. Nguyen, et al., Impedance analysis of the distributed resistivity of coatings in dry and wet conditions, Electrochim. Acta (2015), http://dx.doi.org/10.1016/j.electacta.2015.02.109

solution could produce conductive domains and reveal a structural inhomogeneity, as well as induce the formation of additional defects or the increase of their size. The primary aim of this work has been testing this hypothesis by measuring the impedance of the same coating under dry and wet conditions, i.e. in the metal/coating/metal configuration, and then in the commonly used metal/coating/electrolyte configuration, the latter for increasing immersion times. The coating chosen to perform the experiments was a two-component water-based anticorrosive primer containing several pigments, known to provide an effective anti-corrosion protection to the 2024 aluminium alloy [7]. The dry coating properties (ε_c and ρ_c) were first determined by impedance spectroscopy. Then, the impedance evolution upon immersion of coated samples in either 0.5 M or 0.05 M NaCl solutions was followed.

There is no *a priori* physical reason why the electrolytic solution uptake must lead to a resistivity profile accurately described by a power law, which would cause a strictly constant phase angle. Therefore, an exponential variation of the coating permittivity along its thickness was considered as a possible alternative, when a CPE did not account for the observed behaviour. Such an exponential dependence results in the well-known Young impedance [8] characterized by a phase angle slightly dependent on frequency [9].

The present study is part of a wider program aimed at developing and characterizing chromate-free coatings for 2024 aluminium alloy. Studies on the same epoxy-polyaminoamide waterborne paint, without chromates, are in progress and investigations on coatings containing environmentally friendly inhibitors are planned.

2. Experimental

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

2.1. The coating samples

The coating was a two-component water-based paint used as an anticorrosive primer. The base was a polyaminoamide (Versamid® type) and the hardener was a bisphenol A epoxy polymer. The coatings were manufactured by Mapaero SAS. Different pigments were added to the organic matrix: titanium oxide (12 wt.%), talc (11 wt.%), silica (1 wt.%) and strontium chromate (16 wt.%). The ratio of the pigment volume concentration (PVC) to critical pigment volume concentration (CPVC) was equal to 0.61. The CPVC is the pigment concentration at which there is just enough binder in the dry coating to completely fill all the voids between the pigment particles [10,11]. The PVC to CPVC ratio is an important parameter which controls the film barrier properties.

The coatings were deposited onto a 2024 T3 aluminium alloy (henceforth called "AA2024") currently used in the aerospace industry. 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 × 1.6 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 and cured at room temperature. The coatings were 20–21 μm thick.

2.2. Electrochemical impedance measurements

For the dry coating, a two-electrode configuration was used. A cylindrical Plexiglass tube was fixed on top of the coated sample, exposing a surface area of 5.94 cm^2. The well was filled with mercury (1 cm height) and the electric contact was done with a copper wire. Impedance measurements were performed with a Solartron 1255 Frequency Response Analyzer connected with a 1296 Dielectric Interface. Impedance diagrams were obtained at a dc potential of 0 V over a frequency range of 1 Hz to 10^5 Hz with 10 points per decade and using a 100 mV peak-to-peak sinusoidal voltage.

For the impedance measurements in the conventional metal/coating/electrolyte configuration, a classical three-electrode cell was used in which the coated specimen served as the working electrode. A cylindrical Plexiglas tube was fixed on top of the coated sample, exposing a surface area of 24 cm^2, and filled with either 0.5 M or 0.05 M NaCl solutions. A saturated calomel electrode and a large platinum sheet were used as reference and counter electrode, respectively. The electrochemical cell was open to air and was kept at room temperature with an average value of 17 °C which may have undergone fluctuations by ±2 °C. Electrochemical impedance measurements were carried out using a Biologic VSP apparatus. The impedance diagrams were obtained, for exposure times ranging from 2 to 504 h, under potentiostatic conditions, at the corrosion potential, over a frequency range of 65 kHz to 1 Hz with 8 points per decade, using a 30 mV peak-to-peak sinusoidal voltage perturbation. To confirm consistency with the Kramers–Kronig relations, the measurement model analysis described by Agarwal et al. [12–14] was used. All data were found to satisfy the Kramers–Kronig relations. A relatively good reproducibility of the results was observed in the present work and the results shown for a single coating were typical of other nominally identical coatings. Nevertheless, as observed by Tait [15], variability is observed for industrial coatings. The concepts

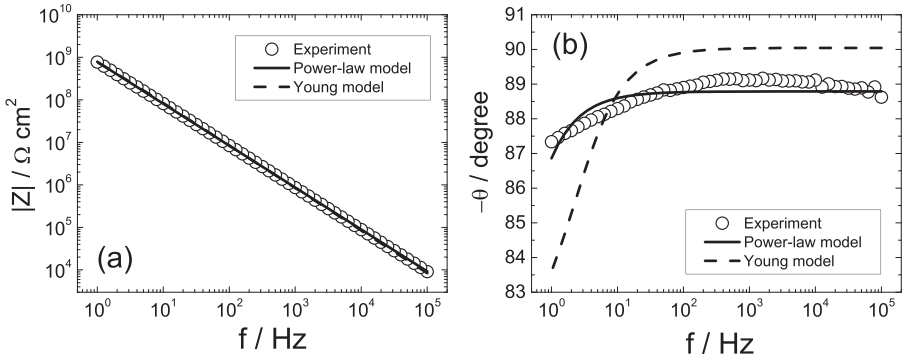

Fig. 1. The impedance modulus (a) and phase angle (b) obtained for the dry coating (21 μm thick) as functions of frequency. The experimental data (o) are compared with the regression results: power-law model, Eq. (2) (solid line) and Young model, Eq. (5) (dashed line).

Please cite this article in press as: A.S. Nguyen, et al., Impedance analysis of the distributed resistivity of coatings in dry and wet conditions, Electrochim. Acta (2015), http://dx.doi.org/10.1016/j.electacta.2015.02.109

Download English Version:

https://daneshyari.com/en/article/6610713

Download Persian Version:

https://daneshyari.com/article/6610713

Daneshyari.com