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Critical aspects in the electrochemical study of unstable coated metallic substrates

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ABSTRACT

Electrochemical methods are largely employed for the study of coated metallic substrates. Electrochemical techniques are very useful for investigation of coating performances also in the field of corrosion protection of aluminum alloys where replacement of chromate based coatings is an important issue. Application of sol–gel technique has recently made available thin inorganic protective coatings that can be considered as an alternative to chromate systems. Therefore, it is important to evaluate the electrochemical behaviour of defect free inorganic films which can be considered an inert material. As a consequence, investigation of this inert material might generate critical aspects related to rapid fluctuations of its open circuit potential and current density during open circuit potential and potentiodynamic polarization measurements. Moreover, the unstable nature of the sol–gel very thin films is a critical issue also in electrochemical impedance measurements carried out under potential control because variation of the open circuit potential of the system during data acquisition might lead to sample damage. Impedance measurements under current control is an alternative method for data acquisition. This technique is considered in the present paper for the investigation of AA2024 substrate coated with a thin sol–gel layer and for chromate conversion coated alloy.

The measurements under current control enable to avoid sample damage due to system polarization that might occur when the open circuit potential significantly changes during the measurement. Moreover, the current control approach guarantees the stability of the system during the impedance measurement. However, measurements under current control carried out using the equipment and the software available in our laboratory have some drawbacks. The frequency range available for the measurements is reduced for data acquisition under current control. In addition, the output signal/noise ratio can be altered for measurements at high frequency. Moreover, input parameters must be carefully selected depending on the system investigated for measurements under current control. Nevertheless, impedance measurements under current control might be very useful for the study of unstable systems.

1. Introduction

Aluminum alloys like AA2024 are widely employed in aerospace industry for the favourable weight/mechanical properties ratio. By alloying aluminum with other metals, physical and chemical properties are changed and mechanical properties can be improved [1]. The alloys of the 2xxx series undergo thermal treatments in order to precipitate hardening particles in the matrix. The hardening mechanism is related to alloying elements like copper and magnesium. However, alloying with copper and magnesium in combination with existence of intermetallics containing iron and silicon render AA2024 susceptible to localized corrosion [2–4].

In order to improve AA2024 corrosion behaviour it is necessary to protect this alloy with a coating. Nowadays, the protective system employed in aerospace industry consists of three different layers: the inner layer is deposited on the metallic substrate using a chemical conversion process or by anodizing. The intermediate layer is essentially an organic primer containing corrosion inhibitors and other compounds. The outer one is an organic topcoat.

A conversion coating should provide three different properties: first of all, it should promote adhesion between the metallic substrate and organic coating. Moreover, the conversion layers should provide good barrier properties and possibly self-healing ability. Chromate based coatings are extensively employed in the aircraft industry because they guarantee a good combination of properties. The self-healing ability is due to the presence of a residual amount of Cr^{6+} in the conversion coating that is able to repair the oxide layer in case of damage. Unfortunately, conversion coatings con-

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taining Cr^{6+} are dangerous and not environmental friendly [5–7]. Therefore, industrial processes involving Cr^{6+} species are restricted for aircraft applications.

Development of alternative technologies and chemical conversion processes is one of the most interesting topics in research about aluminum protection in order to replace chromium based systems. Different methods like plasma deposition, anodizing or sol–gel synthesis have been employed to produce alternative systems to chromate based conversion coatings [8–10]. In particular, sol–gel technology enables to obtain inorganic systems or hybrid inorganic-organic systems at low temperature [11–15]. In some cases, it is possible to produce thin homogeneous inorganic films for long time protection of metallic substrate by controlling deposition parameters and curing temperature for the densification of the sol–gel layer [16].

Electrochemical characterization of thin inorganic films deposited by sol–gel technique is often problematic due to difficulty to reach a steady state condition. Moreover, properties of these systems are strongly dependent on deposition parameters. Therefore, surface reactivity of these systems might be affected by film defects, loss of adhesion and possible formation of nano-cracks during immersion in an aggressive solution [17,18]. Electrochemical studies of corrosion behaviour of thin inorganic sol–gel films can employ two different methods: DC and AC techniques. Among AC techniques, electrochemical impedance spectroscopy (EIS) enables to obtain information about corrosion behaviour of the system investigated as a function of immersion time [19]. Moreover, it is necessary to validate impedance data in order to obtain reliable information. This can be done if the electrochemical system verifies three fundamental conditions: causality, linearity and stability [19]. The condition of causality imposes that system response must only be due to the input perturbation signal and noise. Moreover, the response must not contain signal components deriving from spurious source. The condition of linearity requires that the input perturbation and the output response must be described by a set of linear differential laws. This condition implies that the impedance, which represents the transfer function of the system, must be independent from the amplitude of the input signal perturbation. The condition of stability imposes that the system must return to its original condition when the input perturbation is removed. The three fundamental conditions mentioned above imply that a number of boundary requirements must be also satisfied. If the angular frequency ω tends to zero or to infinite, the impedance measured must be finite-valued. Finally, the impedance spectrum must be a continuous function in the range between $\omega = 0$ and $\omega =$ infinite; that is, impedance spectrum does not contain singularity over all frequency range [19].

Many mathematical methods have been developed to verify the fundamental conditions for impedance spectra obtained experimentally, like Kramers–Kronig relations [19]. Orazem et al. suggested the use of these relations in order to verify the validity of impedance spectra carried out by means of stepped sine excitation [20–22]. An alternative approach for the validation has been proposed by Popkirov and Schindler [23–25]. If an electrochemical system does not satisfy one of the fundamental conditions, impedance spectra are necessarily altered because the output response does not represent the real situation. Although a lot of electrochemical systems are not linear, EIS measurements can be equally performed applying an input perturbation of small amplitude. Indeed, the behaviour of an electrochemical system can be approximated to a quasi-linear system reducing the amplitude of input perturbation. Theoretically, the amplitude of input perturbation should tend to zero in order to improve the approximation for a non-linear system. At the same time, the output signal/noise ratio leads to poor measurement accuracy when the input signal amplitude is too small [25]. Urquidi-Macdonald et al. have demonstrated that impedance spectra performed on corroding iron electrode in 1 M H_2SO_4 with an amplitude of perturbation in the range from 5 mV to 150 mV lead to very different responses [26]. The quasi-linear behaviour of this system becomes non-linear when a large amplitude perturbation is applied. As a consequence, different impedance spectra are detected with respect to the non-linear condition.

Impedance spectra can be recorded for the electrochemical studies in the frequency and in the time domain. The frequency domain method is based on a voltage or current sinusoidal perturbation applied to the sample. The input signal is separately applied for each frequency. In this method, each impedance value is calculated at the end of every perturbation step [27,28]. The time domain method – also known as white noise method – is based on Fast Fourier Transform (FTT). In this last case, a frequency-rich perturbation signal is applied on the sample at the same instant time [25,29–32].

Experimental activities described in this work have been developed in order to find an instrumentation set-up which is able to assure reliable and reproducible impedance results. Impedance measurements were performed with the frequency domain method (FRA) on a very complex electrochemical system. This system consist of a very thin ZrO_2 sol–gel film deposited on a reactive substrate like AA2024. The combination between an homogenous ceramic thin film and a reactive substrate constitutes a system which exhibits transient open circuit potential during impedance measurements. In particular, this paper focuses on experimental aspects associated to the test conditions and to critical system features in order to improve accuracy of impedance measurements. Moreover, this paper assesses the possibility of acquiring reliable electrochemical information using current control method on not completely stationary systems, which are usual studying corroding metals. The paper is not focused on checking system linearity or system causality both under voltage control and under current control. Nevertheless, there is a common procedure to perform impedance measurements under voltage control to avoid linearity loss. Impedance measurements carried out under voltage control on conversion coatings are usually performed applying a perturbation with 10 mV amplitude which it is normally considered small enough to keep the system response in the linear behaviour. Considering the impedance measurements performed under current control in this work, the amplitude of the currents set in the experimental procedure has been chosen as the lowest values providing a reliable response possibly within a linear behaviour. However, the paper does not propose a check validation of the impedance data but it considers an alternative method to acquire reliable impedance data when not stable systems are considered.

2. Experimental

AA2024-T3 was employed as substrate for deposition of ZrO_2 based film. Chemical conversion coatings and pre-treatments used to improve corrosion behaviour of metals require surface preparation of materials. Before deposition of sol–gel film, AA2024 sample underwent surface preparation consisting in an alkaline cleaning, an alkaline etching and an acid etching.

ZrO_2 sol–gel films were deposited on AA2024 employing a water-based solution containing the precursor of the metal oxide. The solution used to produce inorganic films was 0.4 M $ZrO(NO_3)_2$ in water. Film deposition was carried out by means of spraying technique controlling parameters like air pressure gun, distance between gun and sample and general set-up of the robot. Optimization of the spraying process enables to obtain very homogeneous