

On the application of electrochemical impedance spectroscopy to study the self-healing properties of protective coatings

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Abstract

Active corrosion protection based on self-healing of defects in coatings is a vital issue for development of new advanced corrosion protection systems. However, there is a significant lack of experimental protocols, which can be routinely used to reveal the self-healing ability and to study the active corrosion protection properties of organic and hybrid coatings.

The present work demonstrates the possibility to use EIS (electrochemical impedance spectroscopy) for investigation of the self-healing properties of protective coatings applied on a metal surface. The model EIS experiments supported by SVET (scanning vibrating electrode technique) measurements show that an increase of low frequency impedance during immersion in the corrosive medium is related to the suppression of active corrosion processes and healing of the corroded areas. Thus, EIS can effectively be employed as a routine method to study the self-repair properties of different protective systems. The 2024 aluminium alloy coated with hybrid sol-gel film was used as a model system to study the healing of artificial defects by an organic inhibitor (8-hydroxyquinoline).

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1. Introduction

The necessity to eliminate hexavalent chromium from corrosion protection systems offered a powerful incentive to the development of new protective coatings, which combine good barrier properties with active corrosion protection ability originated from self-healing of corroded areas.

Different strategies have recently been used to impart an active protection component to different coatings. In some cases inhibitors can be directly added to the film [1–3]. However, addition of active inhibiting species to the coating formulation very often leads to degradation of barrier properties of the coating and deactivation of the corrosion inhibitors [4,5]. Different encapsulation strategies using nanoporous layers [6], ion-exchangers [7] and nanocontain-

ers [5,8] are suggested to avoid these negative effects and to obtain a corrosion protection system with good barrier properties and effective self-healing mechanism.

Various experimental techniques are used to study corrosion protection performance of protective coatings. Accelerated corrosion tests are very effective to compare the corrosion protection performance of different coatings. However, they do not give any information on the mechanisms of protection. Improvement of protective properties due to a better adhesion or due to a self-healing ability, for example, cannot be differentiated. A conventional DC polarization method is usually not applicable for coated substrates due to important limitations arising from a high IR drop. This method cannot give any useful information on the active corrosion protection and the self-healing ability of protective coatings. Electrochemical impedance spectroscopy (EIS) is widely used to characterize the corrosion protection performance of coating systems. This powerful technique allows not only a comparison between

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performances of different systems but also can give important information on kinetics of evolution of the coating degradation and the corrosion activity during immersion in the corrosive media. The high frequency part of the spectrum is usually related to the barrier properties of the coating, while the low frequency segment reflects the corrosion activity on the metal surface [9]. Several authors, for different corrosion protection systems containing active anticorrosive components, found that the low frequency impedance can increase during immersion [10–13]. Sometimes this increase follows a drop of the impedance caused by a breakdown of the coating with subsequent increased corrosion activity [5,6,14,15]. However, there is no direct confirmation that the increase of the low frequency impedance is related to the active corrosion protection provided by the inhibiting species released from the coating.

The term “self-healing” can be interpreted differently. The classical understanding of self-healing is based on complete recovery of the functionalities of the coating due to real healing of the defect. However, the hindering of the corrosion activity in the defect by the coating itself employing any mechanisms can be also considered as self-healing. Since, the corrosion protective system recovers its main function, namely the corrosion protection, after being damaged. In this work, the second definition of self-healing based on the active corrosion protection originated from inhibiting species is used.

In this work, we tried to design a series of model experiments to correlate the increase of the low frequency impedance during immersion with the self-healing conferred by a corrosion inhibitor. A corrosion inhibitor was added, at different stages of the corrosion process, to the electrolyte where aluminium alloy coated with a hybrid sol–gel film was immersed. SVET (scanning vibrating electrode technique) was also employed to confirm the EIS results on micro-level demonstrating the effect of organic inhibitors on the local corrosion activity in artificial defects.

2. Experimental

2.1. Model coating system

A hybrid protective film on AA2024 was prepared using controllable sol–gel route as reported elsewhere [6]. The only difference in this study was that titanium propoxide was used instead of zirconium propoxide. The hybrid sol–gel formulation was applied to the substrate by dip-coating with following curing for 1 h at 120 °C.

The 8-hydroxyquinoline was employed here as an effective corrosion inhibitor for AA2024 [16].

2.2. Experimental techniques

The EIS measurements were carried out at room temperature in a Faraday cage using Gamry FAS2 Femtostat with PCI4 Controller during immersion in 0.5 and 0.05 M

NaCl solutions. A three-electrode arrangement, consisting of a saturated calomel reference electrode, a platinum foil as a counter electrode and the exposed sample as a working electrode with a surface area of 3.4 cm², was used. The impedance measurements were performed at an open circuit potential with applied 10 mV sinusoidal perturbations in the frequency range of 10⁻²–10⁵ Hz with 10 steps per decade.

The SVET measurements were carried out in different NaCl solutions using an apparatus manufactured by Applicable Electronics Inc. (USA), controlled by the ASET software developed by ScienceWares Inc. (USA) and employed micro-electrodes of MicroProbes Inc. (USA). SVET measures potential differences in the solution due to ionic fluxes that arise from electrochemical reactions occurring in the corroding metal surface. The measured potential differences, ΔV , can be related to the ionic currents, I , that originate them by proper calibration. The micro-electrode had a spherical black platinum tip of 10 μm in diameter and vibrated in two directions (normal and parallel to the surface) with 20 μm amplitude and average distance of 200 μm above the sample. At each point the system waited 0.2 s before the measurement and the sampling time was 0.4 s. All data were recorded by ASET on PC. Experimental results are presented in the form of 2D maps of ionic currents. The maps were generated by QuikGrid (freeware, www.perspectiveedge.com) using data from the electric field normal to the surface. Positive (red) values correspond to the anodic activity and negative values (blue) to the cathodic activity.

The artificial scratches were created by a sharp metallic needle (tip diameter about 50 μm) under constant load.

3. Results and discussion

3.1. EIS measurements

Recent results obtained on AA2024 coated with double-layer hybrid sol–gel system containing an organic corrosion inhibitor (benzotriazole) demonstrated very interesting behavior of the impedance spectra during immersion [6]. An evolution of the impedance spectra for one of the samples with benzotriazole-containing interlayer is presented in Fig. 1. The Bode plot for the coated alloy before defect formation has three distinguishable time-dependent processes. The time constant at high frequencies is related to the capacitive response of the sol–gel film. The resistive plateau at 10²–10³ Hz represents the pore resistance of this sol–gel film. The relaxation process at about 1–10 Hz is attributed to the capacitance of the intermediate oxide layer present at the metal/coating interface. The resistance of such interlayer, which is situated at lower frequencies, is very important from the corrosion protection standpoint, since it is the last barrier for the corrosive species before reaching the metal surface. The third time constant is weakly defined at lowest frequencies and is related to the corrosion activity.

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