



Assessment of healed scratches in intrinsic healing coatings by AC/DC/AC accelerated electrochemical procedure

Mina Abdolah Zadeh, Sybrand van der Zwaag, Santiago J. García *

Novel Aerospace Materials group, Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629HS Delft, The Netherlands

ARTICLE INFO

Article history:

Received 24 August 2015

Revised 28 October 2015

Accepted in revised form 1 November 2015

Available online 9 November 2015

Keywords:

Self-healing

Dual network

Hybrid

ACET

Sol-gel

Disulfide

ABSTRACT

In the last years several intrinsic and extrinsic healing coatings have been presented in the literature. While extrinsic coatings have attracted more attention when dealing with electrochemical characterization techniques, protective intrinsic healing coatings have mainly been analyzed by traditional electrochemical impedance spectroscopy (EIS). In this article we introduce the potential use of the AC/DC/AC accelerated electrochemical protocol as a suitable tool for the fast evaluation of the goodness of the polymer-polymer interface (i.e. scar) in a healed scratch. For the purpose we employed a hybrid healable dual network coating containing disulfide linkages as the responsible reversible groups for the necessary local mobility and subsequent scratch interface sealing. The results obtained show the high discriminating power of AC/DC/AC of the level of interface sealing at the scratch in much faster times than traditional EIS.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Passive protective coatings are among the most widespread approaches for corrosion protection of metallic substrates. Such coatings restrict ingress of water and corrosive species to the metal-coating interface, limiting corrosion initiation [1,2]. Due to the electrochemical nature of the corrosion processes, electrochemical characterization techniques are well-suited for evaluation of the coating's protective performance. Yet, the traditional direct current (DC) measurements (e.g. polarization curves), where electron-conducting processes are described in terms of ohmic resistance, fail to provide adequate information on poorly conducting coatings [3].

Alternating current (AC) measurements on the other hand offer comprehensive information on the properties of non-conductive (polymeric) coatings [4]. Electrochemical impedance spectroscopy (EIS) as the most common AC method, is a well-established technique for evaluation of coating systems [5–9]. In an EIS measurement, the complex impedance of a coating system is measured over the desired frequency range. In combination with equivalent circuits, the EIS data can provide detailed information on the coating's barrier performance, stability, degree of degradation, thickness, porosity, adhesion and the electrochemical processes occurring at the metal surface [10–14]. Yet, as a result of non-destructive nature of the EIS measurements (provided that the measurement is well-performed), the monitoring process of an intact coating system can be as long as months to years.

To reduce the measurement time, a variant of the EIS technique was introduced in the 90s by Hollaender for rapid assessment of the coated food/beverage cans [15,16]. Such variant consists of cycles of EIS (AC) – cathodic polarization (DC) – EIS (AC), leading to its common name AC/DC/AC procedure. The procedure was later adopted by Suay, Rodriguez and Garcia for evaluation of water-born and powder coatings as well as cataphoretic paints through introduction of a long relaxation period and adopting it into a 24 h test [17–22].

In the AC/DC/AC test procedure (or ACET), the coating system's initial state is registered with a first EIS run, then the sample is cathodically polarized at a constant potential (DC) for a given time. The polarization step aims at promoting local cathodic reactions at the metal surface leading to formation of blisters, coating delamination and further corrosion processes around existing defects. Thereafter, a new EIS run registers the coating's new state [15]. The process is generally repeated six times for a 24 h test [22] although more cycles can be implemented depending on the evaluated coating system. As a result of the accelerated aging promoted by electrochemical stresses, such an approach provides valuable information on the properties of the coating systems in a very short time when compared to traditional EIS measurements [9,15,17–24].

Accelerated screening tests also yielding information on the failure mechanisms are particularly valuable when developing new (self-healing) coatings [25]. In this paper we introduce the potential of the AC/DC/AC procedure as an efficient electrochemical technique for evaluation of the goodness of the healed interface of intrinsic healing coatings. To this aim the durability and sealing efficiency of the healable hybrid sol-gel coating were studied using the AC/DC/AC procedure

* Corresponding author.

E-mail address: s.j.garciaespallargas@tudelft.nl (S.J. García).

and the results are compared to those obtained using conventional EIS. Furthermore, the cross-section of the hybrid sol–gel coatings tested using these two electrochemical techniques were further analyzed using scanning electron microscope (SEM), revealing testing technique dependent failure modes of the coatings. The results obtained suggest that the AC/DC/AC procedure is suitable as a fast evaluation technique of the degree of healing achieved in self-healing intrinsic coatings. In combination with complimentary techniques, the AC/DC/AC procedure provides valuable information on the restoration of barrier and adhesion properties in short periods of time.

2. Experimental

2.1. Materials

Epoxy resin based on Epikote™ 828 (184–190 g eq.^{−1}) and Ancamine®2500 curing agent (105–110 g eq.^{−1}) were provided by Akzo Nobel Aerospace Coatings (ANAC) and used as received. (3-Aminopropyl)trimethoxysilane (97%, MW = 179.29 g mol^{−1}) and pentaerythritol tetrakis(3-mercaptopropionate) (>95%, MW = 488.66 g mol^{−1}), hereon, APS and tetra-thiol respectively, were purchased from Sigma-Aldrich, The Netherlands, and used without further purification. Bis[3-(triethoxysilyl)propyl]tetrasulfide (99%, MW = 538.95 g mol^{−1}, total sulfur content > 20%), hereon BS, and ethanol were purchased from Capture Chemicals, China, and VWR, The Netherlands, respectively and used as received. Unclad AA2024-T3 was received from Akzo Nobel and used as metallic substrate. More details about the synthesis procedure, polymer characterization and healing potential of the healable hybrid dual network sol–gel coatings employed in this study can be found elsewhere [26].

2.2. Coating preparation

Prior to application of the coating, the AA2024-T3 panels of 3 × 4 cm² were ground mechanically using SiC paper (grade 1000) to remove the native oxide layer and further degreased with ethanol. The panels were then immersed in 2 M NaOH solution for 10 s and thoroughly rinsed with double distilled water to increase the surface density of the hydroxyl groups (OH[−]) on the AA2024-T3 substrates [27].

The dried AA2024-T3 panels were coated with healable hybrid sol–gel films. The polymers were prepared as described elsewhere [26]. The organically modified silicone alkoxides (OMSAs) were sequentially (APS followed by BS) added to the epoxy resin with the OMSAs:epoxy resin weight ratio of 1:1, keeping BS:APS molar ratio at 3:1. The mixture was stirred using a magnetic stirrer at 300 rpm for 3 h at room temperature. The organic crosslinker (Ancamine®2500) was then added to the mixture keeping the amine hydrogen equivalent (AHE) to epoxy equivalent (EE) ratio at 1.1 and the mixture was stirred in a high speed mixer at 2500 rpm for 5 min. Tetra-thiol was then added in a tetra-thiol:epoxy resin weight ratio 0.56:1 and the mixture was further mixed in the high speed mixer for 40 s at 2500 rpm. The resulting mixture was then cast on the cleaned AA2024-T3 panels using a calibrated standard aluminum single blade. The coated samples were dried at room temperature for one hour and cured for 48 h at 70 °C yielding coatings with an average dry thickness of 60 ± 2 μm. The chemical structure of the OMSAs and an idealized form of the resulting hybrid dual network are presented in Fig. 1.

To evaluate the hybrid sol–gel coating sealing efficiency, controlled 3 mm long scratches with an average width of 50 μm were created using a micro-scratch tester equipped with a sharp razor blade. The penetration depth of the razor into the coating was adjusted such that the artificial scratch reached the metallic substrate. To activate the gap closure and therefore the healing process, the scratched samples were clamped between two glass plates applying a constant uniform pressure of 30 kPa. The assembly was then placed for a given time (1, 2 or 8 h) in an air circulation oven operating at 70 °C. Selective breaking of the

reversible bonds upon application of the thermo-mechanical stimulus induced macroscopic flow in the crosslinked hybrid sol–gel coating enabling closure and fusion of the cut surfaces once the healing stimulus was removed [26].

2.3. Coating characterization

2.3.1. Electrochemical impedance spectroscopy (EIS)

The intact and healed coating systems were electrochemically characterized *in duplo* showing reproducible results. The EIS measurements were carried out at room temperature in a conventional three-electrode cell configuration consisting of a saturated Ag/AgCl reference electrode, a carbon black rod with diameter of 50 mm as the counter electrode and the coated AA2024 substrate as the working electrode. The samples were placed horizontally in the electrochemical cell with an exposed area of around 0.8 cm². A Faraday cage was employed to avoid the interference of external electromagnetic fields. A stagnant 0.5 M NaCl aqueous solution in equilibrium with air was employed as the testing electrolyte. The measurements were performed using an Autolab PGSTAT 302 N potentiostat/galvanostat coupled to a frequency analyzer (FRA) in the frequency range of 10^{−1}–10⁵ Hz, with a 10 mV (rms) sinusoidal perturbation respect to the open circuit potential. 10 data points were acquired per frequency decade. The impedance plots were fitted using different equivalent circuits with the Nova software package from Metrohm-Autolab B.V., following the most probable equivalent circuit (MPEC) selection approach [28].

2.3.2. AC/DC/AC

The AC/DC/AC measurements were performed at room temperature following reported and well-established procedures [17,20,21]. The tests were performed using a PGSTAT 302 N potentiostat/galvanostat, in a conventional three-electrode cell containing stagnant 0.5 M NaCl aqueous solution as the testing electrolyte. The AC/DC/AC test routine started with the first AC run after 1 h pre-exposure to the electrolyte for OCP equilibration. The AC measurements (i.e. EIS) were performed using the procedure described above. After the first AC run the test specimens (intact and healed coatings) were cathodically polarized at a constant potential of −4 V for 20 min. Subsequent to the cathodic polarization, a potential relaxation period of 3 h was implemented. The variation in open circuit potential (OCP) versus time was recorded during the relaxation step. The cycle was completed with a new AC run (EIS). A schematic representation of one EIS-Polarization-relaxation-EIS cycle is shown in Fig. 2. This test sequence was repeated at least 6 times (lasting 24 h in total).

2.3.3. Optical microscopy

The intact, scratched and healed hybrid sol–gel coatings were examined using a Keyence VHX-2000 series digital microscope after damage, healing and electrochemical testing. Images were captured in reflection mode with a 500× objective and the micrographs were analyzed using VHX-2000 software.

2.3.4. Scanning confocal microscopy

An Olympus laser scanning confocal microscope (OLS 3100) was employed to analyze the surface topology of the hybrid sol–gel coatings after the AC/DC/AC procedure. The images were captured with 5× and 10× objectives and were analyzed using LEXT software.

2.3.5. Scanning electron microscopy

A high resolution JOEL SEM (JSM-7500F) operating at 5 kV was employed to analyze the morphology of the electrochemically tested hybrid sol–gel coatings across the coating thickness.

Download English Version:

<https://daneshyari.com/en/article/1656296>

Download Persian Version:

<https://daneshyari.com/article/1656296>

[Daneshyari.com](https://daneshyari.com)