STUDY OF THE FILIFORM CORROSION OF 6016 ALUMINIUM ALLOY COVERED BY CATAPHORETIC COATING: APPLICATION IN AUTOMOTIVE INDUSTRY

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Introduction

In automotive industry, bodywork in aluminium parts is more and more used. This evolution can be explained by the research of a decreasing weight and by the aluminum recycling which is more cost-effective than that of steel. In addition aluminum is recycled without loss of its properties. The corrosion protection of parts of the car body is often obtained by a cataphoretic primer. Aluminium alloys are known to be particularly sensitive to a specific type of corrosion: filiform corrosion. This corrosion is produced between the coating and the substrate by formation of filaments. Galvanic corrosion cell develops between the head front of the filament (anode, oxidation of the aluminium) and the tail (cathode, reduction O_2 in OH^- ions). The aim of this work is to study by Electrochemical Impedance Spectroscopy and Scanning Kelvin Probe two parameters which influence the initiation and the spreading of the filiform corrosion such as the curing temperature of electrocoating and the metal surface pretreatement.

Experimental

The 6016 aluminium alloy samples were degreased with acetone and etched in a commercial acid bath (Henkel Ridoline 124N + Novox Activator 12B). Different pretreatments were applied on the substrates: without pretreatment, commercial silane, based sol-gel film (environmental friendly protection) whose synthesis was developed in the laboratory [1] and a solution with 3-aminopropyltriethoxysilane. The aluminium plates were covered with a commercial anticorrosive and without lead cataphoretic electrocoating (PPG industries, France). The applied conditions were determined in order to obtain a film thickness of 20 µm. The curing temperatures were 155°C, 175°C and 195°C.

The samples were submitted to the normalized filiform corrosion test (ISO/DIS 4623-2). A scratch of 40 mm length and 1 mm width was produced in longitudinal and traverse directions. Filiform corrosion was inoculated by exposure to HCl vapours for 1 h and the samples were then placed in a humidity chamber with 82 ± 3 % relative humidity and 40 ± 2 °C. Visual observation was carried out after 21 days of exposure and the extent of filiform corrosion was quantitatively assessed by measuring the filaments length.

A conventional three-electrode cell was used for the electrochemical tests. The working electrode was the investigated sample. The counter electrode was a platinum plate and all potentials were measured with respect to an Ag/AgCl reference electrode. The impedance measurements were carried out over frequencies ranging from 100 kHz to 10 mHz using a 5 or 20 mV amplitude signal voltage in a Faraday cage. The impedance spectra were acquired by using a potentiostat coupled with a frequency response analyser (Parstat 2273 from Ametek), computer-controlled with Powersuite® software. EIS measurements were carried out on scratched and intact coated samples.

The Volta potentials were measured by using a commercial Scanning Kelvin probe (SKP) from “UBM Messtechnik”. The potentials were given with respect to the standard hydrogen electrode.

Results and Discussion

The curing temperature of the cataphoretic coating was performed at 155°C, 175°C and 195°C in order to modify its mechanicals properties (Tg values, internal stress and residual stress) [2]. The sensitivity to filiform corrosion of aluminium substrate without pretreatement and covered by a cataphoretic electrocoating was studied by using the normalized test and by electrochemical impedance spectroscopy on scratched samples. After optimizing the experimental parameters [2], the active area of various systems in function of immersion times in electrolyte solution was determined by EIS. The lowest active area was obtained at 175°C. A good correlation was observed between the results obtained by the normalized test (21 days) and by EIS within a shorter time (24 h).

The SKP technique was used to study the mechanism of corrosion filiform. The measurements revealed that filiform corrosion of the painted aluminium starts from the formation of a galvanic couple: cathode (the defect) – anode (boundary of the defect-intact paint) and is the same whatever the curing conditions. The mechanism of the filiform corrosion is the anodic undercutting of the coating by the filament. The adhesion coating-substrate increased with the curing temperature. For curing temperatures lower than 175°C, a disbonding phenomenon was observed. For the curing higher than 175°C, increase the length of the filaments.

A more adherent system is more resistant to filiform corrosion? In order to answer this question, 3 pretreatments were applied before electrocoating of aluminium alloy. Dc polarization and OCP measurements shows that pre-treatments inhibit cathodic and anodic partial reactions on the alloy surface in water electrolyte. The protection properties offered by electrocoatings are very good whatever the pre-treatment due to the good interaction between the coating and the homogeneous silane layer. The sensitivity to filiform corrosion of complete systems was evaluated by a normalised filiform corrosion test. The disbonding phenomenon is not observed due to the improvement of adhesion properties but the length of the filaments is function of the pretreatment. The aminosiloxane pre-treatment is able to significantly increase the de-adhesion area of the coating compared with a non-treated interface. The based sol-gel slightly influences the rate of FFC. Commercial Oxsilan layer inhibits the corrosion under the electrocoating.

The SKP was employed to characterize the modified interfaces. The passivating based sol-gel silane treatment increases the potential of the Al surface and Al/paint interface. In opposite, aminosiloxane decreases the potential of the surface and interface. The effect is explained by change of the structure of the double electric layer metal/polymer due to different modes of the siloxane adsorption. The mechanism of the FFC of the Al alloy coated by paint with different pre-treated interfaces was studied by SKP. It was determined that in all cases the anodic undermining is the mechanism of paint de-adhesion. The cathodic oxygen reduction localizes at the metal surface in the defect. The counter anodic reaction takes place at the surrounding metal/paint interface. The aminosiloxane decreases the potential of the interface that increases the electromotive force of galvanic corrosion. In addition aminosiloxane (anion-exchanger) is able to accelerate the migration the chloride ions destroying the metal passivity. The spreading of Cl^- leads to activation of the interface and anodic de-adhesion of the paint. The inhibiting oxsilane treatment passivates the interface and inhibits the chloride spreading.

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