



Cut-edge corrosion study on painted aluminum rich metallic coated steel by scanning vibrating electrode and micro-potentiometric techniques

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ABSTRACT

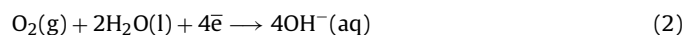
Aluminium-rich metallic coated steels were found to be especially sensitive to cut-edge corrosion in various climates for both painted and unpainted material. The aim of this work is to study the corrosion process in the cut-edge and the effect of aluminium presence in the metallic coating. In this frame, painted zinc metallic coated steel samples with different amount of Al were studied by scanning vibrating electrode technique coupled with a scanning ion-selective electrode technique (SVET/SIET). SVET and micro-potentiometric pH measurements were performed quasi simultaneously. The experiments were performed in continuous immersion in 0.05 M NaCl. As a result, differences in pH and activity for the studied systems could be linked to the presence of aluminium. Formed corrosion products were identified by Raman spectroscopy, FTIR spectroscopy, SEM-EDX and by analyzing the local pH in the area of precipitation.

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1. Introduction

Al-rich coated steel has various applications in automotive industry (e.g. aluminized steel for exhaust systems) and in general industry (e.g. furniture, tanks, air conditioning, etc.) [1]. The development of those products, chiefly based on Zn–Al alloys, responds to the market's demand of more versatile products that can face the leaching effect of zinc under high chloride concentrations. An additional reason is the rising cost of zinc in the recent years. However, Al-rich coated steel shows a special sensitivity to localized corrosion occurring at the cut-edges, where the metallic substrate is exposed to the atmosphere.

It is widely accepted that in organic coated galvanized steel, the undermining of the paint layer is due to the anodic dissolution of zinc (1) with cathodic oxygen reduction, localized frequently on the steel substrate (2):



Zinc coatings on steel can offer two kinds of protection mechanism against corrosion. A first one known as sacrificial protection is due to preferential zinc dissolution versus the steel substrate. A second way of protection consists of the formation of protective layers of zinc corrosion products on the steel. In the particular case of cut-edge corrosion, it was claimed that, in galvanized steel, an unfavorable anode to cathode ratio provoked a poor sacrificial action by zinc [2]. The secondary mechanism of protection that allows for the formation of protective films of zinc corrosion products and of water soluble inhibitors in the primer layers can play an important role on cut-edge corrosion protection [3,4]. Those mechanisms are highly dependent on the surrounding electrolyte, like the electrolyte layer thickness.

The study of the corrosion mechanism in the cut-edge is a complex process as it involves the degradation of both metallic and polymeric materials. Edavan and Kopinski [5] proposed a mechanism in which the initiation of the corrosion creep is due to a galvanic coupling between the steel substrate and the metallic coating and the propagation is lead by local electrodes formed and distributed under the paint film. The oxygen supply and the necessary electrolyte required for the electrochemical reactions will be

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Table 1
Metallic coatings composition in weight (%).

	Al	Zn	Si
Hot Dip Galvanized	0.5	99.5	0.0
AluZinc	55.0	43.4	1.6
AluPur	100.0	0.0	0.0

provided by diffusion through the paint film from the surrounding atmosphere at the advancing creep front.

Various conventional electrochemical methods, e.g. electrochemical impedance spectroscopy are generally used to study corrosion mechanisms in organic coated systems. However, in highly localized processes those techniques lack enough spatial resolution and only an average behavior on the studied surface can be achieved. In view of this, attention was focused on the application of localized electrochemical techniques in corrosion studies.

One example of a local technique widely used in the last years for the study of corrosion is the scanning vibrating electrode technique (SVET), which allows to quantify the distribution of local ionic current densities by measuring local potential gradients. Developed by biologists in its present form [6,7], SVET was adapted for corrosion studies by Hugh Isaacs in 1980s [8,9]. Since then it has been used to study many aspects of cut-edge corrosion as its initiation in coil coated products [10], the effect of differential aeration due to the change of porosity [11] or photodegradation [12], the link to the microstructural changes [13,14], the effect of corrosion inhibitors [15,16] and modeling of cut-edge corrosion [17,18]. Ogle et al. performed consecutive localized current density and pH measurements to study the effect of corrosion products in galvanized steel [2,4]. In their work, they were able to correlate local pH changes with the current density in the anodic and cathodic areas. In all the mentioned references, painted and unpainted galvanized steel was used as base material.

This work aims to study the effect of aluminum additions to zinc metallic coated steel in the cut-edge corrosion mechanism. Three different metallic coated steel systems are considered with contents of aluminum from 0.5% until 100% weight. Quasi-simultaneous measurements of ionic currents and pH distribution were performed. A platinized platinum vibrating probe was used for SVET. This probe is not capable to detect chemical concentrations, therefore a pH-selective microelectrode was placed next to the SVET probe to map ionic current density and pH quasi-simultaneously. A detailed description of this technique is given by Lamaka et al. [19].

After immersion tests and SVET–SIET measurements, an analysis of corrosion products is carried out by Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM/EDX). A more profound analysis of the results can be reached by taking into account the equilibrium chemistry. In this frame, thermodynamical diagrams of distribution of ionic species in solution were built as a function of pH to find a correlation between predicted corrosion products and detected ones.

2. Experimental

2.1. Samples

Three metallic coated steel products with varying content of aluminum supplied by Arcelor-Mittal were studied. The steel substrate thickness was 0.4 mm while the metallic coating had a thickness of 15–20 μm in the case of Hot Dip Galvanized steel and AluZinc and 40 μm for AluPur. The metallic coating compositions are shown in Table 1.

An epoxy-based coating (PRIMEPOX P7) supplied by DuPont was applied on the bare substrates previously cleaned with two different NaOH-based solutions at 55 °C: Ridoline S5086 (Henkel, pH 13) in the case of Hot Dip Galvanized steel (HDG) and Gardoclean C72 (Chemetall, pH 9.5) for AluZinc (AZ) and AluPur (AP). The paint layer was applied by spraying, on both sides of the sample a thickness varying between 25 and 30 μm was obtained. Following the paint specifications, the curing step was done in the oven at 60 °C during 45 min.

For SVET–SIET measurements, the metallic samples were cut into 0.45 mm band and mounted in an epoxy resin. Then, they were gradually polished in several steps using 120 μm and 320 μm sand papers and finished in two steps on a cloth with 9 and 3 μm diamond suspensions.

2.2. SVET/SIET measurements

A commercial scanning vibrating electrode technique equipment (manufactured by Applicable Electronics™) and controlled by ASET software (Science Wares™) was used to perform SVET and SIET measurements. This set-up allows for quasi-simultaneous measurements of local current density and local pH as described in Ref. [19]. Briefly, the vibrating probe of SVET and the glass-capillary microelectrode of SIET were positioned at a distance of 50 μm in order to avoid the cross-talk effect, break of the glass electrode by the vibrating probe and excessive solution stirring. A time lag between acquiring each current density and pH data-point was only 1.5 s. Thus, one SVET–SIET scan yielded two independent maps showing ionic current density and pH distribution. All experiments were performed in a Faraday cage at room temperature (21 ± 3 °C). Experiments were performed during continuous immersion in 0.05 M NaCl for 40 h, mappings were obtained every 2 h. Reproducibility of the evolution of local current and pH was checked, four valid experiments were taken to analyze the data. Only one set of data for each sample is presented in this article.

Insulated Pt–Ir probes (Microprobe, Inc.) with platinum black deposited on a spherical tip of 15 μm diameter were used as vibrating electrode for the SVET system. The probe was placed 100 ± 3 μm above the surface, vibrating in the planes perpendicular (Z) and parallel (X) to the sample's surface. The amplitude of vibration was 18 μm , vibration frequencies of the probe were 124 Hz (Z) and 325 Hz (X).

The local activity of H^+ was detected by positioning pH-selective microelectrodes 50 ± 5 μm above the surface. The localized pH measurements were carried out using two different types of pH-selective glass-capillary microelectrodes filled with (1) 4-nonadecylpyridine-based or (2) tridodecylamine-based ion-selective liquid membrane. All reagents for the membranes preparation were selectophore grade products from Fluka. More details on the preparation of the microelectrodes can be found elsewhere [20]. The need to use two different types of pH-selective membranes arises from different pH ranges of the membrane linear response. The response of the microelectrode with the membrane based on 4-nonadecylpyridine is linear in the pH range from 2 to 10 while tridodecylamine-based electrodes show linear response within pH 5–12 [21]. Tridodecylamine-based membrane is usually used by corrosion scientists for pH monitoring of steel [2,4] and magnesium alloys [22,23] where pH rarely reaches values lower than 5. However, this membrane cannot assure unbiased pH monitoring in the case of aluminum alloys as pH of anodic dissolution may reach values as low as 3 [20,21]. Thus, a tridodecylamine-based microelectrode was used for tracking pH changes in the case of Hot Dip Galvanized steel and 4-nonadecylpyridine-based membrane was used for AluZinc and AluPur samples.

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