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The combined use of scanning vibrating electrode technique and micro-potentiometry to assess the self-repair processes in defects on “smart” coatings applied to galvanized steel

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ABSTRACT

Model weldable primer coatings for galvanized steel were modified with submicron containers loaded with corrosion inhibitors. This procedure aims at introducing a new functionality in the thin coatings self-repair ability. The assessment of this property demands new protocols and new approaches, combining conventional electrochemical methods with electrochemical and analytical techniques of micrometer spatial resolution. Thus, in this work model defects were created in the coatings by using a focused ion beam (FIB). The coated samples, containing the model defects, were immersed in a NaCl 0.05 M solution and the corrosion inhibition ability was studied using the scanning vibrating electrode technique (SVET) and the scanning ion-selective electrode technique (SIET). SVET–SIET measurements were performed quasi-simultaneously. Qualitative chemical analysis was performed by SEM combined with EDS. Complementary studies were carried out by electrochemical impedance spectroscopy (EIS) to assess the effect of the containers filled with corrosion inhibitors on the barrier properties of the coatings. The electrochemical results highlight the importance of the combined use of integral and localized electrochemical techniques to extract information for a better understanding of the corrosion processes and corresponding repair of active microscopic defects formed on thin coatings containing inhibitor filled containers.

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1. Introduction

Organic and inorganic coatings have been widely applied for the protection of metal alloys against corrosion with significant progress in recent years. However, despite essential improvements in anti-corrosion coating technologies, problems persist in the long-term protection of metals in aggressive environments at very high cost. An increased interest has been observed in approaches that combine different classes of materials, achieving more complex and feed-back active structures in order to obtain new synergistic effects with respect to the functional performance. A key strategic topic is the combination of nanostructured materials and eco-friendly hybrid and/or organic polymers to develop new coatings that enhance the product performance and introduce new functionalities as for example self-healing ability.

Nowadays, the study of different coating systems (pretreatments, primers, inorganic and hybrid sol–gel films, conductive polymers and water based coatings) with self-healing ability is an important topic [1], with a significant increase in the number of publications in the last five years.

Based on literature it is possible to identify two main types of electrochemical mechanisms for the self-healing of corrosion processes:

a) Healing due to the formation of protective layers of corrosion products, which block the access of aggressive species and/or oxygen towards the active sites [2–4].
b) Healing due to the formation of protective species, resulting from the presence of organic or inorganic corrosion inhibitors, often incorporated into “smart” particles [5–13].

These mechanisms of self-healing have been studied in different aggressive environments, mainly on aluminum and zinc alloys, including cut edges. It has been shown that the corrosion mechanisms and, consequently, the mechanisms of self-healing are

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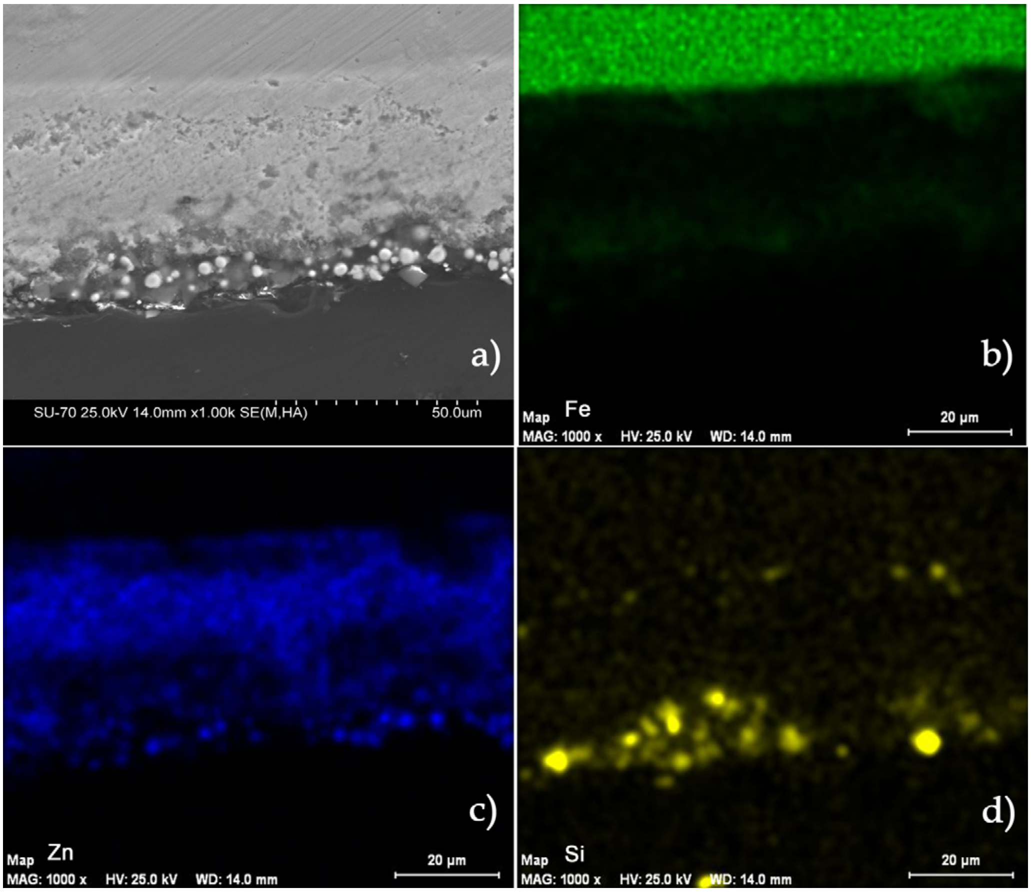

Fig. 1. SEM micrograph of cross-section of reference coating M0 (a), and corresponding EDS elemental mapping of Fe (b), Zn (c) and Si (d).

dependent upon the substrate composition and nature of the corrosion products formed [2,3,14]. According to [2], corrosion of zinc coupons immersed in NaCl electrolytes reveals slight acidification of the anodic zones and major alkalinization of the cathodic sites. Corrosion products precipitate between anodic and cathodic areas, where pH is favorable for formation of insoluble species.

In coated metallic substrates, both corrosion and self-healing mechanisms can be localized over very small areas and generally involve changes in the electrochemical potential, current density and acid–base equilibrium reactions. Furthermore, the processes may become even more complex due to cathodic delamination or anodic undermining phenomena under buried interfaces. The effective characterization of the self-repair ability is an acknowledged need due to the novelty and dynamic behavior of these systems. In this perspective, the combined use of integral and spatially resolved electrochemical techniques becomes fundamental. Some of the most successful spatially resolved electrochemical tools that have been used to investigate localized corrosion phenomena in uncoated and coated substrates are shortly addressed below.

The scanning vibrating electrode technique (SVET), that detects local changes of the current density due to the potential differences originated in the surface as consequence of the ionic fluxes generated between the anodic and cathodic sites, has become one of the most effective and widely used techniques to detect localized corrosion phenomena in bare and coated substrates [2–4,13,15–24].

The micro-potentiometric measurements with ion-selective microelectrodes can be performed by using scanning ion-selective electrode technique (SIET) and SECM in potentiometric mode. This method provides information about local activity (concentration) of specific ions in solution (e.g., H^+) making possible to trace changes in the acid–base equilibriums associated with the electrochemical processes [2,3,8,16–20,25–28]. Mg^{2+}, Zn^{2+}, Na^+ and Cl^- selective microelectrodes have also been reported to be used for studying localized corrosion [16–18,29,30].

The localized electrochemical techniques described above present advantages and limitations, and the need of complementary application has been stressed in literature [2–4,16–20,24,28,29]. In this work a complementary combination of different electrochemical techniques was used to study the corrosion and self-repair processes in model defects. For this purpose, model weldable primers were applied to galvanized steel substrates. Additionally the primers were modified with submicron containers loaded with different corrosion inhibitors.

The barrier properties of five different coatings were first assessed by electrochemical impedance spectroscopy. Based on EIS ranking, the corrosion mechanisms and the self-repair ability of two best coatings and the reference sample were studied using quasi-simultaneous SVET and SIET measurements, complemented with SEM/EDX analysis. The results highlight the need of new experimental protocols and the synergistic combination of SVET and micro-potentiometry with conventional electrochemistry and scanning electron microscopy, providing new information both on the corrosion processes and the self-repair effects occurring on defects formed in coated galvanized steel.

2. Experimental

2.1. Materials

The substrate used for coating application consisted of hot dip galvanized steel, thickness 0.8 mm, coated with 22 µm zinc layers

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