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Electrochemical electrolyte spreading studies of the protective properties of ultra-thin films on zinc galvanized steel

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ABSTRACT

Reactive electrolyte spreading along the surfaces of different conversion films on zinc galvanized steel in humid air was monitored visually and with a height-regulated scanning Kelvin Probe. Electrochemical impedance spectroscopy and current density-potential curves revealed that decelerated spreading kinetics are connected with increasing pore resistances of the pre-treatment layers and decreasing oxygen reduction current densities in the electron transfer controlled potential region. After a few days the progress ranking of electrolyte spreading along uncoated conversion films reflected the progress tendencies of cathodic delamination observed on epoxy coated conversion layers after long-time exposure to the same corrosive environment. Such correlation was not discovered for pre-treatment films that do not provide relevant electrochemical barrier properties. The results suggest that oxygen reduction driven electrolyte wetting is an option for accelerated performance testing of anticorrosive ultra-thin films on metal substrates that can be subject to cathodic delamination.

1. Introduction

Adequate characterization of polymer coated metal compounds modified by adhesion promoting and corrosion protective thin films remains a challenge due to the limited availability of analytical approaches for buried interfaces. The residual electrochemical activity of the pre-treated substrate surface, barrier properties of the organic coating and its adhesion as well as molecular and morphologic characteristics of the organic/inorganic interface structure synergistically determine the corrosion resistance [1–6]. Recently launched two-step pretreatment procedures such as the deposition of amorphous iron oxide prior to the formation of Zr- or Ti-based barrier layers on zinc were developed to offer superior performance for specific applications. However, they also result in complex interface designs which require even more detailed understanding and careful analysis [7,8].

In general, standardized salt spray exposure and long-term weathering tests have to be passed to achieve approval for the use of conversion chemistry based protection systems e.g. at car bodies or building facades [9]. As such procedures are time-consuming, industrial research will especially benefit from short-term and cost-efficient routines to quickly review progress in daily product development. In this context, the comparison of ion transport processes at polymer/metal interfaces seems to offer promising options for accelerated testing and interface characterization. It was observed that the ion mobility sensitively responds to the electrochemical activity of the substrate material and its oxide properties [10–12], to the permeability of the polymer with respect to water and oxygen [13,14], to paint adhesion as well as to mechanical properties of its macromolecular network [13–15]. Moreover, previous publications reported that transport mechanisms detected at polymer covered zinc and steel substrates resemble those observed on uncoated Zn and Fe surfaces during the exposure to humid air [10,11]. Ion convection starts from electrolyte droplets deposited/formed on metal surfaces or from electrolyte covered defects in the polymer coating that extend to the metal substrate. It is initiated by the reduction of atmospheric oxygen and the formation of hydroxide species in the periphery of the electrolyte reservoir. A flow of cations from the reservoir centre, where active dissolution of the base material occurs, toward the cathodic sites of the local galvanic cell then ensures charge compensation. This promotes an extension of the oxygen reduction zone. For droplet spreading along the substrate surface such finding was explained by a reduction of the oxide/electrolyte interface tension with increasing pH above the isoelectric point of the oxide due to OH^- formation [16,17]. Cation ingress into polymer/oxide/metal interface sections adjacent to an electrolyte covered coating defect occurs preferentially on zinc, exclusively on iron and is commonly regarded as an important part of the cathodic delamination mechanism [18–23]. Fig. 1 provides a schematic illustration of relevant ion transport processes for metal substrates with and without organic coating. In-situ monitoring of electrode potentials at electrolyte/metal and polymer/metal interfaces

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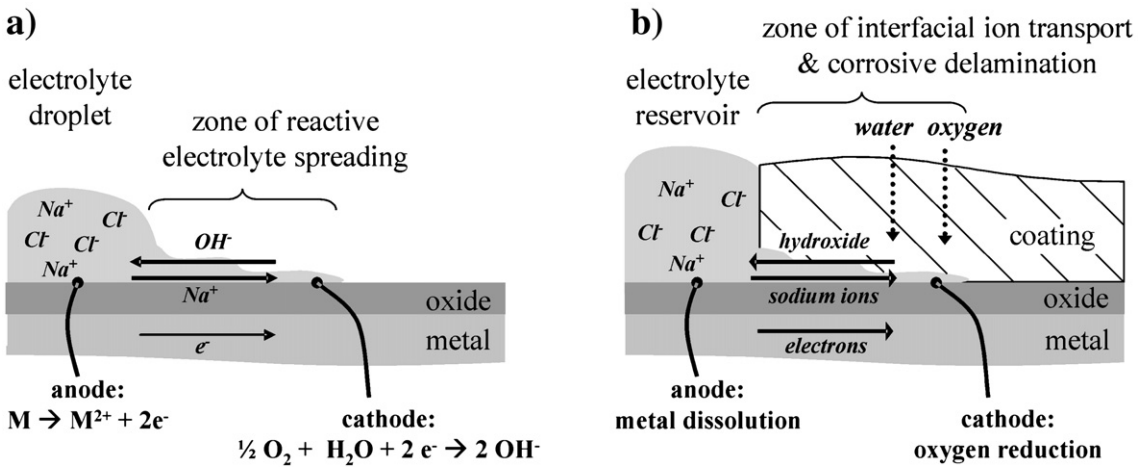

Fig. 1. Schematic illustration of electrolyte transport mechanisms on zinc and iron substrates in humid air (relative humidity: typically > 90%). a) Reactive electrolyte spreading along the bare metal surfaces, starting at a highly viscous droplet of NaCl electrolyte. b) Cathodic delamination along a polymer/oxide/metal interface, starting at a coating defect covered with NaCl electrolyte. Please be aware that the O_2 and H_2O activity in the polymer phase will be significantly lower than in humid air.

by the Scanning Kelvin Probe (SKP) and subsequent investigation of elemental distributions resulting from ion transport reflect established state-of-the-art approaches for analysis [10–12,18–23].

Stability rankings for different interface designs on iron and steel samples were indeed accessible by cathodic delamination studies [13,14], but occurred to be problematic for zinc substrates so far [14,24]. The present publication consequently focuses on the introduction of an analogous approach for conversion chemistry pre-treated zinc electro galvanized steel. Electrolyte spreading was initiated on pre-treatment layers with different barrier properties. The results were compared to the characteristics of polarization curves as well as impedance spectra recorded on these anticorrosive films and correlated with cathodic delamination rankings obtained from ion transport studies at epoxy/conversion layer/zinc interfaces. These data will demonstrate the practicability as well as the limits of the electrolyte spreading approach for accelerated performance testing of Zr-/Ti-based conversion chemistry layers.

2. Experimental

2.1. Sample preparation

Zinc electro galvanized steel sheets with a coating thickness of approx. 7.5 μm were supplied by voestalpine Stahl Linz GmbH (Linz, Austria). After alkaline spray cleaning with a solution that contained 2% Ridoline 1250 BR and 0.2% Ridosol 1270 (from Henkel AG & Co.

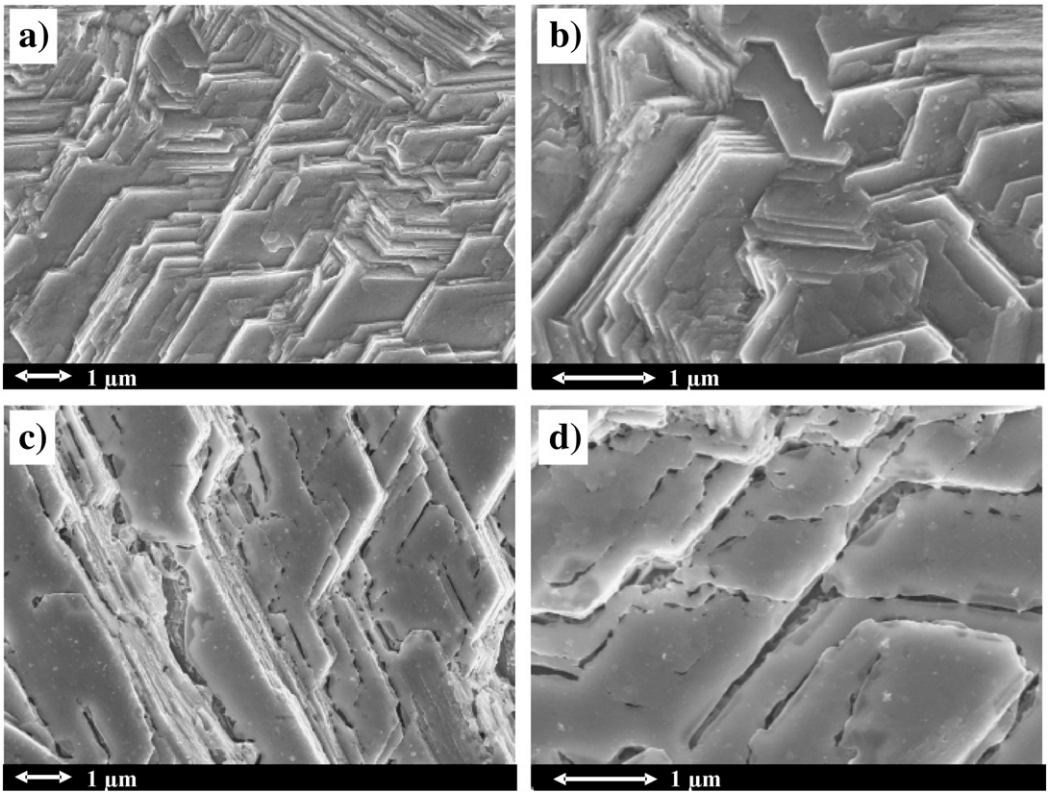

Fig. 2. SEM images of sample surfaces used for experiments discussed in the present publication. a) and b): Zinc electro galvanized steel. c) and d): Zinc electro galvanized steel pre-treated according to procedure (a).