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Corrosion behaviour of galvanized steel studied by electrochemical microprobes applied on low-angle cross sections

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ABSTRACT

The combined use of the microcapillary cell (MEC) and scanning vibrating electrode technique (SVET) and low-angle cross sections was employed to elucidate the role of each coating region on the protection of the cut-edge corrosion of galvanized steels. Different compounds are involved in the blocking action of the corrosion products: Zincite (ZnO) on the steel substrate, hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) at the coating/steel interface, and Simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2$) and ZnO on the different coating regions in different proportions. The coating surface is also active at the initial stage and during long-term protection and thus, must be considered in experimental simulation of the cut-edge corrosion.

1. Introduction

Hot-dip galvanizing applied to steels compared to other coatings presents the lowest long-term cost for effective corrosion protection in a wide range of moderately aggressive environments [1], as in the case of atmospheric, soil and natural waters corrosion. Therefore, so obtained Zn coatings (HD Zn) can be used in a broad range of applications. The corrosion resistance conferred by hot-dip zinc (HD Zn) coatings is provided by a thick compact and perfectly adherent metallic layer bonded to the substrate that seals the steel surface from the corrosive action of the environment. When the coating is damaged during service life, the less noble zinc sacrificially corrodes to protect the steel substrate. Different extents of substrate's surface area may be exposed depending on the type of damage, increasing from coating cracks to scratches, cut-edges and to larger areas, as those caused by the coating evaporation during welding processes. The specific electrochemical properties of exposed phases of the coating/substrate system and their interactions determine the global corrosion rate and, therefore, it is necessary to characterize them to understand galvanized steel corrosion.

The corrosion of HD Zn coatings has been largely investigated by conventional electrochemical techniques that allow obtaining the overall electrochemical behaviour of the corroding surface [2–6].

However, to separately evaluate the corrosion behaviour of each single phase of the galvanized steel, electrochemical microprobe techniques, such as the scanning vibrating electrode technique (SVET) and the microcapillary electrochemical cell (MEC) are complementarily helpful. SVET *i*-maps are based on measurements of the ohmic drop in the solution to calculate the local current density and so, are limited to solution conductivities usually around 10–50 mS cm⁻¹, corresponding roughly to chloride concentrations [Cl⁻] ≤ 0.1 M). On the other hand, the current density at MEC is constrained to small capillary sections, and to avoid ohmic drops inside the capillary, the technique is more adequate for highly conductive electrolytes ([Cl⁻] ≥ 0.1 M).

There are only a few studies aiming to understand the individual and combined behaviour of the different coating regions, generally concerning the cut-edge corrosion phenomenon [7–13]. In all these cases, only the perpendicular cross section of the coated steel was exposed. Thus, the usual thickness of each coating layer was below the lateral resolution of SVET and MEC methodologies.

In the present study, SVET and MEC techniques were complementarily employed to evaluate the corrosion behaviour of galvanized steel in chloride solutions. The MEC technique was used to measure the separate response of each region, whereas SVET was used to measure local current densities of each region, but under the galvanic coupling of all phases

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Table 1
Chemical composition of the interstitial free (IF) steel.

Element	C	Mn	P	S	Al	Si	N	Nb	B	Cu	Cr	Ni	Mo
Wt.%	0.036	0.210	0.018	0.006	0.040	0.007	0.004	0.001	0.000	0.005	0.016	0.004	0.001

Further, by the use of low-angle cross sections, the dimensions of the different regions of the coating/substrate system were amplified, aiming to approach the lateral resolution of the techniques used (50–100 μm). A 0.1 M NaCl solution was used for MEC experiments at the lower concentration and conductivity limits of this technique. SVET, however, was used at a concentration of 0.01 M NaCl, at which a lower solution aggressivity and corrosion rates are expected, thus enabling the acquisition of current density maps of the whole low-angle cross section, without significant modification of the corrosion state during the experiment. Additionally, surface analysis by X-ray diffraction on microscopic areas was carried out before and after exposure of samples to dilute chloride solutions.

2. Experimental procedure

HD-Zn coated steel sheets were provided by *ArcelorMittal-Vega S.A.*, São Francisco do Sul, Brazil. The substrate of the HD Zn coating was interstitial free steel (IF) with the composition shown in Table 1. The coating was produced in the industry using a continuous process by immersing the 1 mm thick IF steel sheet in a liquid zinc bath (Zn-0.2 wt. % Al) at a temperature of $460 \pm 5^\circ\text{C}$. The coating thickness (7 μm) and roughness were controlled with an N_2 jet knife and a final cold rolling “skin” pass. The samples were cleaned with ethanol and distilled water.

The micro-electrochemical behaviour of different phases of the hot-dip galvanized steel was evaluated using a microcapillary electrochemical cell (MEC). The MEC technique consists of a small glass tip (microcapillary) coupled to a small polymethyl methacrylate cell with a volume around 3.5 ml mounted on an optical microscope. A capillary tip diameter of 80 μm was chosen in a compromise between mechanical strength and ability to independently access each coating phase. The cell and microcapillary were completely filled with the electrolyte to perform the electrochemical tests using an *AUTOLAB PGSTAT 30* potentiostat. Tests were performed in 0.1 M NaCl solution using a platinum wire as counter electrode and Ag/AgCl in 3 M KCl as the reference electrode. All potentials shown in this manuscript are referred to the 3 M Ag/AgCl reference electrode ($E_{\text{Ag}/\text{AgCl}}$). The samples had a total geometric area of approximately 1 cm^2 . In order to increase the size of the exposed regions of the coating, after embedding in epoxy, samples were carefully grinded with SiC emery paper in an angle of around 1° with the original surface, except for a fraction of the original coating surface, which was preserved. This *low-angle* was achieved by covering 1/4 of the sample length with a 70 μm thick scotch tape before starting the grinding procedure (see Fig. 1). Subsequently, samples were polished with 1 μm diamond paste and rinsed with ethanol and distilled water.

Local surface analysis was performed on each layer described in Fig. 1, before and after sample immersion for 57 h in an aerated 0.001 M NaCl solution in order to simulate environmental conditions found in natural fresh waters (mean values from 0.3 to 3 mmol l^{-1} [14]). For this, the following techniques were used: Scanning electron microscopy (SEM, *Zeiss EVO MA15*), energy dispersive X-ray spectrometry (EDS, *OXFORD*, at 15 kV electron beam energy), micro X-ray diffraction ($\mu\text{-XRD}$, *Bruker D8 Advance diffractometer*, Cu- α radiation, $0.03^\circ/\text{step}$). $\mu\text{-XRD}$ patterns were analysed with the help of *Phillips X'Pert HighScore* software.

Scanning Vibrating Electrode Technique (SVET) was performed to map local anodic and cathodic current densities (I) during immersion of samples in a 0.01 M NaCl solution at open circuit potential conditions. An *Applicable Electronics Inc.* equipment controlled by the *ASET*

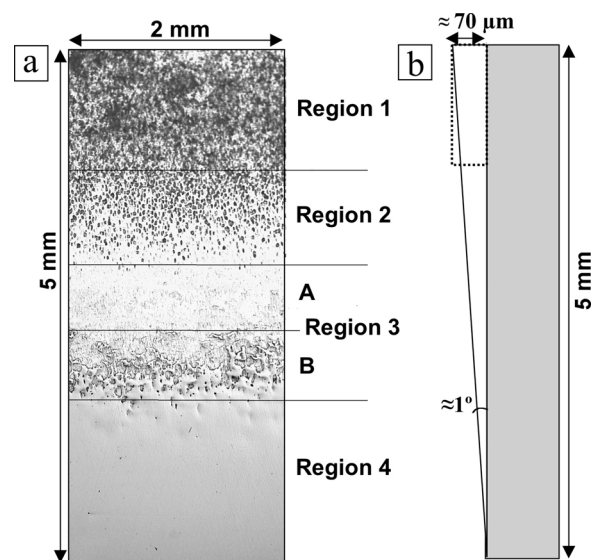


Fig. 1. Low angle ($\approx 1^\circ$) cross section: a) Optical micrograph with differential interference contrast of the top view. The four sample regions are identified: I. original outer coating surface, II. Outer coating region, III-A. inner coating region, III-B. interface region containing a small portion of IF steel substrate and IV. IF steel substrate. b) Schematic dimensions for *low-angle* cross section preparation.

software (*Science Wares Inc.*) was used to perform the experiments. The vibrating microelectrode for i determinations was a Pt-Ir wire from *MicroProbes Inc.* with a spherical tip with $\varnothing = 10 \mu\text{m}$ diameter, prepared as described elsewhere [15].

The distance between the microelectrode tip and sample surface was always 50 μm and the scanned area was about $5 \times 2 \text{ mm}$ in the case of I -maps (grid of 60×20 points, distance between points $\approx 60 \mu\text{m}$). Thus, only a fraction of the sample surface was exposed to the electrolyte during the measurements, as shown in Fig. 1. The acquisition time of each consecutive I -map was 15 min. Therefore, this is the exposure time difference between left and right borders of each I -map. The number of grid points was limited to 1200 so as not to excessively extend the acquisition time of each I -map. For the SVET-measurements, a 1.7 ml cell was adapted to the samples previously embedded in epoxy resin. Experiments were started within 20 s after filling the cell with the 0.01 M NaCl solution. All electrochemical tests were performed at room temperature around 25°C .

Voltametries and OCP transients were repeated at least three to five times, while SVET measurements were performed several times on two different samples. The results shown here express their typical behaviour.

3. Results and discussion

3.1. Coating structure

Fig. 1a shows a low magnification optical micrograph of the *low-angle* cross section, and Fig. 1b, the approximate dimensions of each exposed sample region. The surface was classified in four regions, with respect to the exposed layer region. Accordingly:

Region 1 is the original surface of the coating in the “as received” condition,

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