SVET and ECSM Measurements Under Simultaneous Strain on Hot-Dip Zn based coatings.

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Introduction

Zinc coatings are widely used to protect on carbon steels against atmospheric corrosion due to their excellent corrosion resistance and low cost. In the industry, the ductility of hot-dip Zn based coatings (HD-Zn) is also important, as it enables deep drawing processes typical of the automotive industry. A good formability of the coated steel sheet is required in order to reduce cracking and to maintain the adherence of the coating[1]. Besides of that, steel sheets are frequently bended in service and the resulting strains assume its highest amplitude on the surface region, where the coating is. Thus, a more realistic approach to determine the corrosion protection of Zn coatings to steel should take into account the ductility and adhesion of the coating under simultaneous applied strain. Moreover, a more complex situation than the usual distribution of cathodic and anodic reactions on a Zn-Fe couple should be expected, as Fe and Zn dissolution and O_2 evolution can occur at different rates on the different Fe-Zn phases formed in the different types of HD-Zn coatings.

In the present work, the scanning vibrating electrode technique (SVET) was used to study comparativelly the corrosion under simultaneous straining of different HD-Zn coatings on interstitial free steel. Current maps and additionally [Fe^{2+}] and [O_2] distributions were determined *in situ* on the corroding coatings.

Experimental

HD-Zn coated steel sheets (galvanized/GI, Galvanealed/GA and Galvalume) were provided by *ArcelorMittal*. Current density maps were acquired in a 0.01 mol/L NaCl using an *Applicable Electronics Inc.* equipment. The vibrating microelectrode for *i*-determinations was a Pt wire from *MicroProbes Inc.* with a spherical tip of 10 µm diameter. A similar electrode polarized at +0.55 and -0.6 V ($E_{Ag/AgCl}$) was used for the amperometric determinations of, respectively, [Fe^{2+}] and [O_2] distributions, as described elsewhere[2]. The electrode diameter can be roughly assumed as the lateral resolution of *i*-maps and concentration distribution measurements.

For the SVET-straining tests, flat specimens for uniaxial tensile tests where carefully machined. A small sized (Ø = 12.3 mm, h = 5.1 mm) *barnacle* cell with an electrolyte volume of 0.6 mL was attached to the coating surface. A circa 1 mm^2 area was exposed to the electrolyte, delimited with the use of a *3M Scotch tape*. For the strain values control, the distance between scratches or other marks located under the tape near the exposed area was measured in an optical microscope for each strain step value. After each strain step of around 0.8 %, one or two *i*-line scans and a following *i*-map were acquired.

Results and Discussion

Current density line scans show that localized anodic and cathodic elements are increasingly formed as strain steps are progressively applied, as shown in the example of **Fig. 1** for a GI coating (galvanized iron) before and after the first strain step of ε = 0.008. The distance between two consecutive anodic areas is around 15 µm and similar to the cathodic ones. This distance decreases to around 11 µm after the second strain step (ε = 0.017), becoming then lower than the lateral resolution of the used SVET procedure. It was later confirmed by SEM observation that these elements are associated to cracks formed on the coating due to the progressive straining.

If we assume that the cathodic elements correspond to substrate areas exposed by cracking of the upper more fragile Fe-Zn phases, and the anodic elements, respectively, to the surrounding Zn reach areas, the current density increase after each strain step can be attributed to current density of the exposed area. The current density line scans were integrated respective to the scanned distance and normalized to this distance. The so determined current density values were plotted *versus* the applied deformation ε and are shown for the GI coating in **Fig. 2**. Critical εv were determined for each coating by extrapolation of the i x ε curves to i = zero. The determined average anodic and cathodic i for strain are similar and thus, also the critical εv determined by extrapolation of cathodic or anodic i.

It is easy to show that the slope of the i x ε curves, when referred to the perceptual deformation, $\varepsilon = \Delta L/L_0 \cdot 100\%$, is the i-value on the newly exposed area, $\Delta A = \Delta L \cdot width$, due to straining and cracking, while the slope referred to the absolute ε values, is the i-increase referred to the initial sample surface, $A_0 = L_0 \cdot width$. The so calculated cathodic current on the exposed steel substrate for the example of **Fig. 2** is 8.2±0.2 $\mu A/cm^2$.
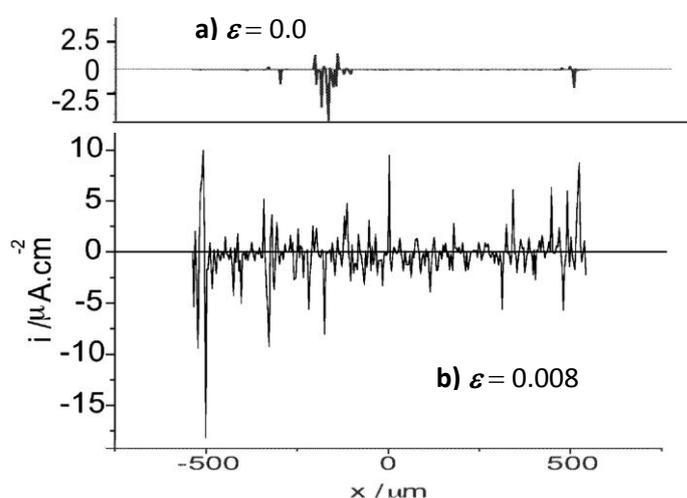

Fig. 1 Current density line scans before and after the first strain step of 0.008 (8%).
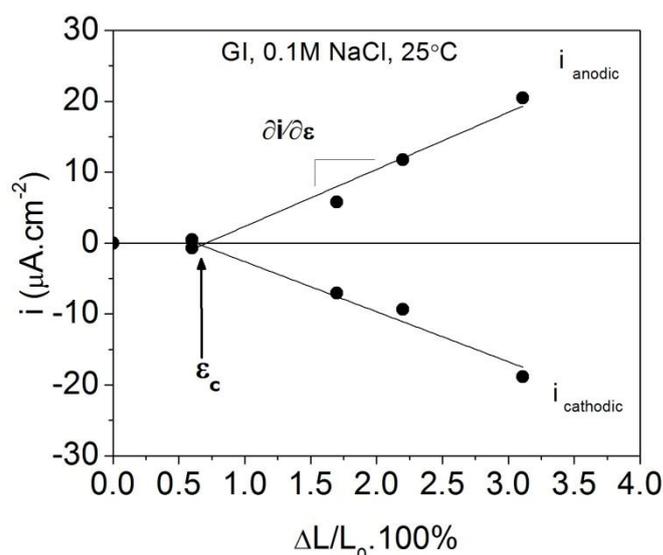

Fig. 2 Average current density *versus* applied strain for GI in 0.01mole/L NaCl.
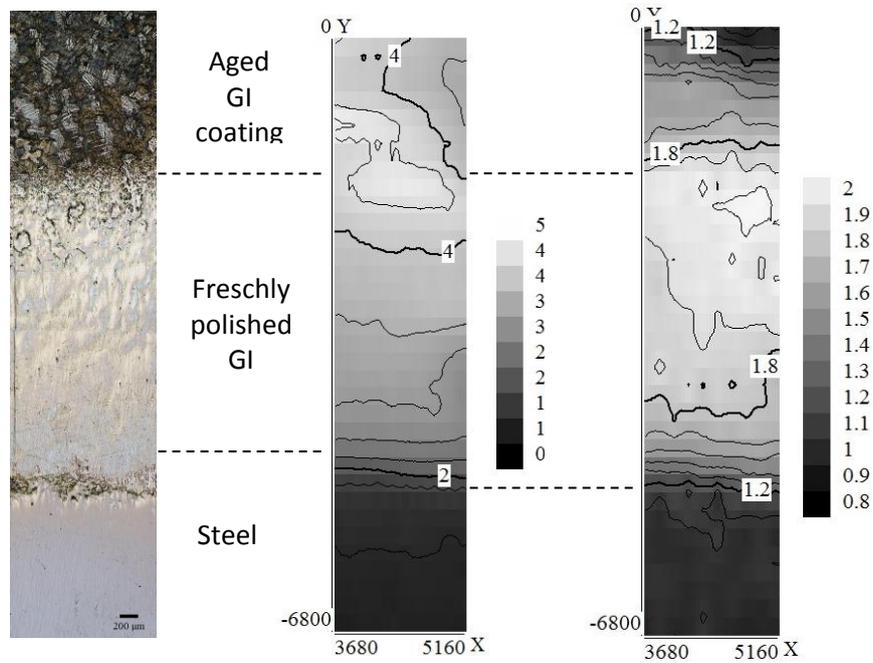.

Fig. 3 Left: Surface of passivated GI sample. Middle: Fe^{2+}-i_d after 1 and Left: 30min exposure.

Fig .3 shows the diffusion limited current density for the Fe^{2+} oxidation to Fe^{3+} on GI samples passivated with chromate. The sample was polished with a grazing angle of only circa 1° exposing fresh polished Zn coating between the passivated upper surface and the steel surface on the bottom. The measurement shows that the Fe dissolution from the Fe-Zn η phase takes place simultaneously to the Zn dissolution mainly from the fresh η phase surface. Thus, the protection of the steel substrate by Zn dissolution is a complex process.

References
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2. A.M. Simões, A.C. Bastos, M.G. Ferreira, Y. Gonzáles-García, S. Gonzáles, R.M. Souto, *Corrosion Science* 49 (2007) 726-739.