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Role of steel and zinc coating thickness in cut edge corrosion of coil coated materials in atmospheric weathering conditions; Part 1: Laboratory study

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1. Introduction

Long-term corrosion resistance of coil coated steel sheets widely used in building and appliance industries is assured by a synergistic protection effect provided by metallic zinc and organic paint. The barrier and galvanic protection of steel substrate by zinc coatings is particularly important at cut edges where a relatively large area of bare steel and small area of zinc and organic coating are exposed to a corrosive medium. In presence of a conductive electrolyte, the anodic reaction of metal oxidation prevails on zinc. It shifts steel corrosion potential to more negative values protecting it from corrosion [1–3]. The cathodic reaction of oxygen reduction dominates on steel. Because it usually controls the overall rate of the atmospheric corrosion process, the galvanic current is proportional to the area of steel cathode and little affected by the anode area [1]. This is known as the catchment principle.

The rate of zinc dissolution and progress of paint delamination can be estimated from models if the cut edge geometry, rate of oxygen diffusion, solubility of oxygen and electrochemical properties of the system are known [4–8]. Still, long-term observations often reveal lower delamination distances than estimated from

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ABSTRACT

Cathode surface area and its ability to reduce oxygen controlled the rate of zinc dissolution and paint delamination from cut edges of hot dip galvanised steel sheets. Zinc corrosion products deposited on steel in atmospheric exposure conditions inhibited oxygen reduction decreasing galvanic current and zinc dissolution and paint delamination. The opposite effect was observed for iron corrosion products. The initial steel substrate and zinc coating thicknesses affected the availability of zinc ions for formation of the protective film.

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models. This is believed to be due to a protective nature of zincbased deposits on steel [2,5,9–13]. Released zinc ions diffuse and migrate to the steel surface and form a film limiting the rate of oxygen reduction. This can be seen as a self-healing process. However, formation of a layer of zinc corrosion products can also increase the resistance to ionic current and decrease the efficiency of galvanic protection. It can lead to local steel activation and formation of iron corrosion products, red rust [4].

Although the principal mechanism of cut edge corrosion is the anodic dissolution of zinc, there are evidences suggesting that cathodic delamination of a paint film can also play a role. No organic paint is able to hinder the oxygen transport to the paint/metal interface completely. After formation of a protective layer of corrosion products inhibiting oxygen reduction on steel, an intact zinc coating underneath the paint film can become an additional cathode [14,15]. Although zinc is generally anodic to steel, formation of a cathodic front that makes only a minor contribution to the total current preceding the anodic dissolution front is not ruled out by some authors [12,15-21]. Tahara and Shinohara analysed composition of corrosion products at cross sections of cut edges of painted hot dip galvanised steel panels exposed to a subtropical marine environment [21]. Energy dispersive x-ray spectroscopy (EDS) mapping showed a higher concentration of sodium at the interface of the paint film and non-corroded zinc coating indicating it was a cathodic site. Samples exposed at a more benign site with







a lower salt deposition were free of sodium at the interface. Beside exposure conditions, paint delamination can be influenced by the porosity and thickness of polymeric coatings, leaching of corrosion inhibitors from primer paints and other factors [12,19,22–24].

The aim of this study was to investigate the role the metallic coating thickness can play in long-term cut edge protection of coil coated products. In Part 1, series of laboratory experiments are described. They were designed to gain better understanding of the edge creep mechanism and the role of cut edge geometry in atmospheric corrosion necessary for interpretation of field exposures reported in Part 2 [25]. Scanning electrochemical methods were used to determine the distribution of cathodic and anodic areas across cut edges. Visual and electron microscopy and surface-sensitive analytical techniques were applied to measure distribution of corrosion products and morphology of corroding surfaces.

2. Experimental

2.1. Materials

Line-produced hot dip galvanized (HDG) panels differing in substrate and zinc coating thicknesses are listed in Table 1. All zinc coatings contained about 0.2 wt.% Al. The thickness of steel substrate varied from 0.2 to 2.5 mm and the zinc coating weight from 100 to 275 g/m^2 (both sides). It corresponds to $7-20 \,\mu\text{m}$ of zinc on each side of a steel panel. The materials are denominated as steel substrate thickness/zinc coating thickness in μ m. For example, 700/10 corresponds to 700 μ m (0.7 mm) steel with 10 μ m zinc coating on each side. All panels were non-passivated and except for 2500/20, skin-passed.

The panels were painted in laboratory conditions following a procedure applied in coil coating lines. After alkali cleaning in Gardobond S5183 of Chemetall at the concentration of 15 g/l and at 55 °C, they were conversion coated in 5 vol.% Cr-free Granodine 1455 pretreatment solution of Henkel with the target coating weight of 5 mg/m² Ti. Conventional industrial Cr-free polyester primer and polyester topcoat paints were cured by convection at the peak metal temperature (PMT) 224 °C to obtain the dry film thickness (DFT) 5 and 20 μ m, respectively. Backside was painted with the primer paint with DFT of 7 μ m.

Paint adhesion to the metal substrate verified according to the ISO 4624 standard [26] was appropriate for all materials. Microhardness of topcoat paints varied from 165 to 205 N/mm² for steel substrates up to 1.5 mm in thickness evidencing complete paint curing. For 2.5-mm substrates, it reached around 140 N/mm². Although the value shows on slight under-curing, barrier properties of the paints can still be considered sufficient.

All prepainted panels in Table 1 were exposed at a marine field site for 5 years [25]. Selected materials were used for laboratory experiments described below.

Table 1	
Sample denomination; steel substrate/zinc coating thickness [μ m].	

Substrate thickness [mm]	Coating weight, both sides [g/m ²] (coating thickness, each side [μ m])		
	100(7)	140 (10)	275 (20)
0.2	200/7	-	-
0.35	-	-	350/20
0.5	500/7	500/10	500/20
0.7	700/7	700/10	700/20
1	1000/7	1000/10	1000/20
1.5	1500/7	1500/10	1500/20
2.5	2500/7	2500/10	2500/20

2.2. Galvanic current and dc polarization measurements

Potentiostat Gamry Reference 600 was used for dc electrochemical experiments. Polarization curves were measured on edges of coil coated specimens pre-exposed at the field site. Potentiodynamic curves were measured in 0.5 M NaCl electrolyte from -0.1 V vs. open circuit potential with a sweep rate 0.1 mV/s. The working electrode was a 20-mm long edge. After the polarization measurement, fresh cut edge of the same dimension was prepared using mechanical cutter and the polarization measurement was repeated. Saturated calomel electrode (SCE) and platinum wire were used as reference and counter electrodes.

Galvanic current was monitored between zinc (cast, 99.95 wt.% purity) and steel (low-carbon hot rolled) electrodes in a galvanic sensor with a potentiostat in a zero-resistance ammeter mode. The sensor comprised two co-planar electrodes with equal area of 1 cm^2 embedded in epoxy resin and separated by a 100-µm Mylar membrane [27].

Anodic dissolution of pre-painted steel panels with zinc coatings of different thicknesses was studied in 0.5 M NaCl. Painted panels 700/7, 700/10 and 700/20 (Table 1) were anodically polarized using external 304L stainless steel cathodes with areas 95 and 51 cm². Potential of the painted panel and galvanic current flowing between the panel and cathode were monitored and the extent of zinc coating dissolution visually inspected. The panel potential was monitored using SCE.

2.3. Scanning Kelvin probe

Scanning Kelvin probe (SKP) is an efficient method to detect anodic and cathodic locations across corroding metal surfaces in situ in atmospheric conditions even under polymer coatings [22,28,29]. SKP can measure corrosion potential of corroding metal surfaces, redox potential of surfaces in contact to a redox couple, e.g. Fe₃O₄/Fe₂O₃, and potential of passive metal in dry air.

Paint delamination from cut edges was studied by SKP in humid air at 95% RH by an instrument from UBM Messtechnik. Surface contour and Volta potential distribution was measured over areas close to corroding cut edges. The reference electrode was a Ni-Cr alloy needle with a tip diameter of $80-100 \,\mu$ m. Lateral resolution of the probe was about $100 \,\mu$ m. Vibration amplitude was $20 \,\mu$ m at frequency of 2 kHz. The probe potential was calibrated relatively to a Cu/CuSO₄ electrode. The potentials are reported versus the standard hydrogen electrode (SHE).

2.4. Scanning vibration electrode technique and scanning ion-selective electrode technique measurements

Selected pre-painted samples were embedded in epoxy resin and polished with emery paper down to 1000 grit. Scanning vibrating electrode technique (SVET) equipment from Applicable Electronics was used to assess distribution of galvanic current across the cut edges. The setup allowed for quasi-simultaneous measurements of local current density (SVET) and pH by scanning ion-selective electrode technique (SIET) over cut edges in aqueous electrolyte [30-32]. A SVET-SIET scan yielded two independent maps showing ionic current density and pH distribution. An insulated Pt-Ir probe from Microprobe, Inc. with platinum black deposited on a spherical tip of $15 \,\mu m$ in diameter was used as the SVET electrode. The probe vibrated in the vertical (Z) and horizontal (X) planes relative to the sample surface at 124 Hz (Z) and 325 Hz (X) with amplitude of $18 \,\mu$ m. Localized pH measurements were carried out with a pH-selective glass capillary microelectrode with tip orifice diameter of $1.8 \pm 0.2 \,\mu$ m and 4-nonadecylpyridine-based H⁺-selective liquid membrane. Nernstian slope of $-58 \pm 1 \text{ mV/pH}$ was observed. The SVET probe and pH microelectrode were sepaDownload English Version:

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