On the Corrosion Performance of Module-Mounting Assemblies for Ground-Mounted Photovoltaic Power Station

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Abstract

The present paper reports the corrosion performance results of construction materials employed for the manufacture of mounting assemblies for ground-mounted photovoltaic (PV) power stations. For this purpose, the corrosion behavior of industrial hot-dip Zn-coated steel sheets was compared with that of Magnelis® type steel coating. Experiments involved samples in continuous exposure in 3 wt% NaCl solution along with regular assessment of their corrosion parameters by means of major (impedance spectroscopy, linear and Tafel polarization plots) electrochemical techniques. Analyses of surface/cross-sectional morphology and elemental compositions of metal-coated samples were carried out by means of SEM and EDX spectroscopy techniques.

Keywords PV mounting assembly · Hot-dip Zn-coated steel · Magnelis® coating · Corrosion performance

Introduction

Photovoltaic (PV)-based systems are most likely the fastest growing among renewable energy technologies. Ground-mounted photovoltaic solar assemblies possess a number of advantages over conventional rooftop PV systems. This is primarily because they could be constructed on a much larger scale, which is very important for utility-size power stations. In addition, ground-mounted PV structures have several other benefits over roof-mounted arrays, including flexible adjustment of solar panel angles and orientation, easy and safe maintenance, better performance (through facilitated cooling), and additional space for possible future system expansion [1–4].

Generally, the PV arrangement consists of solar modules held in place by frames being attached to ground-based mounting supports, typically including concrete-embedded pole mounts. As the PV modules are normally designed for an operational lifespan of 25–30 years, similar robustness would also be expected from structural components of the photovoltaic system. The most important elements of the PV racking structure comprise Zn-coated steel, aluminum sheets and profiles, stainless steel (SS), and copper fasteners. As it is important for the structural components (e.g., Al- and Zn-coated steel sheets) of the ground-mounting system to exhibit superior corrosion performance under typical environmental conditions, it is also important that individual metal elements are not susceptible to galvanic corrosion [5, 6].

In this work, we have comprehensively examined the corrosion behavior of two commercial hot-dip Zn-coated steel sheets in reference to Magnelis®-coated carbon steel material, exposed in 3 wt% NaCl solution, under changing pH and temperature conditions. Magnelis® is an innovative, Zn-based composite coating, modified by ca. 3.5 wt% Al and 3 wt% Mg elements. The coating (originally introduced to the market by ArcelorMittal Company) is believed to offer superior to typical Zn layer protection against corrosion, in a number of harsh environments [7].

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Experimental

For the purpose of this work, samples of commercial Zn(Magnelis®)-coated steel specimens were prepared as follows:

1. *Sample A*: Magnelis®-coated steel (S250GD: 1.0242 grade): $30 \times 30 \times 2.95$ and $50 \times 50 \times 3.02$ mm (ArcelorMittal; ca. 25–30 μm coating thickness)
2. *Sample B*: regular hot-dip Zn-coated steel (DD11: 1.0332 grade): $30 \times 30 \times 3.15$ and $50 \times 50 \times 3.15$ mm (ca. 80–90 μm Zn thickness)
3. *Sample C*: air-knifed postprocessed [8], hot-dip Zn-coated steel (DD11: 1.0332 grade): $30 \times 30 \times 3.01$ and $50 \times 50 \times 3.01$ mm (ca. 20 μm thick Zn coating)

Prior to commencing the corrosion experiments, all metal-coated samples were degreased with ethanol. Then, they were dried in a desiccator, followed by weighing on a precision Sartorius CP224-OCE balance with 0.1 mg accuracy. Electrical connections to electrodes were provided by means of threaded steel wires, covered with shrinkable polyethylene tubes (all electrode corners were properly taped with a polymer, acid-resistant adhesive tape). Continuous corrosion exposure of Zn(Magnelis®)-coated steel sheet samples was carried out at room temperature (ca. 20 °C) in 3 wt% NaCl solution (in laboratory glass beakers), prepared by dissolving NaCl salt (Polish Chemical Compounds, p.a.) in distilled water for a total period of 78 days. Initial and intermittent pH adjustments (to obtain the set pH values of 4, 7, and 9) were performed through addition of aqueous, 0.1 mol dm⁻³ HCl and NaOH solutions, correspondingly (prepared with Polish Chemical Compounds, p.a. chemicals).

Corrosion measurements for the examined metal-coated samples involved periodic recording of their corrosion potentials (E_{cor}), measured vs. saturated calomel electrode, SCE. In addition, freely corroding Zn(Magnelis®)-coated steel samples were subjected to intermittent, instrumental evaluation of their corrosion current (I_{cor}) and other important electrochemical parameters. These experiments involved linear polarization and a.c. impedance spectroscopy tests and sporadic recording of Tafel polarization plots. All instrumental measurements were carried out in a three-compartment HDPE-made electrochemical cell, either at room temperature (RT) or at 50 °C by means of the Solartron 12.608 W Full Electrochemical System, consisting of 1260 frequency response analyzer (FRA) and 1287 electrochemical interface (EI). The voltammetric Tafel polarizations were conducted on selected samples over controlled ranges of the working electrode potential (± 300 mV vs. open circuit potential, ocp), at a sweep rate of 0.5 mV s⁻¹. On the other hand, linear polarization experiments involved micropolarizations carried

out at ± 10 mV around the open circuit (corrosion) potential, at a scan rate of 0.1 mV s⁻¹. For a.c. impedance measurements (performed at the corresponding ocp values), the generator provided an output signal of 5 mV amplitude and the frequency range was swept between 50 (or 100) kHz and 20 mHz. The instruments were controlled by ZPlot 2.9 or Corrware 2.9 software for Windows (Scribner Associates, Inc.). Presented results were obtained through averaging of multiple measurement trials, received independently at two metal-coated electrodes. Data analysis was performed with ZView 2.9 or Corrview 2.9 software package, where the impedance spectra were fitted by means of a complex, non-linear, least-squares immittance fitting program, LEVM 6 [9]. In addition, electrode potential measurements were conducted by means of Fluke 85 III true rms multimeter, whereas oxygen content, electrolyte conductivity, and pH evaluations were carried out with HI 9146, HI 9835, and HI 2002-01 meters from Hanna Instruments, correspondingly.

Furthermore, comprehensive scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDX) analyses were carried out for fresh metal-coated samples and those after completion of the exposure to the corrosion environment by means of Merlin FE-SEM microscope (Zeiss), equipped with Bruker XFlash 5010 (with 125 eV resolution) EDX supplement. Preparation of cross-sectional metallographic specimens involved sample cutting (Struers Secotom 10) and polishing (Struers Labopol-21) with fine grit silicon-carbide abrasive paper, down to 2500 grade.

Results and Discussion

Spectroscopic Examinations of Unexposed and Corrosion-Tested Composite Samples

Figures 1, 2, 3, 4, 5, and 6 and Tables 1 and 2 present the results of comparative, cross-sectional, and surface spectroscopy (SEM/EDX) examinations of Magnelis®-coated steel sheet (sample A) and two commercial hot-dip Zn-coated (samples B and C) steel sheets. Hence, cross-sectional SEM/EDX analysis of fresh Magnelis®-coated (ca. 25–30 μm thick) steel sample is shown in Fig. 1a, b, whereas Fig. 1c, d illustrates analogous but surface spectroscopy examination of the sample A. It could also be seen in Table 1 that the surface of Magnelis® coating (unexposed to the corrosion environment) is primarily composed of Zn (ca. 74 wt%), Al (5.5%), Mg (3%), C (6%), and oxygen (10.5%) elements. Furthermore, approximate cross-sectional composition (not shown in this manuscript) of the Magnelis® coating came to Zn (49%), Fe (18%), Al (3%), Mg (0.5%), C (26%), and oxygen (4%).

On the other hand, cross-sectional SEM/EDX analyses of regular (sample B, 80–90 μm) and air-knifed (sample C,

Fig. 1 **a** Cross-sectional SEM micrograph picture showing Magnelis®-coated (ca. 25–30 μm thick) carbon steel specimen, taken at $\times 7000$ magnification for a fresh (unexposed to electrolyte) electrode (SE: secondary electron imaging mode; MAG: sample magnification; HV: high voltage or acceleration voltage; WD: working distance). **b** As in **a** above, but EDX mapping presenting the sample's elemental analysis within individual zones: steel and Magnelis® coating. **c** SEM micrograph picture showing Magnelis®-coated (ca. 25–30 μm thick) carbon steel surface, taken at $\times 10,000$ magnification for a fresh (unexposed to electrolyte) electrode. **d** As in **c** above, but EDX mapping presenting the surface's elemental analysis (primarily Zn, Mg, and Al)

20 μm), fresh hot-dip Zn-coated steel samples are shown in Figs. 2a, b and 3a, b, correspondingly (while their respective SEM surface characterizations are given in Figs. 2c and 3c).

As compared to sample A, cross-sectional views for both sample B and sample C (Figs. 2a and 3a) indicate that Zn coatings are in general less homogeneous and

Fig. 2 **a** Cross-sectional SEM micrograph picture of a regular hot-dip Zn-coated (ca. 80–90 μm thick) carbon steel sample, taken at $\times 1737$ magnification for a fresh (unexposed to electrolyte) electrode. **b** As in **a** above, but EDX mapping showing the sample's elemental analysis within individual zones: steel and regular hot-dip Zn coating. **c** SEM micrograph picture of a regular hot-dip Zn-coated (ca. 80–90 μm thick) carbon steel surface, taken at $\times 1000$ magnification for a fresh (unexposed to electrolyte) electrode (dwell: dwell time given in μs ; spot: spot size given in nm)

Fig. 3 **a** Cross-sectional SEM micrograph picture of air-knifed hot-dip, porous Zn coating (ca. 20 μm thick) on carbon steel surface, taken at $\times 10,000$ magnification for a fresh (unexposed to electrolyte) electrode. **b** As in **a** above, but EDX mapping presenting the sample's elemental analysis within individual zones: steel and air-knifed hot-dip Zn coating. **c** SEM micrograph picture of air-knifed hot-dip Zn-coated (ca. 20 μm thick) carbon steel surface, taken at $\times 1000$ magnification for a fresh (unexposed to electrolyte) electrode

less compact (especially air-knifed hot-dip Zn in Fig. 3a) than that of Magnelis® coating shown in Fig. 1a. In addition, in contrast to sample A, specimens B and C are also

characterized by significantly increased surface concentrations of zinc (see corresponding EDX results presented in Table 1 for details).

Fig. 4 **a** Cross-sectional SEM micrograph picture of Magnelis®-coated (ca. 25–30 μm thick) carbon steel electrode, taken at $\times 10,438$ magnification for corrosion-tested electrode (exhibiting radical reduction of the coating's thickness). **b** As in **a** above, but EDX mapping presenting the sample's elemental analysis within individual zones: steel and Magnelis® coating. **c** SEM micrograph picture of Magnelis®-coated (ca. 25–30 μm thick) carbon steel surface, taken at $\times 1000$ magnification for corrosion-tested electrode (significant degradation/morphology change of coating is clearly visible). **d** As in **c** above, but EDX mapping showing the surface's elemental analysis for corrosion-tested electrode with locally decayed coating and increased oxygen level

Fig. 5 **a** Cross-sectional SEM micrograph picture of regular hot-dip Zn-coated (ca. 80–90 μm thick) carbon steel surface, taken at $\times 1500$ magnification for corrosion-tested electrode (the coating's outer layer damage and loss of homogeneity are clearly visible). **b** As in **a** above, but EDX mapping presenting the sample's elemental analysis within individual zones: steel and regular hot-dip Zn coating (significant surface oxidation is observed). **c** SEM micrograph picture of regular

hot-dip Zn-coated (ca. 80–90 μm thick) carbon steel surface, taken at $\times 1000$ magnification for corrosion-tested electrode (significant degradation/morphology change of Zn coating is clearly visible). **d** As in **c** above, but EDX mapping presenting surface's elemental analysis for corrosion-tested electrode with clearly recognizable numerous microcathode (Fe) sites and extensive surface oxidation

Fig. 6 **a** Cross-sectional SEM micrograph picture of air-knifed hot-dip Zn-coated (ca. 20 μm thick) carbon steel sample, taken at $\times 5000$ magnification for corrosion-tested electrode (outer layer surface deterioration of Zn coating could be observed). **b** As in **a** above, but EDX mapping illustrating the sample's elemental analysis within individual zones: steel and air-knifed hot-dip Zn coating (significant surface oxidation is observed). **c** SEM micrograph picture of air-knifed hot-dip Zn-coated (ca. 20 μm thick) carbon steel surface, taken at $\times 250$ magnification for corrosion-tested electrode showing locally damaged Zn coating. **d** As in **c** above, but EDX mapping showing the surface's elemental analysis for corrosion-tested electrode with appearance of a number of steel-based microcathodes and extended surface oxidation

Table 1 Surface EDX elemental analysis for unexposed: Magnelis®-coated, regular and air-knifed hot-dip Zn-coated steel sheets (surface samples A, B, and C)

Element	Series	Unn. C [wt%]	Norm. C [wt%]	Atom. C [at.%]	Error (1 Sigma) [wt%]
Surface sample A					
Carbon	K-series	5.56	6.12	19.26	0.82
Oxygen	K-series	9.52	10.47	24.75	1.15
Magnesium	K-series	2.72	3.00	4.66	0.17
Aluminum	K-series	5.00	5.51	7.72	0.26
Iron	K-series	0.07	0.07	0.05	0.03
Zinc	K-series	67.38	74.15	42.89	2.25
Phosphorus	K-series	0.25	0.28	0.34	0.04
Chromium	K-series	0.32	0.36	0.26	0.04
Silicon	K-series	0.04	0.05	0.07	0.03
Total		90.87	100.00	100.00	
Surface sample B					
Carbon	K-series	10.71	11.69	38.10	2.24
Zinc	K-series	72.64	79.24	47.45	2.51
Oxygen	K-series	4.87	5.32	13.01	0.99
Aluminum	K-series	0.47	0.51	0.74	0.06
Iron	K-series	0.16	0.17	0.12	0.04
Lead	M-series	2.83	3.08	0.58	0.15
Total		91.67	100.00	100.00	
Surface sample C					
Carbon	K-series	8.05	8.48	27.86	1.55
Zinc	K-series	77.37	81.55	49.20	2.67
Oxygen	K-series	8.52	8.98	22.13	1.30
Aluminum	K-series	0.08	0.09	0.13	0.04
Iron	K-series	0.06	0.06	0.04	0.03
Chromium	K-series	0.80	0.85	0.64	0.07
Total		94.88	100.00	100.00	

Extended, 78-day exposure of Magnelis®-coated steel sample in 3 wt% sodium chloride solution led to a significant surface depletion of zinc, aluminum, and magnesium elements along with a radical increase of oxygen and iron surface concentrations (compare the results given in Table 1 with those in Table 2 for details). In addition, the coating got essentially thinner and locally lost its continuity, which can be supported by comparative analysis of figure pairs: 1a/1b and 4a/4b, and 1c/1d and 4c/4d, respectively. Analogous observations (reduction of coating thickness, significant depletion of Zn content along with a radical increase of surface oxygen levels) could be made for samples denoted as B and C [see Tables 1 and 2 for details; compare figure pairs: 2a/2b and 5a/5b (5c/5d), and 3a/3b and 6a/6b (6c/6d), correspondingly].

Electrochemical Corrosion Characteristics of Zn(Magnelis®)-Coated Steel Samples

Figure 7 presents variation of open circuit (or corrosion) potentials (E_{cor}) in time recorded for regular and air-knifed hot-dip Zn-coated, and Magnelis®-coated steel sheet electrodes,

subjected to extended exposure in 3% NaCl solution (electrolyte conductivity, κ varied between 30 and 35 mS cm⁻¹), at various pH values. Fluctuation of the corrosion potential of Zn-based coatings is governed by combined characteristics of anodic and cathodic processes in relation to the formation of surface-adsorbed corrosion products. Here, for all examined electrodes, the corrosion potential exhibited a cathodic shift (from an initial potential value of ca. -1.050 ± 0.010 V) toward less negative values during the exposure, with the most pronounced potential change exhibited by the air-knifed hot-dip Zn-coated steel electrode, recorded at a somewhat acidic pH value of 4. Nevertheless, for the all samples, the corrosion potential remained within the range that provided cathodic protection to iron substrate through dissolution of Zn(Magnelis®) coating [10–13].

A.c. impedance behavior of Zn(Magnelis®)-coated steel electrodes is shown in Fig. 8a–d and Tables 3 and 4 [Fig. 8e shows two constant phase element (CPE)- R component equivalent circuit model used for fitting the impedance data]. Thus, the Nyquist impedance plots (Fig. 8a, c) consist of two somewhat depressed semicircles. A high frequency semicircle

Table 2 Surface EDX elemental analysis for corrosion tested: Magnelis®-coated and regular and air-knifed hot-dip Zn-coated steel sheets (surface samples A, B, and C)

Element	Series	Unn. C [wt%]	Norm. C [wt%]	Atom. C [at.%]	Error (1 Sigma) [wt%]
Surface sample A					
Oxygen	K-series	41.19	41.22	63.50	4.63
Magnesium	K-series	0.08	0.08	0.08	0.03
Aluminum	K-series	0.13	0.13	0.12	0.03
Chlorine	K-series	3.40	3.41	2.37	0.14
Iron	K-series	21.37	21.38	9.44	0.66
Zinc	K-series	26.57	26.60	10.02	0.92
Silicon	K-series	0.22	0.22	0.19	0.04
Carbon	K-series	6.95	6.96	14.28	1.08
Total		99.92	100.00	100.00	
Surface sample B					
Oxygen	K-series	37.70	38.19	61.12	4.26
Aluminum	K-series	0.09	0.10	0.09	0.03
Iron	K-series	0.11	0.11	0.05	0.03
Zinc	K-series	52.15	52.83	20.69	1.75
Carbon	K-series	8.19	8.30	17.70	1.23
Silicon	K-series	0.03	0.03	0.03	0.03
Chlorine	K-series	0.43	0.44	0.32	0.04
Total		98.70	100.00	100.00	
Surface sample C					
Oxygen	K-series	29.27	32.37	56.52	3.27
Aluminum	K-series	0.15	0.17	0.18	0.03
Iron	K-series	0.94	1.04	0.52	0.06
Zinc	K-series	52.47	58.01	24.79	1.77
Carbon	K-series	6.72	7.43	17.27	0.96
Silicon	K-series	0.09	0.09	0.09	0.03
Chlorine	K-series	0.56	0.62	0.49	0.05
Chromium	K-series	0.24	0.26	0.14	0.04
Total		90.44	100.00	100.00	

Fig. 7 Changes of electrode corrosion potential (E_{cor}) in time for hot-dip Zn-coated and Magnelis®-coated steel electrodes, continuously exposed in 3 wt% NaCl solution, at RT and various pH conditions

Fig. 8 **a** Complex-plane impedance plots for fresh (day 0) hot-dip Zn-coated and Magnelis®-coated steel electrodes, recorded at corresponding corrosion potentials, at RT in 3 wt% NaCl solution and pH = 7. **b** As in **a** above, but Bode phase-angle plots. **c** As in **a** above, but recorded at pH = 4. **d** As in **c** above, but Bode phase-angle plots. **e** Two CPE- R element equivalent circuit model used for fitting the impedance data for hot-dip Zn-

coated and Magnelis®-coated steel electrodes, corrosion-tested in 3 wt% NaCl solution. The circuit includes two constant phase elements (CPEs) to account for distributed capacitance; R_{coat} and CPE_{coat} elements are related to the resistance and capacitance of surface corrosion products; R_{ct} and CPE_{dl} correspond to the reaction charge-transfer resistance and interfacial double-layer capacitance parameters, and R_{sol} is solution resistance

corresponds to the reaction charge-transfer resistance (R_{ct}) and interfacial double-layer capacitance (C_{dl} ; presented as CPE in Fig. 8e), whereas a medium-low frequency arc feature is associated with the resistance (R_{coat}) and capacitance (C_{coat} ; given as CPE) of corrosion products accumulated on the electrode surface, as the corrosion process continues [14–19]. It could be seen in Fig. 8a (also, refer to Bode phase-angle plots in Fig. 8b) that for freshly immersed composite electrodes (examined at RT under neutral pH conditions), the Magnelis®-coated steel sample is characterized by radically increased values of both the R_{ct} (2807 $\Omega \text{ cm}^2$), as well as the R_{coat} (5130 $\Omega \text{ cm}^2$) resistance parameter, compared with those of the air-knifed (929 and 5095 $\Omega \text{ cm}^2$, respectively) and the regular hot-dip Zn-coated (815 and 852 $\Omega \text{ cm}^2$,

correspondingly) electrodes (see Table 3 for details). As the corrosion process makes its progress, both resistance parameters tend to become significantly reduced. The above could be related to increased corrosion rate under the unstable layer of the surface corrosion products (also refer to Figs. 4c, d, 5c, d, and 6c, d). In addition, periodic increase of the R_{ct} (R_{coat}) parameter (see, e.g., the recorded resistance results for the Magnelis®-coated electrode, on days 35 and 63, and for the regular hot-dip Zn-coated steel specimen, on days 0, 21, and 35) could imply sporadic thickening of the corrosion product(s) layer and thus more effective surface blocking from its contact with the corrosive NaCl electrolyte.

Furthermore, temperature augmentation from RT to 50 °C resulted (understandably) in significant reduction of both

Table 3 Average corrosion parameters for hot-dip Zn-coated and Magnelis®-coated steel sheet electrodes, in contact with 3 wt% NaCl solution at pH = 7, obtained from a.c. impedance spectroscopy measurements

<i>t</i> /days	$R_{ct}/\Omega \text{ cm}^2$	$R_{coat}/\Omega \text{ cm}^2$	$C_{dl}/\mu\text{F cm}^{-2} \text{ s}^{\varphi 1-1}$	$C_{coat}/\mu\text{F cm}^{-2} \text{ s}^{\varphi 2-1}$
Air-knifed hot-dip Zn-coated (20 μm) steel sheet: RT (50 °C)				
0	929 (423)	5095 (2418)	98 (168)	965 (1237)
21	442 (371)	1920 (1500)	109 (145)	1029 (1027)
35	509 (177)	1400 (1059)	366 (644)	4575 (4408)
63	313 (56)	500 (399)	325 (107)	4872 (3056)
Regular hot-dip Zn-coated (80–90 μm) steel sheet: RT (50 °C)				
0	815 (356)	852 (1153)	140 (165)	2660 (1160)
21	472 (187)	1303 (482)	105 (521)	2821 (5808)
35	300 (231)	1389 (645)	158 (625)	474 (5450)
63	135 (67)	714 (328)	209 (1280)	46 (2689)
Magnelis®-coated (25–30 μm) steel sheet: RT (50 °C)				
0	2807 (424)	5130 (3654)	32 (123)	548 (575)
21	1075 (215)	2820 (1928)	101 (452)	2661 (6044)
35	333 (95)	600 (428)	635 (829)	1764 (3690)
63	524 (175)	717 (480)	509 (655)	2039 (4290)

resistance parameters for all three examined composite materials. The latter is a general consequence of temperature dependence of the rates of corrosion (electrochemical) processes; however, it also implies that increased ambient temperature considerably inhibited the formation (and/or stability) of surface-adsorbed layer of the corrosion products. In addition, the recorded initial values of the double-layer capacitance parameter ($32\text{--}168 \mu\text{F cm}^{-2} \text{ s}^{\varphi 1-1}$, see Table 3 again) were significantly higher than $20 \mu\text{F cm}^{-2}$, a generally used C_{dl} value in literature for smooth and homogeneous surfaces [20, 21]. The above might suggest major contribution from the C_{coat} pseudocapacitance parameter along with a simultaneous effect of increased microscopic roughness of the zinc (Magnelis®) coatings. Then, as the corrosion exposure continued, the C_{dl} parameter kept rising, whereas the C_{coat} exhibited considerable fluctuation for all examined samples and at both studied temperatures. In addition, the recorded values of dimensionless φ_1 and φ_2 parameters of the CPE elements (in relation to the so-called capacitance dispersion effect [22–24]) oscillated around 0.50–0.95.

The corrosion process of zinc coating commences with the oxidation of Zn to form Zn^{2+} cations, whose reaction under neutral or alkaline conditions is balanced by the process of oxygen (in this work, the concentration of dissolved oxygen in electrolyte fluctuated between 7.0 and 7.5 ppm) depolarization reaction (Eq. 1):

Hence, the major corrosion product for zinc coating involves the formation of zinc hydroxide (stabilized by increased pH value upon the cathodic reaction), which then becomes converted to ZnO, according to Eq. 2 [14–17, 25–28]:

However, in the presence of chloride ions and dissolved CO_2 , the formation of other zinc products, including hydrozincite: $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and simonkolleite: $\text{Zn}_5(\text{OH})_8\text{Cl}_2$,

Table 4 Average corrosion parameters for regular hot-dip Zn-coated and Magnelis®-coated steel sheet electrodes, in contact with 3 wt% NaCl solution at pH = 4 and (pH = 9), obtained at room temperature from a.c. impedance spectroscopy measurements

<i>t</i> /days	$R_{ct}/\Omega \text{ cm}^2$	$R_{coat}/\Omega \text{ cm}^2$	$C_{dl}/\mu\text{F cm}^{-2} \text{ s}^{\varphi 1-1}$	$C_{coat}/\mu\text{F cm}^{-2} \text{ s}^{\varphi 2-1}$
Regular hot-dip Zn-coated (80–90 μm) steel sheet				
0	278 (312)	1264 (1117)	354 (308)	1967 (2891)
21	29 (27)	1112 (484)	739 (427)	543 (239)
63	63 (42)	2473 (645)	64 (43)	795 (183)
Magnelis®-coated (25–30 μm) steel sheet				
0	410 (1005)	6415 (7930)	104 (48)	590 (827)
21	165 (596)	3938 (4922)	154 (463)	610 (2580)
63	352 (112)	950 (439)	1245 (24)	1440 (602)

has widely been indicated [14, 16, 17, 25–28]. On the other hand, the presence of Mg and Al additives within Magnelis® coating primarily (except for some more complex molecules, such as pure and mixed hydroxy carbonates) leads to the formation of hydroxide compounds (Eqs. 3 and 4) [16, 25, 27–29]:

It is widely believed [25–28] that the effect of enhanced anticorrosion protection for Al/Mg-doped (e.g., Magnelis®) Zn layers (also, refer to the reported resistance parameters in Tables 3 and 4), as compared to that exhibited solely by the zinc coating, is related to the surface formation of complex, mixed (Mg/Al) hydroxy carbonate precipitates. These compact films could then provide superior protection to the background material, also by tightly filling local cavities within the coating. In addition, precipitated magnesium corrosion products, namely, $\text{Mg}(\text{OH})_2$, MgCO_3 , and $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2$, make a pH value to locally increase to the level of 10–11, which simultaneously results in slowing down the dissolution process of Zn [28].

On the other hand, both regular hot-dip Zn-coated as well as Magnelis®-coated steel electrodes revealed significantly higher susceptibility to corrosion under either slightly acidic (pH = 4) or alkaline (pH = 9) conditions. Thus, in general, such recorded charge-transfer resistance, R_{ct} , exhibited considerably lower values than those derived under neutral conditions (see Nyquist impedance plots in Fig. 8c and the corresponding Bode phase-angle diagrams in Fig. 8d for freshly immersed metal-coated samples, examined at RT and bulk pH of 4, and other details in Table 4). Hence, under the pH deviated from neutral conditions (i.e., for pH = 4 or 9), the charge-transfer process becomes significantly facilitated though changes of the R_{coat} parameter are rather insignificant (as compared to those previously recorded at pH = 7). The latter might result from the fact that bulk pH adjustments in the respective sample examination containers were carried out periodically, whereas the development of corrosion layers proceeded at the interface over an extended period of time, under locally increased (alkaline) pH conditions. For the same reason, the possibility that the cathodic process (even at bulk pH = 4) could be controlled by proton depolarization reaction ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) was not taken into account [14, 28].

The corrosion performance of hot-dip Zn- and Magnelis®-coated carbon steel electrodes was also examined by means of the linear polarization method. The latter technique allowed for the derivation of polarization resistance (R_p) and the corrosion current density (j_{cor}) parameters, as shown in Tables 5 and 6. The polarization resistance is calculated as the inverse of the slope of I (current) vs. E (potential)

Table 5 Calculated average corrosion parameters for hot-dip Zn-coated and Magnelis®-coated steel sheet electrodes, in contact with 3 wt% NaCl solution at pH = 7, obtained from linear micropolarization measurements

<i>t</i> /days	$R_p/\Omega \text{ cm}^2$		$j_{cor}/\mu\text{A cm}^{-2}$	
	RT	50 °C	RT	50 °C
Air-knifed hot-dip Zn-coated (20 μm) steel sheet				
0	4363	2689	6.0	9.7
21	3138	2348	8.3	11.9
35	2378	2469	11.0	10.6
63	1983	1758	13.1	14.8
Regular hot-dip Zn-coated (80–90 μm) steel sheet				
0	2969	1507	8.8	17.3
21	1516	947	17.2	27.5
35	1732	1718	15.1	15.2
63	2911	1689	9.0	15.5
Magnelis®-coated (25–30 μm) steel sheet				
0	6309	3433	4.2	7.6
21	2492	1303	10.5	20.0
35	3635	1616	7.2	16.1
63	3424	1797	7.6	14.5

graph, based on micropolarization (here ± 10 mV vs. ocp) measurements. The corrosion current (I_{cor}) is then derived from the well-known Stern-Geary relationship (Eq. 5):

$$I_{cor} = \frac{b_a \times b_c}{2.303 \times R_p \times (b_a + b_c)} \quad (5)$$

Table 6 Calculated average corrosion parameters for hot-dip Zn-coated and Magnelis®-coated steel electrodes, in contact with 3 wt% NaCl solution at pH = 4 and (pH = 9), obtained from linear micropolarization measurements

<i>t</i> /days	$R_p/\Omega \text{ cm}^2$		$j_{cor}/\mu\text{A cm}^{-2}$	
	RT	50 °C	RT	50 °C
Air-knifed hot-dip Zn-coated (20 μm) steel sheet				
0	3386 (4027)	868 (2656)	7.7 (6.5)	30.0 (9.8)
21	1307 (1738)	565 (777)	19.9 (15.0)	46.2 (33.6)
63	949 (1061)	386 (549)	27.4 (24.6)	67.6 (47.5)
Regular hot-dip Zn-coated (80–90 μm) steel sheet				
0	2269 (2537)	873 (929)	11.5 (10.3)	29.8 (28.1)
21	1349 (1407)	505 (808)	19.4 (18.5)	51.7 (32.3)
63	1282 (1521)	606 (633)	20.3 (17.1)	43.1 (41.3)
Magnelis®-coated (25–30 μm) steel sheet				
0	4501 (5074)	3121 (3592)	5.8 (5.1)	8.3 (7.3)
21	1424 (1606)	890 (723)	18.3 (16.2)	29.8 (36.1)
63	1200 (1335)	486 (674)	21.7 (19.5)	53.6 (38.7)

For Tafel slopes (b_a and b_c) fixed at $120 \text{ mV decade}^{-1}$, this equation simplifies to $I_{\text{cor}} = 0.026 \times R_p^{-1}$.

Thus, when compared to Magnelis®-coated material (with $j_{\text{cor}} = 4.2 \mu\text{A cm}^{-2}$ and $R_p = 6309 \Omega \text{ cm}^2$), freshly immersed hot-dip Zn coatings were characterized (at pH = 7 and RT) by significantly increased corrosion current densities (on the order of 6.0 and $8.8 \mu\text{A cm}^{-2}$) and the reduced values of the R_p parameter—4363 and $2969 \Omega \text{ cm}^2$ for the air-knifed and the regular hot-dip Zn-coated electrodes, correspondingly. The calculated corrosion current density (as well as the R_p parameter) exhibited significant fluctuation over a total period of the corrosion exposure with a tendency to rise (j_{cor}) for both temperature values (RT and 50°C). Understandably, at 50°C , the recorded corrosion current densities were radically greater than those derived at room temperature for all three tested materials (see all details in Table 5). Analogous observations could be made for the corrosion examinations conducted at pH = 4 and 9 (Table 6). However, it should be stressed here that the j_{cor} parameter values obtained under neutral conditions were fundamentally lower than those derived under pH = 4 or 9 (also, refer to the impedance results presented in Tables 3 and 4).

Such recorded corrosion current densities could then be recalculated to linear corrosion rates (V_L), according to Eq. 6:

$$V_L = 8.76 \times 10^6 \frac{k_{\text{Zn}} \times I_{\text{cor}}}{S_A \times d_{\text{Zn}}} \quad / \mu\text{m year}^{-1} / \quad (6)$$

where:

- k_{Zn} is the electrochemical equivalent for Zn in $\text{g A}^{-1} \text{ h}^{-1}$ /
 I_{cor} is the measured corrosion current in A /
 S_A is the electrode's geometrical surface area in m^2 /
 d_{Zn} is the density of zinc in kg m^{-3} /

Fig. 9 Quasi-potentiostatic Tafel polarization curves (recorded at a rate of 0.5 mV s^{-1}) for hot-dip Zn-coated and Magnelis®-coated steel electrodes, exposed in 3 wt% NaCl solution, recorded at RT and pH = 7 on day 63 (the iR correction was made based on the solution resistance derived from the impedance measurements)

Table 7 Calculated anodic and cathodic Tafel coefficients and corrosion current densities for hot-dip Zn-coated and Magnelis®-coated steel electrodes, in contact with 3 wt% NaCl solution at pH = 7 on day 63 of corrosion exposure, obtained from Tafel polarization plots

$b_a/\text{mV dec}^{-1}$		$b_c/\text{mV dec}^{-1}$		$j_{\text{cor}}/\mu\text{A cm}^{-2}$	
RT	50°C	RT	50°C	RT	50°C
Air-knifed hot-dip Zn-coated (20 μm) steel sheet					
145	89	−154	−176	4.8	17.8
Regular hot-dip Zn-coated (80–90 μm) steel sheet					
154	121	−130	−150	6.4	14.9
Magnelis®-coated (25–30 μm) steel sheet					
55	81	−176	−109	6.9	11.6

Hence, the linear corrosion rates assessed at an initial stage of the corrosion process in sodium chloride solution (at pH = 7 and RT) came to about 62, 90, and $132 \mu\text{m year}^{-1}$ for Magnelis® (it should be noted that in order to simplify calculations, both k and d parameters in Eq. 6 for Magnelis® coating were substituted by those of Zn), air-knifed, and regular hot-dip Zn coatings, correspondingly. The above implies that for a fixed coating's thickness of $100 \mu\text{m}$, these layers would only last on the substrate for about 19 (Magnelis®), 13 (air-knifed hot-dip Zn), and 9 (regular hot-dip Zn) months under such aggressive experimental conditions (continuous contact of samples with 3% NaCl solution). However, it should also be stressed that due to significant surface accumulation of corrosion products, comparative (quantitative) evaluation of corrosion rates by the loss of electrode mass (on the order of 0.1 to 0.3 wt%) was not feasible.

Finally, Fig. 9 shows quasi-potentiostatic Tafel polarization plots recorded for hot-dip Zn-coated and Magnelis®-coated steel electrodes, in contact with 3 wt% NaCl solution (at RT and pH = 7) upon completion of the corrosion exposure. In addition, the

Tafel region-derived, temperature-dependent Tafel coefficients, as well as the corrosion current densities, are displayed in Table 7. Hence, the Tafel-recorded j_{cor} values are qualitatively in-line with those derived based on the linear polarization measurements in Table 5. On the other hand, values of anodic Tafel coefficient (Table 7) are generally lower than the cathodic ones, thus indicating that the corrosion process is controlled by the cathodic oxygen depolarization reaction [10, 17, 18].

Conclusions

Based on the laboratory experiments to comparatively investigate the corrosion performance of hot-dip Zn-coated steel sheets with that of Magnelis®-coated electrodes in 3 wt% NaCl electrolyte, the following conclusions were drawn:

1. Prolonged, 78-day corrosion exposure of Zn(Magnelis®)-coated specimens in sodium chloride solution caused considerable physical and morphological changes (including thinning of coatings, formation of local galvanic Zn/Fe cells, and significant depletion of their major constituent elements: Zn, Mg, and Al) to all examined metal-coated materials.
2. Generally, under the employed corrosion environment (including changing pH and temperature conditions), Magnelis®-coated steel outperformed both the examined hot-dip Zn-coated steel materials. The latter was elucidated through facilitated reaction and the coating's resistance parameters, as well as by significantly reduced values of the corrosion current densities for Magnelis®-coated steel electrodes.
3. Superior corrosion performance of Magnelis® material is primarily associated with the surface formation of complex (Mg/Al) hydroxy carbonate precipitates, which provide exclusive protection to the base material (along with partial inhibition of the cathodic oxygen depolarization reaction). In addition, precipitated magnesium corrosion products would locally raise a pH level, thus slowing down the dissolution of Zn.
4. Although the obtained results are more qualitative in nature (simple laboratory corrosion setups, no interaction of variable external weather conditions), a general conclusion is that none of these coatings (including Magnelis®) is suitable for such aggressive corrosion environment (continuous exposure in self-aerated 3% NaCl solution), thus for the conditions of C5-M corrosion category.

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