

Contents lists available at ScienceDirect

Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jalcom

Effect of cerium salts on the cut-edge of zinc-based sacrificial coatings: Influence of Al and Mg alloying elements on galvanic corrosion

Thi Thao Nguyen^{a,b}, Sajjad Akbarzadeh^a, Thu Thuy Thai^b, Yoann Paint^c, Anh Truc Trinh^b, Marie-Georges Olivier^{a,*}

^a Material Science Department, University of Mons, Place du Parc 20, 7000 Mons, Belgium

^b Institute for Tropical Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Viet Nam

^c Materia Nova, Parc Initialis, Mons, Belgium

ARTICLE INFO	ABSTRACT
Keywords: Galvanic corrosion SVET Cerium salts Cut-edge Zinc-based coating	The effect of cerium salts on the cut-edge of zinc-based sacrificial coated steel was investigated by theoretical approach (based on individual polarization curves on the top surface and by Scanning Vibrating Electrochemical Technique (SVET). In both approaches, cerium salts increase the galvanic corrosion of zinc-based sacrificial layer coupled with steel. Furthermore, the anion parts of cerium salts exhibited a synergistic accelerated effect of galvanic activity on the cross-section. The SVET results indicated that the addition of Al, Mg alloying elements promotes localized corrosion and influences the formation and distribution of corrosion products.

1. Introduction

Zinc coatings alloyed with Al and Mg for the sacrificial protection of steel have been developed during the last decades and significantly improved the performance of steel against corrosion compared to pure zinc coating [1-5]. The protection of zinc-based coating on steel not only resulted from the barrier and sacrificial protection but also zinc or alloving element corrosion products formed on the steel surface, significantly contributed to the corrosion protection and prolonged its lifetime [1-4]. Indeed, the presence of dissolved Al³⁺ and/or Mg²⁺ ions buffer the pH in the cathodic sites, favoring the formation of new protective corrosion products such as double hydroxide layer (LDH) of $Zn/Al (Zn_6Al_2(OH)_{16}(CO_3) \cdot H_2O)$ or Mg/Al (Mg_6Al_2(OH)_{16}(CO_3) \cdot H_2O) [1-4], or simonkolleite (Zn₅(OH)₈Cl₂.2 H₂O [2,5,6], which form a compact and adherent layer. In our previous study [7], the corrosion behaviors on the top surface of three types of zinc alloy-coated steel substrate: HDG (Zn + 1.2 wt% Al), ZA (Zn + 9.4 wt% Al), and ZAM (Zn+ 7.1 wt%Al + 4.0 wt% Mg) were investigated in chloride medium by electrochemical measurements. The results proved the better corrosion resistance of ZA and ZAM coatings (with higher Al, and Mg contents) than the HDG layer. In addition, the higher corrosion resistance of ZA and ZAM was assigned to the ZnAl (LDH) formation on the surface of substrates, which offered a more protective film than ZnO or simonkolleite formed on HDG's surface. Furthermore, Lee et al.[5] evaluated

the corrosion behavior on the cut-edge of ZnAlMg (ZAM) alloy-coated steel in chloride medium by cyclic corrosion test (CCT) during 6, 15, 30, and 60 cycles in comparison with pure zinc (GI) steel. The result indicated that the cut-edge of GI steel presented red rust on the exposed cross-section after 30 cycles, no trace of red rust was observed on the cut-edge of ZAM steel till 60 cycles, proving higher cut-edge corrosion resistance of ZAM alloy-coated steel than that of GI steel. Additionally, the authors proposed that higher corrosion resistance may be related to the higher fraction of simonkolleite obtained on ZAM alloy-coated steel compared to GI steel.

Despite the significant reinforcement achieved from the zinc sacrificial coating, the cut-edge or the appearance of scratches where the steel is in direct contact with the aggressive environment are the major issues due to the unfavorable anode-to-cathode surface area ratio. In this case, the cut-edge of zinc-based layer-coated steel is exposed in a corrosive medium, forming a galvanic coupling between steel and zinc-based coating, causing the anodic zinc dissolution and providing sacrificial protection for steel. However, it could not offer sacrificial protection for steel for a prolonged time [8,9] because the zinc layer thickness is much smaller than steel. Therefore, it required supplementary active protection for galvanic coupled metallic materials.

In our previous work [10], the effect of Ce (III) on the top surface and the cross-section of ZnFe-coated steel was investigated by the electrochemical impedance spectroscopy (EIS) and Scanning Vibrating

* Corresponding author. *E-mail address:* marjorie.olivier@umons.ac.be (M.-G. Olivier).

https://doi.org/10.1016/j.jallcom.2024.173711

Received 7 December 2023; Received in revised form 25 January 2024; Accepted 28 January 2024 0925-8388/© 2024 Elsevier B.V. All rights reserved.

Electrode Techniques (SVET) measurements, respectively. The EIS results showed that Ce (III) acts as a corrosion promoter on the top surface of ZnFe-coated steel. Meanwhile, it provided an inhibitive effect on the cut-edge revealed by SVET measurement. Therefore, in an aggressive environment, the role of Ce (III) (as a corrosion inhibitor or a corrosion promoter) depends on the tested position of the sample: on the top surface or the cut edge. Our recent study [11] revealed that cerium (III) presented a promising corrosion inhibitor on the top surface of the zinc-based coatings (Zn, HDG, ZnAl, and ZAM layers). Besides, the inhibition efficiency of Ce (III) depends on the type of substrate and counter-anion. CeCl₃ provided high and durable protection for all four coatings, while Ce(NO₃)₃ acted differently for all samples. Interestingly, Ce(NO₃)₃ presented the simultaneous and antagonistic properties (inhibition of the cathodic reaction and acceleration of the intermetallic particle dissolution) for ZAM layers. In coil coating industry, the sheets are covered by organic coating after the application of the sacrificial layer and the sacrifical layer gives a long-term resistance to the substrate. Nevertheless, the edge of the coils is a critical zone in terms of corrosion resistance as sometimes not completely covered by zinc and organic coating exposing the galvanic coupling to aggressive exposure. This is a major concern for the automotive industry to investigate the cut-edge corrosion because this corrosion can appear quickly and with a high local intensity. Furthermore, some authors [12,13] have investigated the influence of cerium salt on the cut-edge of Zn/(Fe or steel) or modeling between Zn and Fe/steel by SVET measurement. However, from our knowledge, there is no research studying the galvanic corrosion behavior of zinc alloyed with Al and/or Mg-coated steel in the presence of cerium salts. Therefore, to understand in-depth the effect of Ce (III) and its counter anion on the galvanic coupling between steel and various zinc-based coatings, the galvanic corrosion behavior of the cut-edge of zinc-based coated steel in a chloride medium without and with different cerium salts was evaluated by a theoretical approach (based on polarization curves) and a local electrochemical technique (SVET). Besides, the distribution of product precipitation on the tested surface was conducted by EDS mapping and discussed based on a thermodynamic approach.

2. Experimental method

2.1. Materials

In this study, HDG, ZnAl, and ZAM were supplied by ArcelorMittal, Belgium. The element composition of ST37–2 steel consists of Fe (balance), C (0.17 wt%), Si (0.03 wt%), Mn (1.4 wt%), P (0.02 wt%), and S (0.02 wt%), as mentioned in the previous study [10].

Before electrochemical measurement, HDG, ZnAl, and ZAM substrates were degreased with acetone, and then all three substrates were dipped in an alkaline commercial solution (Gardoclean®) at 50 °C for 30 s to carry off the traces of oxide. Meanwhile, the steel surface was electrochemically degreased in an alkaline commercial solution (ATF systoclean) at 60 °C with a current density of 30 mA/cm² for 3 min. The substrate was then rinsed with deionized water. After that, the steel surface was treated in the pickling solution (10 v.% hydrochloric acid + 10 v.% sulfuric acid in water) for 30 s, rinsed, and dried [10]. The thickness of the zinc-based coatings, their chemical composition, and the thickness of steel were determined by a Hitachi SU8020 FE-SEM and Palmer digital CD-15APX, respectively. The roughness of top layers was measured by optical profilometry with a NanoJura instrument. 10 mm length scans were performed at a scan rate of 100 μ m/min.The thickness and the roughness of the top layer, the thickness of the steel, and the coating composition of the top layers are presented in Table 1. The zinc based layers are compact and non porous.

2.2. Electrochemical measurements

A conventional three-electrode set-up was used for the

Table 1

The thickness, roughness of different sacrificial coatings and steels, and the composition on top of different sacrificial coatings.

Substrates	Thickness (µm)		Ra (µm)	Zn/Fe area ratio	Coatin compo %)	Coating composition (wt %)		
	Zn based- coating	Steel			Zn	Al	Mg	
HDG	11 ± 0.2	1740	$\begin{array}{c} \textbf{0.87} \pm \\ \textbf{0.02} \end{array}$	1/80	92.1	1.2	0	
ZnAl	21 ± 0.3	660	$\begin{array}{c} 1.23 \pm \\ 0.05 \end{array}$	1/16	89.2	9.4	0	
ZAM	29.6 ± 0.5	720	$\begin{array}{c} 0.012 \pm \\ 0.002 \end{array}$	1/12	83.7	7.1	4.0	

electrochemical tests, with a saturated calomel electrode SCE as the reference electrode, a platinum grid as the counter electrode, and the steel or zinc-based coatings as the working electrode (surface test: 1 cm²). In a system of zinc-based coating on steel, steel would be considered the cathode, while zinc-based layers behave as the anode providing sacrificial protection. In this case, the cathodic polarization curves were performed for steel (from 0.01 V/ OCP to - 2.0 V/OCP) and only the anodic ones were performed for Zn-based sacrificial coatings (from - 0.01 V/OCP to 2.0 V/OCP, the curve stopped at 10^{-3} A/cm²). In order to check the reproducibility, each test was carried out at least twice to obtain consistent results. A coupling model was established from the cathodic polarization curves of steel and the anodic polarization curves of zinc-based coatings [10]. The intersection points of the anodic and cathodic curves provided the value of the galvanic potential (Eg) and galvanic current density (jg). This approach provides the initial prediction of galvanic corrosion coupling in particular conditions considering the shape of the polarization curves. In these cases, the anode/cathode area ratio equals 1. The electrolyte employed in this part is 0.1 M NaCl (NaCl, VWR Chemicals) in the absence and presence of 5.10^{-3} M cerium salts: cerium chloride (CeCl₃·7 H₂O, VWR Chemicals) and cerium nitrate (Ce(NO₃)₃.6 H_2O Aldrich, > 99%). Concerning the electrolyte containing cerium chloride, the sodium chloride amount was adjusted to limit the chloride ion concentration to 0.1 M. Moreover, the NaCl solution was adjusted at pH = 7 by adding 0.01 M NaOH. While in the case of cerium-containing electrolytes, the pH values measured were 5.66 and 5.44 for CeCl₃ and Ce(NO₃)₃, respectively. The composition of these electrolytes was tabulated in Table 2.

2.3. Scanning Vibrating Electrode Technique (SVET)

The sample preparation (HDG, ZnAl, and ZAM) and the condition of SVET measurements were proposed in a previous work [10]. The cross-section of HDG, ZnAl, and ZAM coated steel was embedded in epoxy resin (Mecaprex) (Fig. 1) and then polished by SiC abrasive paper with grades from 100 to 2400, rinsed with distilled water, and quickly dried by compressed air. Then, they were activated in the Nital solution (3 v.% of nitric acid in absolute ethanol) for 15 s, rinsed with distilled water and ethanol, followed by drying by compressed air. The cut-edge was covered by protective tape (3 M^{TM} ScotchrapTM 50) to homogenize the conditions (the same position and area with 1 mm long) and to limit the tested area to about 1.0 mm² (ZnAl and ZAM) and 1.5 mm² (HDG because the thickness of steel part is wider than that of ZnAl and ZAM).

Table 2

Composition of the different solutions used for the potentiodynamic polarization curves.

	[Cl ⁻] (M)	[NO ₃] (M)	[Ce ³⁺] (M)
NaCl	0.1	x	x
NaCl +CeCl ₃	0.1	x	5.10 ⁻³
NaCl +Ce(NO ₃) ₃	0.1	15.10 ⁻³	5.10 ⁻³



Fig. 1. Cut-edge electrode embedded in epoxy (a) and schematic (b) of the cross-section of the sample used for SVET (the black rectangle and arrow indicated the tested area and the location of zinc-based coatings, respectively).

The composition and resistivity of electrolytes are given in Table 3. For the SVET measurements, the concentration of NaCl solution was 0.015 M, which is lower than the one in the potentiodynamic polarization curve measurements in order to obtain an intense signal. This signal intensity is improved in a solution with a high resistivity (Table 3). In the case of cerium chloride, the sodium chloride amount was adjusted to obtain 0.015 M chloride ions. SVET measurements were conducted by Applicable Electronics (AE), Inc. equipment associated with Science Wares, Inc. ASET software. The tip of the probe was covered by black platinum following the AE system manual to improve its capacitance. The cut-edge tested surface was scanned with a grid of 31×31 measurement points during which the vibration electrode distance from the sample surface was 150 µm. The vibration amplitude was 40 µm associated with a frequency of 80 Hz. Each test was performed at least twice to confirm the reproducibility.

2.4. The cut-edge of zinc-based coated steel characterization

The cross-section of all samples before and after 24 h of exposure was characterized by a Field Emission Scanning Electronic Microscope (FE-SEM, Hitachi SU8020) coupled to an Energy Dispersive X-ray spectrometer analyzer (EDS). The product precipitation on the surface crosssection after 24 h of immersion was characterized by EDS mapping. To better interpret the sequential formation of precipitation products based on the equilibrium chemistry and thermodynamic in the different electrolytes, the Hydra-Medusa software was used.

3. Results and discussion

3.1. Characterization of the cross-section of the sacrificial coating before exposure

The morphology, thickness, and composition on top and crosssection of all three coatings studied have been presented in our previous work [11]. The representative surface morphology and microstructure of the cross-section of all samples significantly differ as shown in Fig. 2. The main compositions of each zone are given in Table 4. As can be observed, the HDG layer presented a homogenous layer of Zn and

Table 3

Composition and resistivity of the different solutions used for the SVET measurements.

	[Cl ⁻] (M)	[NO ₃] (M)	[Ce ³⁺] (M)	Resistivity (Ω cm)
NaCl NaCl + CeCl ₃ NaCl + CeCl ₃	0.015	x x 15 10 ⁻³	x 5.10 ⁻³	604 591

a small amount of Al (0.4-0.5 wt%) with defects on the cross-section surface. The investigated ZnAl and ZAM coatings consist of complex microstructures. Concerning the ZnAl layer, the microstructure is generally characterized by two phases: a proeutectic zinc-rich eta (η) phase (location 1) containing 1.1 wt% Al which was surrounded by a eutectic-type phase (locations 2 and 3) consisting of beta (β) aluminum and eta (η) zinc lamellae [14]. The eutectic phase contains a higher Al amount (at about 6 -7.5 wt%) than the zinc-rich phase. The microstructure of the ZAM layer exhibited a zinc-rich phase (η) (area 1) containing a small content of Al (0.8 wt%) surrounded by an Al-rich phase (4-5 wt%) and an intermetallic MgZn₂ determined by XRD [11]. The binary eutectic (MgZn₂-Zn) and the ternary eutectic (MgZn₂-Zn-Al) phases were not well distinguished from the SEM images. The previous work indicated that Al accumulated in the steel/HDG layer interface, assigned to an Al-rich inhibition layer (Fe₂Al₅) [11]. In this study, it should be noticed that Al is enriched in the interface between zinc-based coating and steel (especially in the ZnAl/steel interface), implying the existence of an Al-rich inhibition layer, which prevents the formation of the brittle Fe-Zn intermetallic layer and leads to better adhesion property of the zinc-based layers [14].

3.2. Effect of cerium salts on galvanic corrosion by a theoretical approach based on polarization curves

3.2.1. Cathodic polarization curves of steel

Fig. 3 represents the cathodic polarization curves of steel after 24 h of immersion in 0.1 M NaCl without and with cerium salts. As can be seen, in the presence of cerium salts, the corrosion potentials shifted toward nobler values compared to the 0.1 M NaCl blank solution with an increase in cathodic current density in all the investigated cathodic range, especially in the case of cerium nitrate.

Regarding the 0.1 M NaCl blank solution, a plateau (region 1) was obtained from -1.01 V to -0.85 V, corresponding to the reduction of dissolved oxygen [10,12,15]. Then, the reduction of water with hydrogen generation took place at a more negative potential [12,15]. Meanwhile, the presence of cerium salts influenced the cathodic behavior of steel by forming a plateau (region 1) and a new wave (in region 2). The first one related to the dissolved oxygen reduction occurred from -0.86 V to -0.71 V in the presence of cerium chloride, while it took place at more positive from -0.83 V to -0.64 V with an increase of cathodic current density by adding cerium nitrate, indicating a rise in the rate of oxygen reduction [16]. The new reduction wave (region 2) was visible around -1.2 V to -0.8 V with a Tafel slope of 0.129 V/dec for cerium chloride, and - 0.134 V/dec for cerium nitrate. It highlighted that this region is only related to the behavior of cerium salts, responding to the reduction of water ligands from the cerium-aqua complex Ce(H₂O) $_{x}^{3+}$ [15,16]. Indeed, Tran et al.[15] supposed that the enhancement of water activation in the presence of rare earth cations could be associated with the formation of aqua-complex, the reduced water molecules issued from the coordination shell of the complex. The water-ligand reaction was described by the following reaction:

$$Ce(H_2O)_x^{3+} + ne \rightarrow Ce(H_2O)_{x-n}^{3+} + n/2 H_2 + nOH^-$$
 (1)

Later, this suggestion was in agreement by Gustavsson et al. [17] and Oliveira et al. [12].

3.2.2. Zinc-based coatings/steel galvanic corrosion

The cathodic polarization curves of steel and the anodic polarization of three sacrificial coatings recorded after 24 h immersed in 0.1 M NaCl without and with cerium salts were demonstrated in Fig. 4. A galvanic coupling model was established at the intersection between the steel's cathode and the sacrificial coating's anode polarization curves, where the coupling potential (E_g) and galvanic corrosion current density (j_g) were identified as highlighted in red in Fig. 4 (a). These values were



Fig. 2. Cross-section SEM images of HDG (a), ZnAl (b), and ZnAlMg (c) coatings.

Table 4

The principal composition of different sacrificial coatings obtained by EDS analysis on the different locations shown on Fig. 2.

Coatings	Coating co			
	Zn	Al	Mg	Fe
HDG – 1	81.8	0.4	-	1.2
HDG - 2	81.1	0.5	-	2.3
ZnAl - 1	83.9	1.1	-	1.5
ZnAl - 2	79.8	6.0	-	0.9
ZnAl – 3	78.7	7.5	-	1.3
ZnAl – 4	65.5	12.2	-	2.8
ZAM - 1	82.5	0.8	-	0.9
ZAM - 2	74.6	4.4	3.0	0.5
ZAM – 3	73.5	5.2	3.1	1.5
ZAM-4	65.5	6.4	0.5	4.8

collected and presented in Table 5.

Regarding the reference electrolyte, the HDG/Fe coupling presented the highest galvanic current density at about $j_g=27 \ \mu A/cm^2$, associated with the most negative coupling potential $E_g=-1.02 \ V/SCE$ after 24 h of exposure. These values slightly decrease measuring around 22 $\mu A/cm^2$ for ZnAl/Fe, and ZAM/Fe couplings. Notably, the movement towards a more positive potential was observed in the case of ZnAl and ZAM ($E_g=-0.98 \ V/SCE$), indicating a slight decrease in galvanic corrosion with steel. Thus, the addition of Al and/or Mg alloying elements in a zinc-based layer could slow down the corrosion rate and prolong the lifetime of sacrificial coatings in 0.1 M NaCl.

Regarding the electrolyte-containing cerium salts, the presence of cerium salts significantly influenced the cathodic polarization curves of the steel by shifting the corrosion potential to a more positive value and creating a second plateau. This second plateau was a result of the reduction of cerium-aqua complex $Ce(H_2O)_x^{3+}$ and led to an increase in cathodic current density, as discussed in Section 3.2.1. Moreover, in the presence of cerium salts, the corrosion potential of zinc-based coatings also exhibited a slight shift towards more positive values, with a more pronounced effect observed when cerium nitrate was present [11], attributed to the anodic inhibition effect of nitrate [18,19]. This resulted in an increase in galvanic current density and a slight shift towards a more positive galvanic potential for both cerium salt, especially in the presence of cerium nitrate, revealing that the presence of cerium salts accelerated the galvanic corrosion. In the presence of cerium chloride, the galvanic potential shifted toward more positive values, at about 0.03-0.09 V/SCE. Moreover, the galvanic current density tended to raise from HDG/Fe to ZnAl/Fe and then ZAM/Fe systems at around 56, 64, and 78 μ A/cm², respectively, corresponding to an increase in galvanic corrosion. Considering the corrosion current ratio, the ZAM/Fe coupling presented the highest galvanic corrosion speed, approximately 3.6 times higher than in 0.1 M NaCl solution. It was followed by ZnAl/Fe and HDG/Fe at 2.9 and 2 times higher, respectively. These results indicate varying corrosion levels among different models. Concerning the electrolyte with cerium nitrate, the galvanic potential significantly shifted toward more positive values at around 0.1- 0.13 V/SCE, relating to the anodic inhibitive effect of nitrate [18,19]. Furthermore, the galvanic corrosion current densities were noticeably higher than in 0.1 M NaCl electrolyte without cerium species and the solution containing cerium chloride. The extra augmentation of galvanic potentials and galvanic current densities compared to the cerium chloride can be associated with the presence of NO₃, which provoked an increase in the conductivity of the solution [12]. Contrary to cerium chloride, zinc-based /steel behaved in different ways in the presence of cerium nitrate. The ZAM/Fe system still presented the highest current value (jg



Fig. 3. Cathodic polarization curves of steel after 24 h of immersion in 0.1 M NaCl without and with 5.10^{-3} M inhibitors.



Fig. 4. Polarization curves of steel (cathodic) and zinc based coatings (anodic) after 24 h of immersion in 0.1 M NaCl without and with 5.10⁻³ M inhibitors.

able 5
otential (Eg) and current density (jg) coupling obtained between steel and zinc sacrificial coatings based on polarization curves

Couples 0.1 M [Cl ⁻]		0.1 M [Cl ⁻]	$0.1 \text{ M [Cl^{-}]} + 5.10^{-3} \text{ M [Ce}^{3+}]$			$0.1 \text{ M [Cl]} + 5.10^{-3} \text{ M Ce (NO_3)}_3$		
	E _g (V)	j _g (μA.cm ²)	E _g (V)	j _g (μA.cm ²)	Corrosion ratio (τ)	Eg (V)	j _g (μA.cm²)	Corrosion ratio (τ)
HDG/steel	-1.02	27.3	-0.93	56.8	2.08	-0.8	165.5	6.06
ZnAl/steel	-0.98	22.1	-0.94	64.1	2.90	-0.79	151.4	6.85
ZAM/steel	-0.98	21.7	-0.95	78.2	3.6	-0.8	169.9	7.83

 $\tau = jginh \ / \ jgo$

In which: j_{g}^{nh} and j_{g}° are the galvanic corrosion current density of with and without inhibitors (the presence of cerium salts)

 $\approx 170~\mu A/cm^2$), followed by the HDG/Fe (jg $\approx 165~\mu A/cm^2$) and the ZnAl/Fe (jg $\approx 151~\mu A/cm^2$). However, observing the corrosion current ratio defined as the ratio between the galvanic corrosion current in presence of cerium salts and the one in the blank solution, the highest corrosion rate was observed on ZAM/steel, came after by ZnAl/steel, and HDG/steel at 7.8, 6.8, 6.0 times, respectively, indicating the presence of Al and Mg promoted the galvanic corrosion in presence of cerium nitrate.

These results demonstrated that although cerium salts played a role as inhibitors on top of zinc-based coatings [10,11,20–22], they accelerated the corrosion in the case of zinc-based coating/steel coupling, leading to an increase in corrosion rate. Furthermore, NO₃ could be an accelerator of galvanic corrosion by leading to a rise in galvanic corrosion current density compared to cerium chloride. Similar results were reported by Oliveira et al.[12]. Two different metals Zn and Fe were in electrical contact. Then, this system was investigated in chloride solution without and with cerium nitrate by SVET measurement. With cerium nitrate, an increase in the anodic and cathodic current densities was observed, indicating the augmentation of the galvanic corrosion rate.

3.3. Effect of cerium salts on galvanic corrosion by SVET measurements

The theoretical approach, based on individual polarization curves, provided the initial prediction of galvanic corrosion in zinc-based coating/steel couples. However, in practice, experimental results depend on various factors, including geometrical considerations such as the surface area ratio of anode/cathode, the solution film depth, and the distance between two electrodes [23-25]. Indeed, Song et al.[25] observed an increase in anodic current density with a reduced area ratio, suggesting the need to avoid large cathodic surface area in practice to prevent significant galvanic corrosion. Conversely, a larger distance between two electrodes results in smaller galvanic current density. These findings align with the report of Jia et al.[23]. In addition, the authors also demonstrated that the galvanic current density rises with an increase in the solution film depth. In order to study further galvanic corrosion behavior on the cross-section of zinc-based coated steel, SVET experiments were characterized on the cut-edge of HDG, ZnAl, and ZAM coated steel in 0.015 M [Cl⁻] solution without and with 5.10⁻³ M cerium salts. To minimize the impact of these factors on galvanic corrosion in practical applications, they were homogenized and detailed in Section 2.3. In this configuration, the anodic area (Sanode) was much smaller compared to the cathodic area (Scathode), and the ratio Sanode/ Scathode increased from HDG/steel to ZAM/steel at about 1/80 (HDG/steel), 1/16 (ZnAl/steel) and 1/12 (ZAM/steel).

3.3.1. Galvanic corrosion behavior of the cut-edge of zinc-based coated steel in 0.015 M NaCl

Fig. 5 indicates the distribution of current density on the crosssection of HDG/steel, ZnAl/steel, and ZAM/steel versus immersion time in 0.015 M NaCl reference electrolyte. The yellow rectangle and arrows indicated the sample (cross-section surface) and the location of



Fig. 5. Current density distribution on the surface of different zinc based coatings coated steel cross-section until 6 h and the optical images of all samples after 24 h of immersion in 0.015 M NaCl.

the zinc-based layer. As can be seen, all samples presented both the anodic areas (j > 0) located in the zinc-based layer and the cathodic areas (j < 0) on steel over immersion time, indicating the sacrificial protection of zinc-based coating, as expected. Both anodic activity (Zn dissolution) and cathodic activity (O₂ reduction on steel) were written as equations below:

$$Zn \to Zn^{2+} + 2e \tag{2}$$

$$O_2 + 2 H_2 O + 4e \rightarrow 4OH^-$$
(3)

At the starting exposure time, the HDG/Fe exhibited the largest anodic corrosion area with the highest intense current density, followed by ZnAl/Fe and ZAM/Fe systems. Although the intensity of anodic density slightly decreased, the anodic activity tended to widen along both sides of HDG layers over the exposure period, increasing the number of active anodes after 6 h of immersion. Besides, the cathodic activity spread out uniformly on the steel surface. For the ZnAl/steel, the anodic activity is focalized on the right-bottom of the ZnAl layer and the corrosion intensity slightly decreases over immersion time; however, there is a relatively broadening trend. Moreover, the cathodic reaction took place at the upper half and broadened to the center of the sample with time. The ZAM/steel presented minor corrosion activity at the beginning of the experiment period. Then, the anodic corrosion developed localized and intensified on a single point upon immersion. After 6 h of immersion, the corrosion activity presented the highest intensity (229 mA/cm^2) on ZAM, followed by ZnAl $(113 \mu\text{A/cm}^2)$ and HDG (101 μ A/cm²) surfaces. The highest intensity of current density and the corrosion behavior on ZAM layers may be associated with the microstructure of the ZAM layer, causing the selective dissolution of zinc-rich phase Zn_2Mg , supporting the pitting corrosion attack [6,9,26,27]. Observing the cross-section surface of all substrates after 24 h immersion, the precipitation distribution was different in each substrate. The grey products formed next along the sides of the HDG and ZnAl coatings and in the right corner of the ZAM/steel sample, which could be assigned to the zinc-based layers [10], corresponding to the anodic area

by SVET measurement. The rest of the substrates (in the center of the steel part), especially in the ZAM/steel system, showed unaffected area in the aggressive environment, meaning that the zinc-based layer still provided sacrificial protection.

3.3.2. Galvanic corrosion behavior of the cut-edge of zinc-based coated steel in the presence of cerium salts

The current density mapping on the cut edge of all samples in the presence of cerium chloride and cerium nitrate is shown in Fig. 6 and Fig. 7, respectively. As can be observed, cerium salts exhibited no change in current distribution on the cut-edge zinc-based coatings compared to the blank electrolyte. The anodic and cathodic activities occurred at zinc-based layers and steel, respectively, as expected. At the beginning of the test, the galvanic corrosion process strongly occurred, especially in the presence of cerium nitrate, leading to a significant increase in anodic current density, which was two and three orders of magnitude higher than that in the blank solution. This increase means that the presence of cerium salts accelerates the Zn dissolution (in the case of galvanic coupling) and induces the generation of OH⁻ in cathodic sites, leading to the formation of insoluble cerium hydr(oxide) as following Eq. 3. This observation is correlated to the results obtained from the theoretical approach in section 3.1.2.

$$Ce^{3+} + 3 OH^{-} \rightarrow Ce(OH)_{3} \downarrow$$
 (3)

Regarding the electrolyte containing cerium chloride, a different current density distribution was observed in samples. No change of anodic positions was observed on HDG and ZnAl layers over immersion time, while it was changed in the case of ZAM coatings. In addition, the HDG/steel system presented the largest anodic areas (with the highest number of active anodes) uniformly distributed along both sides of the HDG layers with great intensity. Meanwhile, in the presence of Al and/ or Mg alloyed elements, the zinc-based coatings (ZnAl and ZAM /steel samples) presented less active anodes, which took place at localized points on the active zinc cut-edge, relating to the pitting corrosion [9]. Moreover, the cathodic region was uniformly distributed on the whole



Fig. 6. Current density distribution on the surface of different zinc based coatings coated steel cross-section until 6 h and the optical images of all samples after 24 h of immersion in 0.015 M NaCl with 5.10^{-3} M cerium chloride.



Fig. 7. Current density distribution on the surface of different zinc based coatings coated steel cross-section until 6 h and the optical images of all samples after 24 h of immersion in 0.015 M NaCl with 5.10⁻³ M cerium nitrate.

steel surface of the HDG/steel sample and partially dispersed on the steel surface of ZnAl/steel and ZAM/steel substrates. Besides, the cathodic current density was much higher than the reference solution, indicating the emergence of an extra reduction reaction. The optical images (Fig. 6)

of the cross-section of all substrates after 24 h of immersion revealed that the appearance of all samples was changed entirely compared to the blank solution. The precipitation distribution was different on the cut-edge of each substrate, which may be related to the thickness of steel

samples and the corrosion mechanism of each zinc based coating due to the presence of alloying elements. It is worthwhile to note that the thicker the steel layer, the wider the corrosion product distribution [9]. The area next to both sides of the zinc-based layer demonstrated no corrosion product. In contrast, the steel surface exhibited a brownish/greyish film. This film covered almost all the steel surface of the HDG/steel substrate (the most expansive layer). Interestingly, it partially covered the steel surface in the case of ZnAl and ZAM/steel models (narrower sample). This film corresponded to the cathodic region measured by SVET. This cathodic activity could be related to the formation of an insoluble cerium hydr(oxide) film that slows down the dissolved oxygen reduction [10,28]. In the presence of cerium nitrate (Fig. 7), the evolution of anodic activity is much higher than in the presence of cerium chloride. Corrosion activity significantly appeared on both sides of the Zn-based layers in all samples. However, the corrosion behavior acts differently on various systems. Regarding the HDG/steel, in the first 3 h of the test, the corrosion activities were increased, then decreased after 6 h of exposure. In the case of ZnAl/steel and ZAM/steel samples, it reduced with time. In addition, the HDG/steel system presented the highest anodic current density with the largest anodic areas compared to ZnAl/steel and ZAM/steel systems, meaning the highest corrosion rate. Moreover, similar to the electrolyte containing cerium chloride, a brownish product film was observed on the steel surface of all samples, correlated to the cathodic activities indicated by SVET measurements, leading to a decrease in cathodic activity with low current density.

The results revealed that the presence of cerium salt strongly increased the galvanic corrosion activity, leading to a rise in the corrosion rate, where a decrease was expected due to the inhibitive effect of cerium salts on the top surface of zinc-based coatings. Furthermore, higher Al and/or Mg alloying element amounts in the zinc sacrificial coating tend to decrease the corrosion activity with less intensity of current density and anodic areas. However, the presence of alloyed elements Al and Mg promotes local/pitting corrosion.

3.4. Surface characterization of the cut-edge of zinc-based coated steel in 0.015 M NaCl without and with the presence of cerium salts

Fig. 8 exhibited the EDS mapping conducted along the cut-edge of HDG, ZnAl, and ZAM after 24 h of exposure in 0.015 M NaCl (same exposure conditions than for SVET experiments). The visual inspection shows considerable differences among the three zinc-based coatings. The cut-edge surface of ZAM/steel presented fewer precipitation products compared to ZnAl/steel and HDG/steel in the reference solution. Regarding the cross-section of HDG-coated steel, there are three distinct

regions: on the top of the Zn laver part, on the Zn laver part next to the steel substrate, and on the steel part. The Zn layer part is rich in Zn, Cl, and O, suggesting the formation of simonkolleite, which is commonly obtained on zinc in a chloride solution [5,10,29]. On the second zone next to the steel substrate, iron is detected with high intensity and along with the presence of Al, which may have originated from the intermetallic Al-rich inhibition layer (Fe₂Al₅) at the steel/coating interface [27], hence forming oxide of iron. In the steel part, there is a uniform distribution of zinc and oxygen, along with a few traces of chlorine. This suggests the presence of a thin layer of zinc hydr(oxide) product, which masks the steel and reduces the intensity of iron. These precipitation products were mentioned in the previous work [10]. In addition, a homogenous distribution of Al was observed on the cut-edge surface. SEM images (Fig. 9 (a)) of zinc-based coating revealed that the original metallic surface of HDG was converted to a homogenous porous layer of precipitation products, with high contents of Zn (9.8 wt%), O (13.9 wt %), Cl (1.2- 6.4 wt%), and Fe contents, and no metallic Zn is dectected by EDS analysis (Fig. 8 (a) and complementary results not shown in the manuscript), indicating a uniform sacrificial protection provided by Zn laver.

Concerning ZnAl coated steel (Fig. 8 (b)), the zinc layer enriched in O with a remarkable intensity of Zn, Al and with a small amount of chlorine was observed, indicating that the precipitation products contain mainly simonkolleite, ZnO [10,29] and probably the presence of Al-rich protecting product which was reported in the literature [30]. Similar to the HDG-coated steel, Fe was rich in the ZnAl layer, which could be due to the dissolution of Fe from the intermetallic Fe₂Al₅ inhibition layer (originated on the steel/ZnAl coating interface) [27] and formed on the ZnAl layer. Interestingly, O was detected on the steel part, but it is not associated with Zn and Cl. However, a small zone containing Zn and O was observed on the steel part, which may relate to the formation of zinc hydr(oxide). The SEM images (Fig. 9 (b)) of the cut-edge surface of the ZnAl layer presented different corrosion behavior. The fact that some regions of the ZnAl layer were preferentially dissolved led to the formation of the porous precipitation products covering the surface. While some zones demonstrated less sign of corrosion and the original metallic morphology, indicating the local selective dissolution [30]. Besides, the original morphology sites presented some minor pits and the even distribution of the grains of precipitation product containing mainly Zn (37.8 - 44.8 wt%) and O (36.5 wt% - 40.1 wt%) by EDS analysis.

In the case of ZAM-coated steel, O, Zn, Al, and Mg were typically distributed on the ZAM layer (Fig. 8 (c)). Besides, the intensity of Zn was higher compared to the ZnAl and HDG layers, proposing the presence of metallic Zn. Notably, the ZAM layer exhibited no trace of Fe, which was



Fig. 8. EDX mapping of one half of HDG (a), ZnAl (b), and ZAM (c) coated-steel cross-section after 24 h of immersion in 0.015 M NaCl.



Fig. 9. Cross-section SEM images of HDG (a), ZnAl (b), and ZAM (c) coatings after 24 h of immersion in 0.015 M NaCl.

detected on HDG and ZnAl coatings. Furthermore, the steel part presented no traces of Zn and O, Mg, and Al content but a high intensity of Fe, indicating no precipitation products on the surface. Indeed, the SEM images (Fig. 9 (c)) illustrated no evidence of the accumulation of corrosion products on the ZAM layer. This observation was also reported by Salgueiro Azevedo et al.[31]. The authors proposed that the corrosion product precipitation requires an increase in pH related to the cathodic reactions. Besides, the SEM images showed a preferential attack of MgZn₂ intermetallic (surrounded η - Zn rich phase), leading to more localized corrosion and the formation of localized active anodes, as expected [1,27,31]. This selective attack is more prominent than that observed on the ZnAl layer. Indeed, the main attack sites could be started from MgZn₂ phases (Mg-rich and Al-rich phases) by forming the pits around 1.5 to 2.5 µm wide. These pits then localized and developed, causing a high local dissolution of MgZn₂, resulting in a larger (about 24 µm wide) and deeper pit, resembling the process of pitting corrosion [6,9,26,27]. While, the η-Zn rich phase remained unaffected in the aggressive solution, confirming the selective ZAM phase dissolution and

the presence of micro-galvanic corrosion, where the anodic activity occurred on the $MgZn_2$ phase and η -Zn rich phase would be the cathode sites, leading to a high dissolution. This result is correlated to the SVET result.

Regarding the presence of cerium salts, especially in the presence of cerium nitrate, the cross-section zinc-based coated steel was covered by a thicker precipitation products layer than that obtained in the blank solution. In the cerium chloride medium, the EDS mapping (Fig. 10) of the cross-section of all the samples relatively presented similarly. A high O content was observed on the zinc layer where Zn and Cl are enriched, supposing the formation of simonkolleite on the anodic areas. However, the ZAM layer exhibited the lowest Cl intensity compared to ZnAl and HDG coatings, corresponding to the poorest simonkolleite amount. Al is still rich in ZnAl and ZAM layers, but the presence of Mg was tiny on ZAM coating, probably related to the low Mg content on ZAM and to being hidden by the other products. Additionally, cerium was also observed on zinc-based layers with the highest intensity on ZnAl coatings, which was also confirmed by EDS measurement. The distribution



Fig. 10. EDX mapping of one half of HDG (a), ZnAl (b), and ZAM (c) coated steel cross-section after 24 h of immersion in 0.015 M NaCl containing 5.10⁻³ M CeCl₃.

of these elements indicated the presence of micro-galvanic corrosion in all zinc-based coatings, resulting in the precipitation of cerium products on the micro-cathodic sites. On the steel regions (cathodic sites), considerable O contents were associated with Ce amount and low Zn and Cl contents, relating to the formation of cerium hydr(oxide) precipitation and simonkolleite. However, low Zn intensity may be related to less Zn-based product precipitation or be masked by cerium hydr(oxide) products.

Approaching closer to the cross-section of the zinc-based layer, the SEM images (Fig. 11 (a)) revealed that HDG layer was strongly consumed, resulting in deep grooves in both sides of HDG coatings and covered by plate-like and needle-like precipitation products with significant Ce (from 9.8 to 11.4 wt%), O (from 44 to 46 wt%), Zn (from 20 -25.1 wt%) and Cl (4.5-10.8 wt%) contents confirmed by EDS analysis. Meanwhile, the ZnAl layer (Fig. 11 (b)) was not well defined and was covered by a thicker and denser layer containing mainly Ce (34.5 wt%), O (28.5 wt%), Zn (20.9 wt%) and with low Cl (0.5 wt%) content determined by EDS analysis. Another region with high Cl (7.0 wt%) but lower Ce (6.6 wt%) was observed by EDS analysis. The observation highlights a notable competition occurring for the formation of corrosion products. Specifically, regions rich in cerium (Ce) content tend to suppress the presence of Cl. This indicates that the prevalence of cerium in certain areas limits the occurrence of chlorine-related corrosion products (simonkolleite). In addition, the plate-like morphology was found in some regions which were enriched by Ce (9.7 wt%), O (37.1 wt %), Zn (31.7 wt%), Al (6.7 wt%), suggesting the product of cerium hydr (oxide), product based on zinc and Al-containing product. In the case of the ZAM layer (Fig. 11 (c)), different morphologies were observed and corrosion unevenly occurred. The precipitation products formed a thick and dense layer in some regions of the ZAM layer which mainly consisted of Ce (31.6 wt%), Zn (34.1 wt%), O (25.6 wt%), and Cl (5.0 wt%). Whereas, some regions of metallic ZAM were still exposed (η-Zn-rich phase) or presented the plate-like crystals containing Ce (15 wt%), Zn (60 wt%), O (11.4 wt%), Cl (1.6 wt%) elements or small round seeds with higher Ce, O contents, suggesting the precipitation of cerium hydr (oxide). The observation of the unaffected zone ($\eta\text{-}Zn$ phase) and corrosion attack in the eutectic phases surrounded n-Zn phase clearly

assigned selective corrosion. Moreover, these observations confirmed the decisive sacrificial anode of zinc-based coating in the presence of cerium chloride.

By contrast, in the presence of Ce(NO₃)₃, the cross-section surface presented more precipitation products compared to the blank solution and the medium with CeCl₃, indicating higher evolution of galvanic corrosion activity. The EDS mapping of the cross-section of all samples after 24 h of immersion in the chloride solution with Ce(NO₃)₃ was shown in Fig. 12. It is evident that similar to the presence of CeCl₃, the zinc-based layer presented the distribution of high Zn, O, and Cl contents, along with the presence of Ce and Al, associating with the presence of simonkolleite, cerium hydr(oxide) and Al-containing products. Interestingly, the distribution of Zn, Cl, and Ce on the cross-section of all samples varies. Cl was mainly detected on the HDG layer, whereas it was distributed in certain parts of ZnAl coating and focused on the center of steel parts in the case of ZnAl. Regarding the ZAM/steel substrate, Cl was observed on the ZAM layer and close to the ZAM coating. Besides, Ce demonstrated the highest intensity of distribution on the ZAM layer, followed by ZnAl and HDG coatings, indicating the presence of numerous micro-anodic and micro-cathodic sites. This phenomenon could be attributed to the different phases present in the structure of the zinc-based layer (due to the alloyed elements Al and Mg). Furthermore, the selective corrosion of Zn₂Mg phase tends to clearly exhibit the presence of Mg. However, Mg was not well detected by the EDS mapping.

On the steel region, the cut-edge surface of the ZAM-coated steel revealed the highest level of precipitation, which was enriched by O and Ce, forming the thickest layer. As a result, the metallic steel surface was masked to a greater extent than the ZnAl and HDG-coated steel samples. The presence of cerium hydr(oxide) precipitation could hinder the formation of zinc oxide products due to the pH local as mentioned in previous works [10,11].

Closer examination of the cross-section of the zinc-based layer, the SEM images (Fig. 13) revealed uneven consumption of the HDG layer. Certain parts were significantly corroded, leading to deep grooves where principally demonstrated the presence of Zn (47.7 wt%), O (24 wt%), Cl (8.1 wt%) with low Ce content (3.4 wt%) measured by EDS analysis. The



Fig. 11. Cross-section SEM images of HDG (a), ZnAl (b), and ZAM (c) coatings after 24 h of immersion in 0.015 M NaCl containing 5.10⁻³ M CeCl₃.



Fig. 12. EDX mapping of one half of HDG (a), ZnAl (b), and ZAM (c) coated steel cross-section after 24 h of immersion in 0.015 M NaCl containing 5.10^{-3} M Ce(NO₃)₃.



Fig. 13. Cross-section SEM images of HDG (a), ZnAl (b), and ZAM (c) coatings after 24 h of immersion in 0.015 M NaCl containing 5.10⁻³ M Ce(NO₃)₃.

morphology of the ZnAl and ZAM layers varied. The ZnAl coating displayed a dense film in some regions and crystalline areas with high Ce (14.8 - 29.7 wt%), Zn (13.5 - 25.5 wt%), O (39.7 - 45.0 wt%) amounts with Cl (2.8 wt%). The ZAM layers exhibited more significant corrosion compared to the presence of CeCl₃. Certain portions of the ZAM layers displayed a dense film with Ce (24.0 wt%), O (32.3 wt%), Zn (29.5 wt %), and Cl (2.2 wt%) as measured by EDS analysis. The interface of ZAM/steel presents a compact layer of plate-like crystalline structure with notable amounts of Ce (25.9 wt%) and O (45.3 wt%), proposing the formation of cerium hydr(oxide) products. Additionally, in certain areas, the original metallic surface was still visible.

4. Discussion

From the results above, the precipitation products formed on the cross-section of HDG and ZnAl coated still are mainly simonkolleite (on zinc-based layer), ZnO or $Zn(OH)_2$ (on steel part), while no trace of product precipitation on ZAM coated steel was observed in the chloride

solution. Whereas, both simonkolleite and cerium hydroxide (in both zinc–based layer and steel surface) were observed on the cross-section of all samples in the chloride medium with cerium salts. To understand the mechanism and the sequential precipitation formation in the studied solutions, the thermodynamic approach was employed. In the literature, several authors have predicted corrosion products based on thermodynamic equilibrium using the Hydra-Medusa database [32–35].

In this study, Hydra-medusa modeling was performed in both electrolytes without and with cerium salts (experimental conditions) (Fig. 14 and Fig. 15). Fig. 14 presented the Hydra-Medusa modeling with different Zn^{2+} concentrations ($[Zn^{2+}] = 5 \text{ mM}$ and $[Zn^{2+}] = 6 \text{ mM}$), $[Al^{3+}] = 5 \text{ mM}$, $[Mg^{2+}] = 5 \text{ mM}$, $[CO_3^2] = 5 \text{ mM}$ in a 15 mM chloride solution. From Fig. 14 (a), the results demonstrate that in the nearly neutral medium (pH= 6–7), Zn^{2+} ions tend to preferentially precipitate with OH⁻ and Cl⁻, leading to the formation of simonkolleite. On the other hand, at higher pH values (pH > 7–8), the formation of zinc oxide (ZnO) becomes favorable, and ZnO precipitation stabilizes. In the presence of aluminum (ZnAl layer), Al(OH)₃ can be obtained and remains stable in a



Fig. 14. Fraction of (a, d) different Zn^{2+} , (b) Al^{3+} , (c) Mg^{2+} precipitation product formed as a function of pH for a system predicted by thermodynamic calculation using the Hydra-Medusa modeling with $[Zn^{2+}] = 6 \text{ mM}$, $[Al^{3+}] = 6 \text{ mM}$, $[Mg^{2+}] = 6 \text{ mM}$, $[Cl^{-}] = 15 \text{ mM}$ and $[CO_{3-}^{2-}] = 5 \mu M$.



Fig. 15. Fraction of different Ce^{3+} precipitation products formed as a function of pH for a system predicted by thermodynamic calculation using the Hydra-Medusa modeling with $[Ce^{3+}] = 5$ mM, $[Zn^{2+}] = 6$ mM, $[Mg^{2+}] = 6$ mM, $[Cl^2] = 15$ mM, and $[CO_3^2] = 5$ μ M.

wide pH range, from acidic to alkaline conditions (pH= 4–12) (Fig. 14 (b)). In the case of ZAM layer, the presence of Mg^{2+} can lead to the formation of Mg(OH)₂ at around pH= 10 and remains stable in a strong alkaline solution (Fig. 14 (c)). As mentioned earlier, for HDG and ZnAl substrates, simonkolleite was observed in the Zn-based parts, while the main corrosion product precipitations were Zn(OH)₂ or ZnO in the steel part. These observations, combined with predictions based on Hydra-Medusa suggest a gradual evolution of local pH from the zinc-based layer (close to neutral, resulting in simonkolleite formation) to the steel part (mild alkaline, resulting in ZnO or Zn(OH)₂ formation). Meanwhile, the absence of product precipitation on the cross-section of ZAM (Fig. 9) can be attributed to two main factors: the concentration of species in the solution and the local pH. The concentration of cations may be low, and the local pH may not reach the required value, thus

being insufficient for precipitation formation. Notably, when maintaining the same species in the solution but altering the concentration of Zn^{2+} from 6 mM to 5 mM (Fig. 14 (d)), the simonkolleite was not obtained. Volovitch et al. [32] conducted a Hydra-Medusa modeling using a higher concentration of species in the solution: $[Zn^{2+}] = 500$ mM, $[CO_3^{2-}] = 500$ mM, $[CI^-] = 1$ mM, both with and without $[Mg^{2+}] = 500$ mM. The result indicated that the presence of Mg^{2+} shifts the pH range for the formation of $ZnCO_3$ from neutral and low basic pH (up to 8) in the acid region (pH <7).

Regarding the electrolyte with cerium salts, a simulation system conducted by Hydra-Medusa modeling with $[Ce^{3+}] = 5 \text{ mM}$, $[Cl^{-}] = 15 \text{ mM}$, $[CO_3^{-2}] = [Zn^{2+}]$, $[Mg^{2+}]$, $[Al^{3+}]$ was exhibited in Fig. 15. As can be seen, $Ce(OH)^{2+}$ was obtained in the pH range from 6 to 8. While $Ce(OH)_3$ is predicted to form at pH values greater than 7. The cerium

species could affect the corrosion kinetics of zinc. As mentioned above, the main product precipitations in the solution with cerium salts are simonkolleite and cerium hydr(oxide), as suggested by EDS mapping. The presence of simonkolleite in both the zinc-based layer and the steel part can be explained by considering that during the initial immersion time, all the samples experience an environment with a pH close to neutral (pH <7). Hence, the most probable precipitation product should be simonkolleite. Over time, the oxygen reduction reaction at cathode sites gradually develops and generates more OH⁻ groups, leading to an increase in local pH to attain the required pH value for Ce(OH)3 formation in the cathodic areas. This range is also the same value required for ZnO formation (Fig. 14(a)). However, the formation of $Ce(OH)_3$ in the solution will be prioritized to ZnO due to the lower solubility product $(K_{sp} Ce(OH)_3 = 1.6 \times 10^{-20}; K_{sp} Zn(OH)_2 = 3 \times 10^{-17})$ [36]. Moreover, the consumption of OH⁻ generated from the oxygen reduction reaction by Ce^{3+} and the formation of $Ce(OH)_3$ can buffer the pH medium, thus preventing the formation of ZnO and stabilizing the simonkolleite products on the zinc-based layers and the steel surface. The formation of Ce(OH)₃ with high intensity in the steel part indicated also the evolution of local pH from anodic to cathodic sites.

5. Conclusion

The effect of cerium salts and the counter-ion on the cut-edge of zincbased sacrificial coatings was initially studied by theoretical approach (based on individual polarization curves of steel and zinc-based coatings), and then by the localized technique (SVET measurement). The major results can be summarized as follows:

- 1. The theoretical approach results demonstrated that the zinc-based alloyed Al, Mg layers presented the best performance for galvanic corrosion in the chloride solution. Besides, cerium salts accelerated the corrosion of zinc when coupled with steel. Notably, in the presence of Ce (III), adding Al and Mg alloyed elements in zinc-based coating decreased the galvanic corrosion. However, a synergistic accelerated effect was observed particularly in the presence of NO₃ ions. The ZAM coating/steel exhibited the highest galvanic corrosion in presence of Ce(III).
- 2. The SVET measurement conducted on the cut-edge of zinc-based coatings coated steel correlated to the results obtained by the theoretical approach and indicated that all the zinc-based layers still provided the sacrificial protection after 6 h immersion in the studied electrolytes. Although cerium salts have been proven to inhibit corrosion on the top surface of zinc-based layer coated steel in our previous work, both theoretical predictions and SVET results confirmed that cerium salts accelerate galvanic corrosion at the cutedge of all the samples, especially in the presence of cerium nitrate (which exhibited higher cathodic current density than cerium chloride on steel. This greater current density indicated an increase in the cerium aqua-complex reduction, leading to a higher corrosion rate), hence increasing the zinc consumption, leading to a reduction in the lifetime of the material in the presence of defect or the cut-edge in the short-term. The presence of NO3 significantly accelerated the anodic activity, leading to a higher amount of cerium hydr(oxide) deposited on the steel surface. Therefore, the anion parts of cerium salts should be chosen carefully. Additionally, cerium salts are not effective corrosion inhibitors to protect zinc-based coated steel in all situations. It is essential to find another way to provide an improved performance for both on the top surface and on the cut-edge.
- 3. The ZnAl and ZAM layers exhibited a reduction in intensity (which could be attributed to the addition of Al, Mg in the zinc-based layer and/or the surface area ratio $S_{anode}/S_{cathode}$) and the number of galvanic corrosion activities. However, the presence of microstructure led to selective dissolution and promoted localized corrosion, resulting in pitting corrosion. EDS mapping and SEM analysis offered significant insights into the alloy design concept and the corrosion

behavior of all sacrificial coatings for the development of alloycoated steel products with better corrosion resistance

CRediT authorship contribution statement

Olivier Marie-Georges Marjorie: Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Conceptualization. Trinh Anh Truc: Writing – review & editing, Validation, Supervision. Paint Yoann: Validation, Investigation. Thai Thu Thuy: Writing – review & editing, Supervision, Methodology. Akbarzadeh Sajjad: Validation, Methodology, Investigation. Nguyen Thi Thao: Writing – original draft, Methodology, Investigation, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

The authors would like to thank ArcelorMittal for providing the metallic substrate and Sebastien Colmant from the Metallurgy Department for his help in preparing the embedded samples. This study was supported by the Académie de Recherche et d'Enseignement Supérieur (ARES Belgium) through the Development Cooperation project between Vietnam and Belgium (PRD 2020–2025: Renforcement de expertise environnementale du centre de compétences en protection contre la corrosion et en électrochimie), and National Foundation for Science and Technology Development under grant number 104.06-2019.20.

References

- [1] S. Schürz, G.H. Luckeneder, M. Fleischanderl, P. Mack, H. Gsaller, A.C. Kneissl, G. Mori, Chemistry of corrosion products on Zn–Al–Mg alloy coated steel, Corros. Sci. 52 (2010) 3271–3279, https://doi.org/10.1016/j.corsci.2010.05.044.
- [2] P. Volovitch, T.N. Vu, C. Allély, A. Abdel Aal, K. Ogle, Understanding corrosion via corrosion product characterization: II. Role of alloying elements in improving the corrosion resistance of Zn–Al–Mg coatings on steel, Corros. Sci. 53 (2011) 2437–2445, https://doi.org/10.1016/j.corsci.2011.03.016.
- [3] A. Marder, The metallurgy of zinc-coated steel, Prog. Mater. Sci. 45 (2000) 191–271, https://doi.org/10.1016/S0079-6425(98)00006-1.
- [4] T. Prosek, D. Persson, J. Stoulil, D. Thierry, Composition of corrosion products formed on Zn–Mg, Zn–Al and Zn–Al–Mg coatings in model atmospheric conditions, Corros. Sci. 86 (2014) 231–238, https://doi.org/10.1016/j.corsci.2014.05.016.
- [5] J.-W. Lee, B.R. Park, S.-Y. Oh, D.W. Yun, J.K. Hwang, M.-S. Oh, S.J. Kim, Mechanistic study on the cut-edge corrosion behaviors of Zn-Al-Mg alloy coated steel sheets in chloride containing environments, Corros. Sci. 160 (2019), https:// doi.org/10.1016/j.corsci.2019.108170.
- [6] M. Salgueiro Azevedo, C. Allély, K. Ogle, P. Volovitch, Corrosion mechanisms of Zn (Mg, Al) coated steel in accelerated tests and natural exposure: 1. The role of electrolyte composition in the nature of corrosion products and relative corrosion rate, Corros. Sci. 90 (2015) 472–481, https://doi.org/10.1016/j. corsci.2014.05.014.
- [7] T.T. Pham, T.D. Nguyen, A.S. Nguyen, T.T. Nguyen, M. Gonon, A. Belfiore, Y. Paint, T.X.H. To, M.-G. Olivier, Role of Al and Mg alloying elements on corrosion behavior of zinc alloy-coated steel substrates in 0.1 M NaCl solution, Mater. Corros. (2023) 1–17, https://doi.org/10.1002/maco.202213549.
- [8] K. Ogle, V. Baudu, L. Garrigues, X. Philippe, Localized electrochemical methods applied to cut edge corrosion, J. Electrochem. Soc. 147 (2000) 3654.
- [9] K. Ogle, S. Morel, D. Jacquet, Observation of self-healing functions on the cut edge of galvanized steel using SVET and pH microscopy, J. Electrochem. Soc. 153 (2005) B1.
- [10] C. Arrighi, T.T. Nguyen, Y. Paint, C. Savall, L.B. Coelho, J. Creus, M.G. Olivier, Study of Ce(III) as a potential corrosion inhibitor of Zn-Fe sacrificial coatings electrodeposited on steel, Corros. Sci. 200 (2022), https://doi.org/10.1016/j. corsci.2022.110249.
- [11] T.T. Nguyen, C. Arrighi, T.T. Thai, L. Dangreau, M.F. Gonon, A.T. Trinh, M. G. Olivier, Inhibitive effect of the Ce (III) chloride and nitrate on the corrosion resistance of Zn alloyed sacrificial coatings: Effect of alloying compounds of the

T.T. Nguyen et al.

- [12] M. Oliveira, A.C. Bastos, S. Kallip, T. Hack, M.L. Zheludkevich, M.G.S. Ferreira, Corrosion inhibition and acceleration by rare earth ions in galvanic couples, J. Electrochem. Soc. 166 (2019) C642–C648, https://doi.org/10.1149/ 2.0761916jes.
- [13] S. Kallip, A.C. Bastos, K.A. Yasakau, M.L. Zheludkevich, M.G. Ferreira, Synergistic corrosion inhibition on galvanically coupled metallic materials, Electrochem. Commun. 20 (2012) 101–104.
- [14] A. Marder, The metallurgy of zinc-coated steel, Prog. Mater. Sci. 45 (2000) 191–271, https://doi.org/10.1016/S0079-6425(98)00006-1.
- [15] M. Tran, P. Dubot, E. Sutter, Activation of water reduction in the presence of REM salts in aqueous solution, Int. J. Hydrog. Energy (2008), https://doi.org/10.1016/j. ijhydene.2007.11.025.
- [16] M. Tran, C. Fiaud, E. Sutter, Cathodic reactions on steel in aqueous solutions containing Y (III), J. Electrochem. Soc. 153 (2006) B83.
- [17] J. Gustavsson, G. Lindbergh, A. Cornell, In-situ activation of hydrogen evolution in pH-neutral electrolytes by additions of multivalent cations, Int. J. Hydrog. Energy 37 (2012) 9496–9503, https://doi.org/10.1016/j.ijhydene.2012.03.061.
- [18] A.J.M.C. Cook, C. Padovani, A.J. Davenport, Effect of Nitrate and Sulfate on Atmospheric Corrosion of 304L and 316L Stainless Steels, J. Electrochem. Soc. 164 (2017) C148–C163, https://doi.org/10.1149/2.0921704jes.
- [19] W. Xu, B. Zhang, Y. Deng, L. Yang, J. Zhang, Nitrate on localized corrosion of carbon steel and stainless steel in aqueous solutions, Electrochim. Acta 369 (2021) 137660, https://doi.org/10.1016/j.electacta.2020.137660.
- [20] B. Hinton, L. Wilson, The corrosion inhibition of zinc with cerous chloride, Corros. Sci. 29 (1989) 967–985, https://doi.org/10.1016/0010-938X(89)90087-5.
- [21] I.A. Kartsonakis, S.G. Stanciu, A.A. Matei, R. Hristu, A. Karantonis, C.A. Charitidis, A comparative study of corrosion inhibitors on hot-dip galvanized steel, Corros. Sci. 112 (2016) 289–307, https://doi.org/10.1016/j.corsci.2016.07.030.
- [22] M. Olivier, A. Lanzutti, C. Motte, L. Fedrizzi, Influence of oxidizing ability of the medium on the growth of lanthanide layers on galvanized steel, Corros. Sci. 52 (2010) 1428–1439, https://doi.org/10.1016/j.corsci.2010.01.011.
- [23] J.X. Jia, G. Song, A. Atrens, Influence of geometry on galvanic corrosion of AZ91D coupled to steel, Corros. Sci. 48 (2006) 2133–2153, https://doi.org/10.1016/j. corsci.2005.08.013.
- [24] Hack, H.P., in: R. Baboian (Ed.), Corrosion Tests and Standards Application and Interpretation, American Society for Testing and Materials, Fredericksburg, VA, 1995, p. 186.

- [25] G. Song, B. Johannesson, S. Hapugoda, D. Stjohn, Galvanic corrosion of magnesium alloy AZ91D in contact with an aluminium alloy, steel and zinc, Corros. Sci. 46 (2004) 955–977, https://doi.org/10.1016/S0010-938X(03)00190-2.
- [26] M. Challis, D.A. Worsley, Cut edge corrosion mechanisms in organically coated zinc–aluminium alloy galvanised steels, Br. Corros. J. 36 (2013) 297–303, https:// doi.org/10.1179/000705901101501640.
- [27] S. Schuerz, M. Fleischanderl, G.H. Luckeneder, K. Preis, T. Haunschmied, G. Mori, A.C. Kneissl, Corrosion behaviour of Zn–Al–Mg coated steel sheet in sodium chloride-containing environment, Corros. Sci. 51 (2009) 2355–2363, https://doi. org/10.1016/j.corsci.2009.06.019.
- [28] L.B. Coelho, M. Mouanga, M.E. Druart, I. Recloux, D. Cossement, M.G. Olivier, A SVET study of the inhibitive effects of benzotriazole and cerium chloride solely and combined on an aluminium/copper galvanic coupling model, Corros. Sci. 110 (2016) 143–156, https://doi.org/10.1016/j.corsci.2016.04.036.
- [29] B. Li, A. Dong, G. Zhu, S. Chu, H. Qian, H. Ch, B. Sun, W. J. Investigation of the corrosion behaviors of continuously hot-dip galvanizing Zn–Mg coating, Surf. Coat. Technol. 206 (2012) 3989–3999, https://doi.org/10.1016/j.surfcoat.2012.03.079.
- [30] N. Lebozec, D. Thierry, D. Persson, J. Stoulil, Atmospheric corrosion of zincaluminum alloyed coated steel in depleted carbon dioxide environments, J. Electrochem. Soc. 165 (7) (2018) C343–C353, https://doi.org/10.1149/ 2.0721807jes.
- [31] M. Salgueiro Azevedo, C. Allély, K. Ogle, P. Volovitch, Corrosion mechanisms of Zn (Mg,Al) coated steel: The effect of HCO3⁻ and NH⁴₄ ions on the intrinsic reactivity of the coating, Electrochim. Acta 153 (2015) 159–169, https://doi.org/10.1016/j. electacta.2014.09.140.
- [32] P. Volovitch, C. Allely, K. Ogle, Understanding corrosion via corrosion product characterization: I. Case study of the role of Mg alloying in Zn–Mg coating on steel, Corros. Sci. 51 (2009) 1251–1262, https://doi.org/10.1016/j.corsci.2009.03.005.
- [33] M. Salgueiro Azevedo, C. Allély, K. Ogle, P. Volovitch, Corrosion mechanisms of Zn (Mg, Al) coated steel: the effect of HCO3– and NH4+ ions on the intrinsic reactivity of the coating, Electro Acta 153 (2015) 159–169, https://doi.org/ 10.1016/j.electacta.2014.09.140.
- [34] J.D. Yoo, P. Volovitch, A. Abdel Aal, C. Allely, K. Ogle, The effect of an artificially synthesized simonkolleite layer on the corrosion of electrogalvanized steel, Corros. Sci. 70 (2013) 1–10, https://doi.org/10.1016/j.corsci.2012.10.024.
- [35] K. Ogle, S. Morel, D. Jacquet, Observation of self-healing functions on the cut edge of galvanized steel using SVET and pH microscopy, J. Electrochem. Soc. 153 (2006) B1–B5, https://doi.org/10.1149/1.2126577.
- [36] K. Aramaki, Treatment of zinc surface with cerium(III) nitrate to prevent zinc corrosion in aerated 0.5 M NaCl, Corros. Sci. 43 (2001) 2201–2215, https://doi. org/10.1016/S0010-938X(00)00189-X.