



Influence of solution pH on the structure formation and protection properties of ZnAlCe hydrotalcites layers on hot-dip galvanized steel

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ARTICLE INFO

Keywords:

Ce-doped ZnAl hydrotalcite layers
Hot-dip galvanized steel
Corrosion resistance

ABSTRACT

This study aims at investigating the influence of the solution pH and cerium cations on the formation and the anti-corrosion properties of hydrotalcite (HT) layers grown by the “in-situ” synthesis method on hot-dip galvanized steel substrate (HDG) in the pH range of 11–13. The anti-corrosion properties of all ZnAlCe HT layers were recorded by electrochemical tests and compared to bare HDG substrate during exposure to 0.1 M NaCl. The pH of precursor baths significantly impacted the orientation, chemical composition, microstructure of HT layers, and the intercalation of cerium cations inside HT with significant differences in their anti-corrosion performance. The ZnAlCe HT, prepared at pH 12, showed an obviously enhanced corrosion protection for HDG substrate compared to the other two HT layers. The anti-corrosion mechanism of HT layers as well as the role of cerium inside HT network was investigated and discussed in this research.

1. Introduction

Due to a more negative corrosion potential than iron, zinc and its alloys are applied as a sacrificial anode coating to protect steel substrates [1]. However, zinc alloys are susceptible to localized corrosion in media containing Cl^- anions, resulting in reduced substrate life expectancy [1,2]. To solve this serious issue, organic and inorganic coatings with higher stability can be applied on zinc alloys surface, such as sol-gel coatings, chemical conversion coatings, and polymer coatings [3–8]. Among the chemical conversion coatings, the hydrotalcite (HT) layers, which are self-healing anti-corrosion coatings, were developed on zinc alloy surfaces [6,9–12].

The HT structure consisted of intercalation of water molecules and different organic/inorganic anions (A^n) sandwiched between the mixture of metal hydroxide (divalent and trivalent/tetravalent cations) layers [13]. Due to their unique structure, the HT characterization can be designed by changing M^{2+} , M^{3+} , and A^n ions as required [13–15]. Recently, various methods have been investigated to prepare HT layers as smart anti-corrosion coatings on surfaces of zinc alloys and galvanized steel. Zheludkevich et al. focused on the one-step method for ZnAl-

NO_3 HT layer developing on pure zinc surface as well as their growth mechanism [9,16]. Their results reported that the structure and surface morphology of ZnAl- NO_3 HT layer depended obviously on synthesis time [16]. Besides, the ZnAl HT layers intercalated with different anions (Cl^- , SO_4^{2-} , $\text{V}_4\text{O}_{12}^{4-}$, and $\text{V}_2\text{O}_7^{4-}$) were prepared on pure zinc substrate by replacing NO_3^- anions [17]. However, the anti-corrosion properties of these ZnAl-HT layers were not evaluated and discussed. Hoshino et al. produced a ZnAl- CO_3 HT conversion layer on electrogalvanized steel (EGS) surface by putting the bare substrate into alkaline solutions and by exchanging NO_3^- anions with CO_3^{2-} ones inside HT network to form ZnAl- NO_3 HT layer in the second stage [18]. They also studied the effect of pH values on the growth behavior and corrosion protection of these ZnAl- CO_3 HT layers [6]. They indicated that ZnO was deposited in higher pH solutions, and, the ZnO deposition can influence the development process, morphological, structural, and protective properties of HT layers [6]. Amanian et al. prepared ZnAl- CO_3 HT layers on EGS substrate at different treatment times and discussed this effect on the formation and corrosion protection of HT layers [19]. The characterization and corrosion protection mechanism of ZnAl- CO_3 HT layers on EGS substrate at different $\text{Al}^{3+}/\text{Zn}^{2+}$ ratios were investigated in our

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<https://doi.org/10.1016/j.surfcoat.2023.129918>

Received 19 July 2023; Received in revised form 7 August 2023; Accepted 12 August 2023

Available online 25 August 2023

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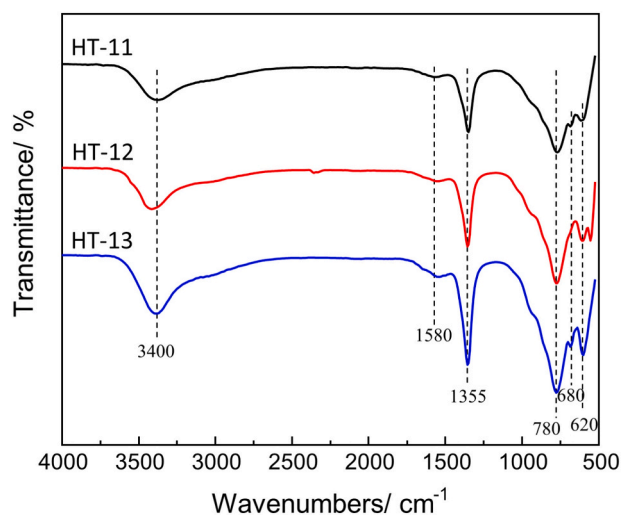


Fig. 1. The FT-IR spectra of HT-11, HT-12, and HT-13 samples.

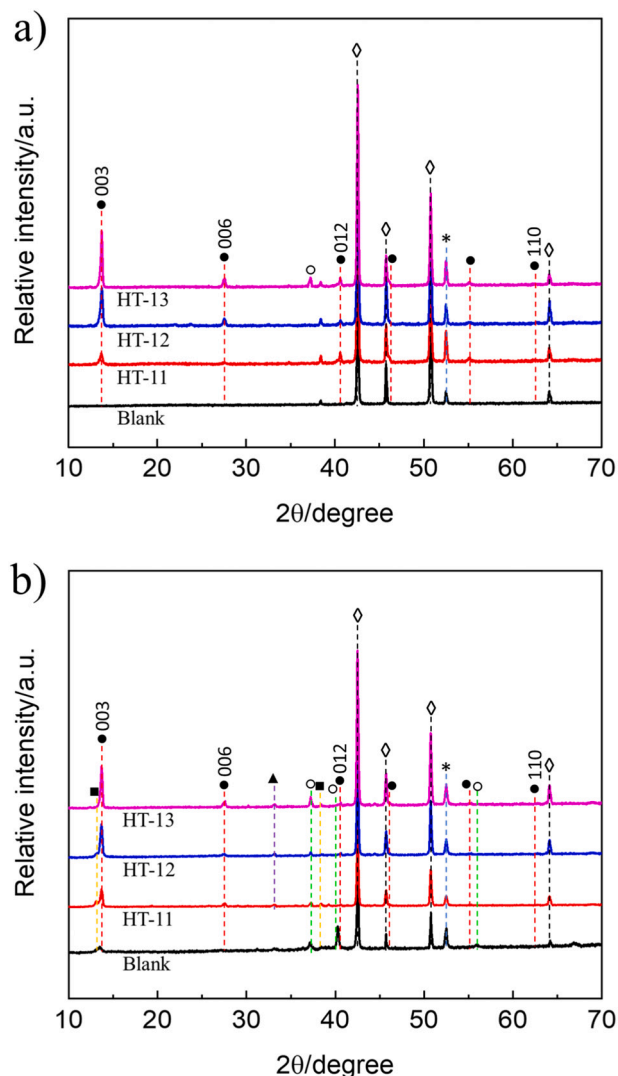


Fig. 2. XRD patterns of bare HDG substrate, HT-11, HT-12, and HT-13 samples before (a) and after (b) 168 h exposure to 0.1 M NaCl. Peaks marked with ●, ◇, *, ○, ■, and ▲ are contributed to Zn—Al HT, Zn, Fe, ZnO, and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O} / \text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$, CeO_2 , respectively.

Table 1

XRD analysis results for original HT-11, HT-12, and HT-13 samples.

Samples	d(003) (nm)	d(006) (nm)	d(110) (nm)	a (nm)	c (nm)
HT-11	0.754	0.377	0.177	0.354	2.262
HT-12	0.756	0.378	0.182	0.364	2.268
HT-13	0.755	0.378	0.178	0.356	2.265

previous study [11]. Our results showed that the “in situ” development of HT layer on the EGS surface required appropriate ratios [11]. Besides, we also discussed the effect of composition and roughness of sacrificial layer on the growth as well as corrosion mechanism of the ZnAl- CO_3 HT layers on zinc alloys coated steel substrates such as hot-dip galvanized steel (Zn, Al: 1.2 wt%), Zn—Al coated steel (Zn, Al: 9.4 wt%), and Zn-Al-Mg coated steel (Zn, Al: 7.2 wt%, Mg: 4.0 wt%) [12]. Huang et al. also prepared ZnAl- CO_3 HT layers on Zn—5Al alloy (Zn, Al: 5.0 wt%) substrate and compared the corrosion resistance properties of HT layer grown on the bare substrate [10]. Their results confirmed that the as-prepared ZnAl HT layer gradually improved the corrosion protection via the physical barrier as well as the deposition of hydrozincite in the defected HT nanosheets, which reduced the creation of cracks on the corrosion product layer [10].

Lanthanide compounds, recognized as environment-friendly inorganic inhibitors, have been widely applied to protect metal surfaces due to the deposition of lanthanum oxides/hydroxides on the cathodic area [8,20,21]. The addition of lanthanide cations, especially Ce and La cations, into the host layer of HT coating was one of the promising methods to improve the corrosion protection of metal substrates [22–26]. Zhou et al. studied the preparation of La-doped ZnAl HT layer on 6061 alloy substrates by the “in situ” growth method and discussed the role of La cations dissolved from the HT lamellar layer on corrosion resistance [22]. They found that $\text{La}(\text{OH})_3$ deposition on the corrosion crack, supplied a secondary protection layer for the substrate, which blocked the surface, avoided the exposure to corrosion medium and decreased the corrosion metal rate [22]. Zhang et al. found that adding Ce cations into the ZnAl HT layer improved the corrosion protection of AA2024 alloy [26]. The Ce cations dissolution from the HT frame caused an increase in the stability of the HT layer [26]. Fedel et al. prepared the “in-situ” Ce-doped MgAl-HT layers on AA6082 and anodized AA6082, and discussed the role of Ce cations on the improvement of the HT layer's corrosion resistance [25,27,28]. Their findings claimed that the Ce cations released from the HT network during the exposure to saline solution, and then self-repaired the Ce oxides/hydroxides at the cathodic regions [27]. Therefore, the Ce-doped HT layer could reduce the electrochemical activity of the metal and delay the substrate degradation [27]. Zahedi Asl et al. investigated the effect of Zn/Ce ratios and pH values of precursor baths on the characterization and protection property of ZnCe-HT layers on AZ31 magnesium alloy [23]. The HT layer formed at low pH values (about 9) had a weak protection property due to its non-uniform microstructure, while the corrosion resistance of HT layer at high pH values (about 11) was enhanced, mainly attributed to the intercalation of larger amounts of Ce cations [23]. However, the deposition of metallic oxides reduced the HT layer quality when the pH values of precursor baths exceeded about 12.5 [23].

According to our knowledge, the preparation and corrosion resistance assessment of “in-situ” La/Ce-doped HT layer on galvanized steel substrates have not been still investigated in-depth. Recent publications have highlighted that Ce-based salts and conversion coatings can be more effective in corrosion inhibition compared to La-based ones [29,30]. Therefore, we investigated the impact of pH values of precursor solutions on the development behavior, microstructure, and corrosion protection of Ce-doped ZnAl HT (ZnAlCe HT) layers on HDG substrate in this paper. The structural and morphological properties of ZnAlCe HT layers were detected by Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electron microscopy/energy dispersive X-ray spectroscopy (SEM/

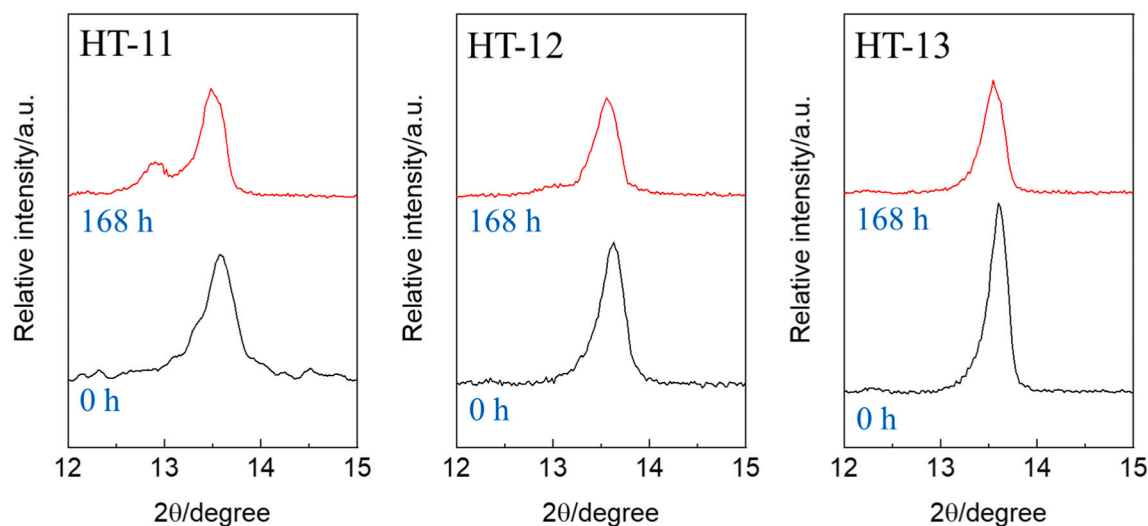


Fig. 3. XRD patterns (12° – 15°) of HT-11, HT-12, and HT-13 samples before and after 168 h exposure to 0.1 M NaCl.

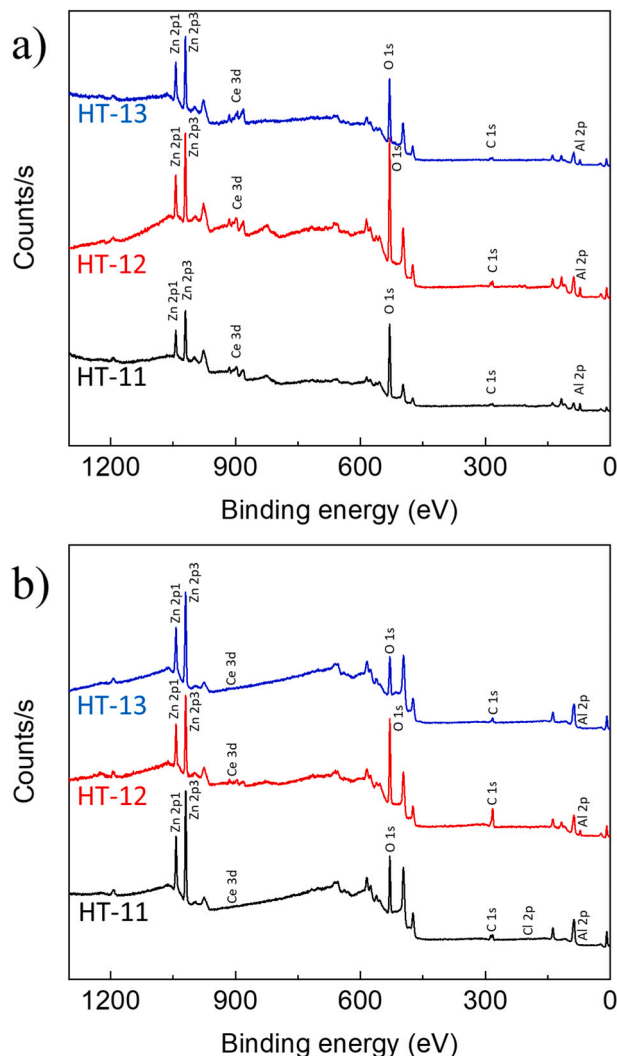


Fig. 4. XPS spectra survey of HT-11, HT-12, and HT-13 samples before (a) and after (b) 168 h exposure to 0.1 M NaCl.

EDS). The corrosion behaviors of layers were recorded by electrochemical methods such as potentiodynamic polarizations and electrochemical impedance spectroscopy (EIS) during 168 h exposure to 0.1 M NaCl. Besides, the role of Ce on the HT layer anti-corrosion mechanism was also studied in-depth by observing corrosion products after 168 h.

2. Materials and methods

2.1. Materials

The HDG plates (92.1 Zn wt%, 1.2 wt% Al, 3.9 wt% C, 2.8 wt% O), provided by Arcelor Mittal (Belgium), were cut into 50 mm × 25 mm × 2 mm pieces. Before growing the HT layer, the samples were cleaned with acetone, commercial Gardoclean alkaline solution, ethanol, and DI water as described in our previous study [11].

All chemicals used in this study are of analytical grade, consisting of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, NaOH, and NaCl.

2.2. Preparing the HT layer on HDG substrates

The ZnAlCe HT layers were produced on HDG surface by the “in situ” development method at pH values of 11, 12, and 13, which were named HT-11, HT-12, and HT-13, respectively. 0.04 mol $\text{Al}(\text{NO}_3)_3$ was dissolved and stirred with 0.16 mol NaOH in 1000 mL DI water for 15 min, and then 0.01 mol $\text{Ce}(\text{NO}_3)_3$, and 0.03 mol $\text{Zn}(\text{NO}_3)_2$ were added in the solution baths. The pH value of solution baths was adjusted in the range of 11 to 13 by addition of 1 M NaOH. The HDG substrates were soaked in mixed solution baths. The mixed solutions were stirred for 6 h at room temperature, and then the substrates continued to be dipped in the reactional solution for 16 h without stirring. Finally, these HT layer coated samples were removed from the reactional bath, rinsed with DI water, and dried at 70 °C.

2.3. Surface characterization

The surface morphology, elemental composition, and thickness of all ZnAlCe HT layers were observed via FE-SEM (Hitachi SU8020) equipped with an energy dispersive X-ray spectroscopy (EDS, Thermo Scientific Noran System 7). Fourier-transform infrared (FT-IR) spectra were recorded using a Nexus 670 Nicolet spectrometer. X-ray diffraction (XRD) pattern was collected on a Bruker D5000 with $\text{CoK}\alpha$ radiation (0.1789 nm) and Fe filter at a rate of $1^{\circ} \text{ min}^{-1}$. Moreover, X-ray photoelectron spectroscopy (XPS) analysis was performed by a PHI VERSAPROBE 5000 spectrometer with a monochromatic Al $\text{K}\alpha$ radiation

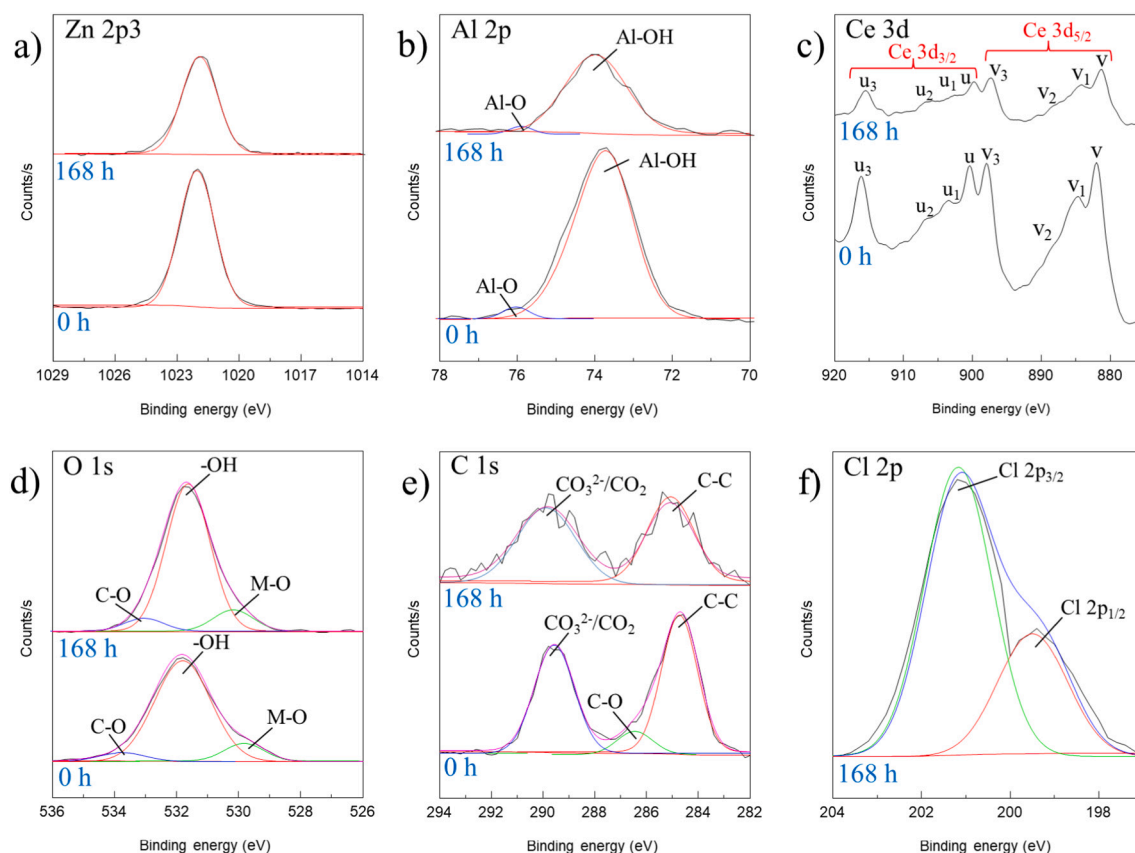


Fig. 5. High resolution XPS spectra of (a) Zn 2p₃, (b) Al 2p, (c) Ce 3d, (d) O 1s, (e) C 1s, and (f) 3d Cl 1s for HT-11 before and after 168 h exposure to 0.1 M NaCl.

at 1486.6 eV. The measurements were collected by an X-Ray source with a beam size diameter of 200 μm and a power of 50 W. Atomic compositions were calculated from peak areas after Shirley background subtraction.

2.4. Electrochemical tests

The corrosion resistance of all the samples in 0.1 M NaCl solution was investigated via electrochemical impedance spectroscopy (EIS) and potentiodynamic polarizations by using a Parstat Model 2273 controlled by Powersuite® software. An Ag/AgCl (sat. KCl) reference electrode, a spiral shape platinum counter electrode, and an exposed area of 1 cm^2 of surface samples as a working electrode were used as three-electrode system. Before EIS measurements, all samples were checked for stability by open circuit potential (OCP) for 15 min. The EIS spectra were recorded between 10^5 Hz and 10^{-2} Hz with an amplitude of 5 mV. The cathodic and anodic polarization curves were separately determined after 24 h and 168 h exposure to electrolyte solution with a scan rate of 0.2 mV s^{-1} starting from open circuit potential (OCP) and ranging from 0.03 V to -0.40 V and -0.03 to $+0.40$ V versus OCP (V/Ag/AgCl), respectively. Each experiment was performed at least three times to check the reproducibility.

3. Results and discussion

3.1. Characterization of ZnAlCe HT layers before and after exposure to 0.1 M NaCl

3.1.1. FT-IR analysis

Fig. 1. presents the FT-IR spectra of all the ZnAlCe HT layers on the HDG surface. No significant differences can be observed in the FT-IR spectra of the samples prepared in the three conditions. The strong

peaks at around 1355 cm^{-1} were attributed to the stretching vibration of C—O from intercalated carbonate anions [11]. All the HT layers exhibited a significant absorption band at about 3400 cm^{-1} , corresponding to the stretching vibration of the hydroxyl groups from metal hydroxyl groups and water molecules [14]. In the case of HT-12, a low peak at about 2300 cm^{-1} , which can be attributed to CO_2 from the air, was observed [31]. Moreover, the characteristic peak for the bending mode of water molecules was observed at around 1580 cm^{-1} [11]. The bands recorded at lower wavenumber ($800\text{--}500 \text{ cm}^{-1}$) were ascribed to the M—O, M—OH, O—M—O, and M—O—M lattice vibrations (M: Zn, Al, and Ce) [15]. However, these HT-12 bands shifted to lower wavenumbers than those of other two samples, which may be related to the Ce cation concentration in the HT-12 network, which showed clear differences compared to the other two samples [23].

3.1.2. XRD analysis

The XRD patterns of all the samples are presented in Fig. 2. Before the corrosion tests, all the ZnAlCe HT samples exhibited the (003), (006), and (110) characteristic peaks of HT layered structure. This confirms that the HT layers were successfully developed on HDG substrates at a pH range of 11 to 13 (Fig. 2a) [6,18]. According to Bragg's equation, the basal spacing $d_{(003)}$ of all the HT layers was about 0.755 nm (Table 1), proving the formation of HT layers intercalated with CO_3^{2-} anions [25]. The a lattice parameter (cation-cation distance in brucite layer), which depends on the size and the ratio of M^{2+} and M^{3+} ions, was calculated: $a = 2 \times d_{(110)}$ (Table 1) [12]. The c lattice parameter (the interlayer distance), which corresponds to the charge, the size, and the orientation of intercalated anions and water molecules, was determined: $c = 3 \times d_{(003)}$ (Table 1) [12]. Compared with the XRD analysis results of HT layers obtained in our previous research [11,12], the c values of all ZnAlCe HT samples were slightly higher, with a difference of about 0.02 nm, indicating that the addition of cerium cations into the HT lamellar

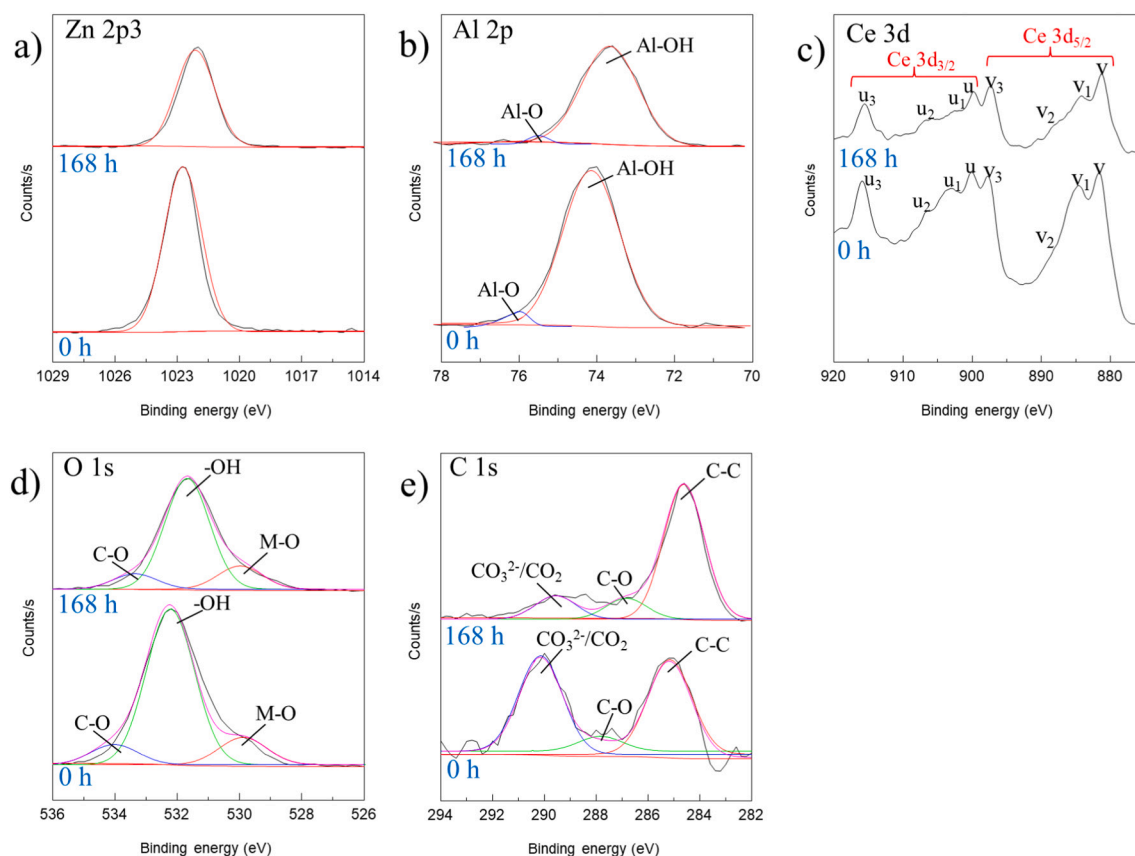


Fig. 6. High resolution XPS spectra of (a) Zn 2p₃, (b) Al 2p, (c) Ce 3d, (d) O 1s, and (e) C 1s for HT-12 before and after 168 h exposure to 0.1 M NaCl.

layer did not induce any significant difference in the orientation of CO_3^{2-} ions. However, the values of all ZnAlCe samples increased obviously, which was related to partial replacement of Al^{3+} ions by $\text{Ce}^{3+}/\text{Ce}^{4+}$ ions. The Ce^{3+} (0.102 nm) and Ce^{4+} (0.087 nm) ionic radii are bigger than Zn^{2+} (0.074 nm) and Al^{3+} (0.053 nm) ones, thus the $\text{Ce}^{3+}/\text{Ce}^{4+}$ intercalation into the ZnAl-HT network led to an increase in the cation-cation distance in the brucite layer [32]. However, no characteristic peaks of cerium oxides/hydroxides were observed. It was reported that the cerium compounds were intercalated within HT network and masked by HT crystals, thus the incident X-rays cannot interact with these cerium compounds and these diffraction peaks were not detected by XRD [33]. The intensity of HT characteristic peaks of HT-13 sample was obviously higher than those of HT-11 and HT-12 ones. It confirms that the amount of HT crystals deposited on the HDG surface at solution pH 13 was larger than those of the other two pH values. Moreover, the zinc oxide (ZnO) peaks were observed on the HT-13 XRD pattern, suggesting that a ZnO/HT composite layer is formed on the surface substrate. It indicated that the pH precursor baths affected the composition of HT layer deposited on HDG surface.

The XRD patterns of all the samples after 168 h of exposure to 0.1 M NaCl are presented in Fig. 2b. The characteristic peaks of HT crystals were still present on the XRD patterns, indicating that all HT layers showed good adhesion. However, the intensity of these HT peaks exhibited a significant decrease. It can be observed that the reflection of (003) characteristic peak was moved to lower 2θ range (Fig. 3). It confirmed that Cl^- ions partially replaced CO_3^{2-} ions and were trapped in interlayer of HT layers [11,12]. The ZnO peaks appeared on the HDG bare substrate and all the HT layers samples, implying the re-precipitation of Zn^{2+} cations dissolved from the substrate and HT layer [2,11]. It can be easily found that the intensity of ZnO peaks of HT-13 samples was sharply higher than those of the other two HT samples. The simonkolleite peaks were observed on the bare substrate and HT-11

samples. In addition, low intensity of cerium oxide (CeO_2) peaks appeared on all HT layer samples, suggesting the ability to self-liberate cerium cations from HT lamellar layer to the environment and their ability to re-precipitate [28]. This hypothesis is discussed in detail in the “corrosion mechanism” section.

3.1.3. XPS analysis

Figs. 4–7. show the XPS patterns of all the ZnAlCe HT grown on the sample at different solution pH. In the wide-scan XPS spectrum of all the original HT layers (Fig. 4a), the Zn 2p, Al 2p, C 1s, O 1s, and Ce 3d peaks were observed, confirming that the cerium cations were successfully incorporated into the HT network at the range of 11 to 13 pH values [23]. The Zn 2p_{3/2} and Al 2p spectra for all the HT samples showed two main peaks at around 1022.5 eV and 74.3 eV, respectively, which were related to the Zn-OH and Al-OH bonds of the HT network [12,22,23]. In addition, it can be observed a low-intensity peak of Al 2p at about 75.6 eV, which can be related to the Al-O bonds [34]. The Ce 3d spectra exhibited the peaks at around 918.0–898.0 eV and 895.0–880.0 eV which ascribed to Ce 3d_{3/2} and Ce 3d_{5/2} (Fig. 5c, 6c, and 7c) [23,35]. This split was attributed to the mixed valences of Ce^{3+} and Ce^{4+} , meanwhile, the (v, v₃, and u) and (v₁, v₂, u₁, u₂, and u₃) multiples corresponded to Ce^{3+} and Ce^{4+} , respectively [36]. The O 1s spectra of all the HT samples consist of three peaks, corresponding to different oxygen species. The O 1s peaks at around 533.0, 531.5, and 529.5 eV related to carboxyl group, metal hydroxide groups (M-OH, M: Zn, Al, and Ce), and lattice O^{2-} bonds (M-O, M: Zn, Al, and Ce), respectively [37,38]. The C 1s main peaks were located at around 289.5, 286.5, and 285.0 eV (Fig. 5e, 6e, and 7e), which correspond to O-C=O, C-O, and C-C bonds, suggesting clearly that the carbonate anions were intercalated in HT structure [39,40]. Like FT-IR and XRD results, no significant structural change was observed on the ZnAlCe HT XPS patterns with different solution pH, confirming that the pH values between 11 and 13

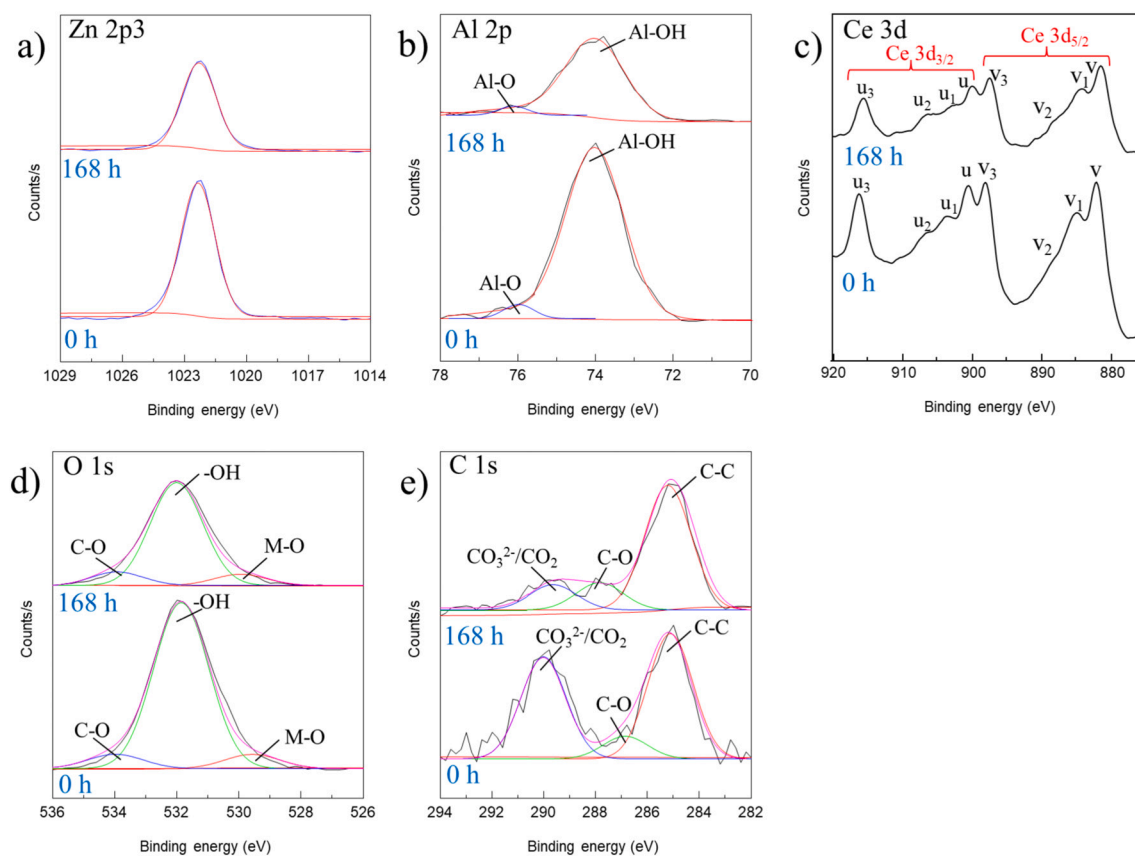


Fig. 7. High resolution XPS spectra of (a) Zn 2p3, (b) Al 2p, (c) Ce 3d, (d) O 1s, and (e) C 1s for HT-13 before and after 168 h exposure to 0.1 M NaCl.

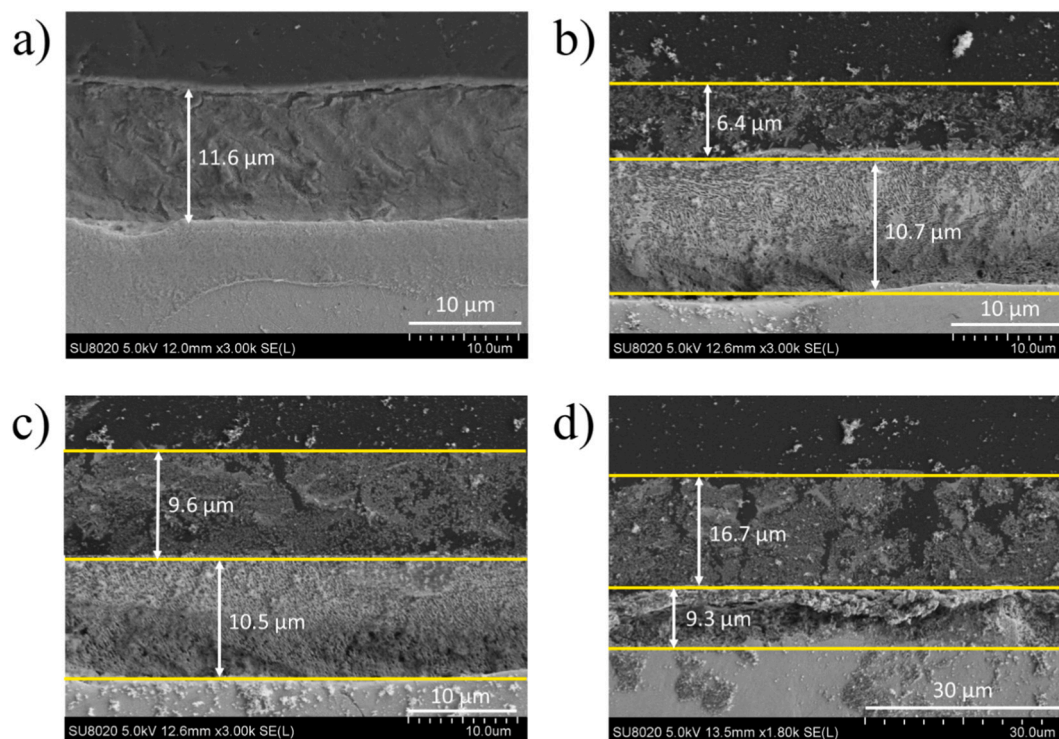


Fig. 8. SEM of the cross-sections of bare HDG substrate (a), HT-11 (b), HT-12 (c) and HT-13 (d) samples.

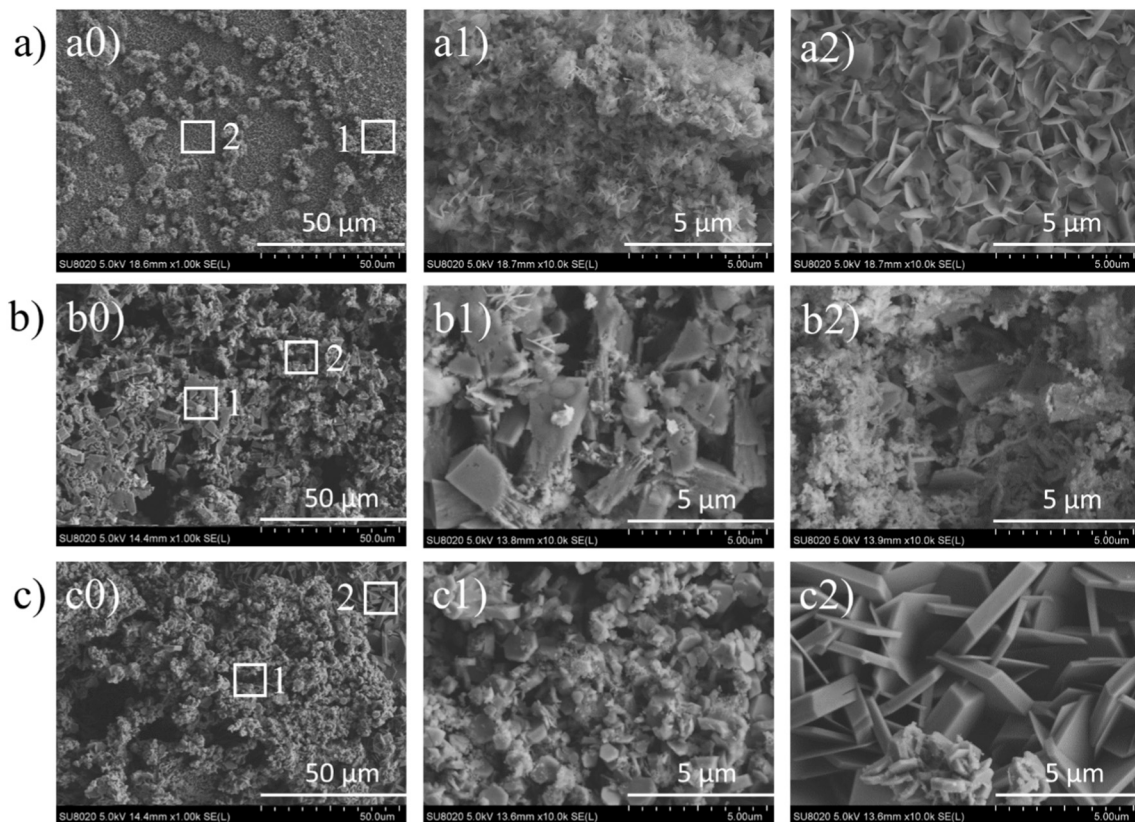


Fig. 9. SEM images of top surface of HT-11 (a), HT-12 (b), and HT-13 (c) samples.

Table 2

Element contents obtained from the EDS results of bare HDG substrate, HT-11, HT-12, and HT-13 samples before and after 168 h exposure to 0.1 M NaCl.

Sample	Element content (wt%)				
	O	Al	Zn	Ce	Cl
Before 168 h exposure to 0.1 M NaCl					
HT-11 1	37.2	7.7	48.9	2.1	–
HT-11 2	28.9	5.9	59.8	1.6	–
HT-12 1	36.5	9.8	43.2	6.4	–
HT-12 2	36.2	9.6	44.4	6.0	–
HT-13 1	36.9	10.2	47.1	2.5	–
HT-13 2	30.6	8.8	55.7	2.0	–
After 168 h exposure to 0.1 M NaCl					
HDG 1	32.8	0.1	63.9	–	0.4
HDG 2	33.0	0.1	63.5	–	0.3
HT-11 1	42.9	6.0	45.9	1.4	0.6
HT-11 2	34.7	4.3	56.4	1.0	0.5
HT-12 1	41.1	8.0	42.4	5.9	0.1
HT-12 2	40.3	7.5	44.1	5.5	–
HT-13 1	40.8	8.4	45.9	1.9	0.1
HT-13 2	35.7	7.1	53.2	1.4	0.1

cannot affect strongly the structural property of HT layers.

All the chemical elements of ZnAlCe HT layers after 168 h immersion in chloride solution were also studied by the XPS patterns (Figs. 4–7). The Zn 2p_{3/2} and Al 2p peaks of all HT samples existed after immersion time. The multiple peaks of Ce 3d_{3/2} and Ce 3d_{5/2} were also observed, suggesting that the cerium cations existed in Ce³⁺ and Ce⁴⁺ valence states after immersion test [35]. Similar to results of our previous study [12], the intensity of characteristic peaks of C 1 s slightly decreased, indicating that the CO₃²⁻ anions in intercalated layer were replaced and released during immersion time. The Cl 2p spectrum was only detected on the XPS survey spectra of the HT-11 sample (Fig. 4b). The Cl 2p

spectrum were deconvoluted into two peaks at around 201.0 and 199.5 eV, which were attributed to Cl 2p_{3/2} and Cl 2p_{1/2}, respectively (Fig. 5f) [41]. Combined with the XRD results, it can be concluded that these Cl 2p peaks were characteristic for simonkolleite corrosion product.

3.1.4. Cross section morphology

All the samples were embedded on cross section by using an epoxy resin from Stuers, ground with 400–4000 SiC papers, and rinsed with DI water [11]. Fig. 8. shows the cross section of bare substrate and ZnAlCe HT layers at different pH values. The solution pH effects can be observed on the cross section. Firstly, the solution pH affected the thickness and the morphology of the zinc alloy coatings. Compared with the bare substrate, it was found that the solutions at pH 11 and 12 did not change considerably the thickness and morphology of zinc alloy coatings. In contrast, the thickness of zinc alloy coating strongly decreased at pH 13 values. Moreover, on the zinc alloy coating of HT-13 sample, crevices appeared and the layer became more porous, because the rate of dissolution reaction of zinc was more intense and a large amount of insoluble ZnO precipitated at this high pH value [6]. These results were in good agreement with the XRD results (Fig. 2a). Secondly, the thickness of HT layers increased with the increase in pH value (Fig. 8). The thickness of HT-13, HT-12, and HT-11 layers were around 16.7, 9.6, and 6.4 μm, respectively. Besides, the crevices and gaps were observed from the cross section of all HT layers, which impacted their corrosion protection.

3.1.5. Surface morphology and elemental composition

The morphology and composition of all ZnAlCe HT samples were investigated by SEM, EDS, and EDS maps. It can be observed that the solution pH significantly impacted the morphology of HT layers (Fig. 9). The SEM (Fig. 9) and EDS (Table 2) results presented the non-uniform deposited layers with all pH values. Moreover, the amount of ZnAlCe HT crystals deposited at solution pH 12 and 13 was larger than that of

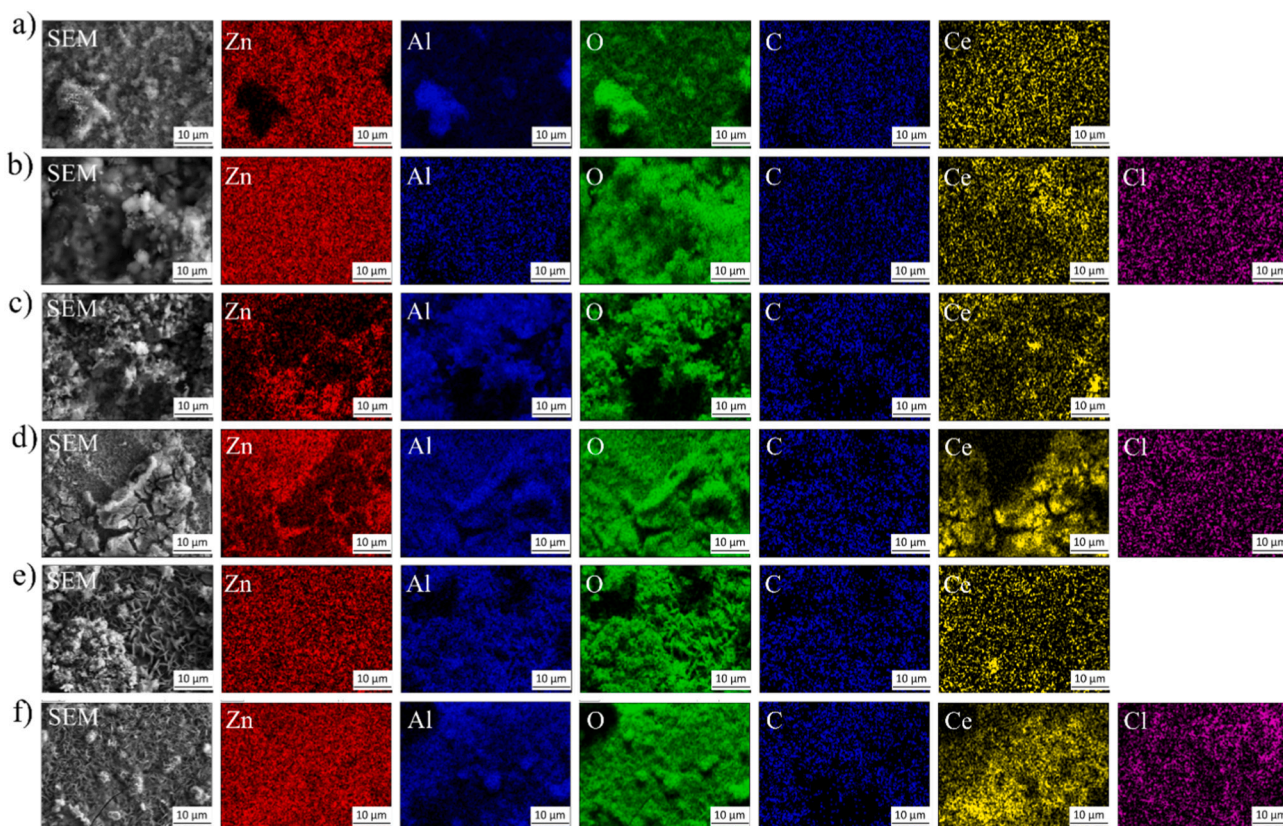


Fig. 10. EDS maps of the surface of HT-11 (a, b), HT-12 (c, d) and HT-13 (e, f) samples before and after 168 h exposure to 0.1 M NaCl.

solution pH 11. The HT nanosheets directly developed perpendicular to the surface substrates at solution pH 11 and 13 (Fig. 9a2 and 9c2). However, the HT-11 crystals had thinner structure compared to HT-13 one. It was also observed from HT-11 and HT-13 samples that the smaller HT hexagonal crystals deposited interlaced structures on the substrate (Fig. 9a1 and 9c1). In contrast, the orientation and shape of HT nanosheets in HT-12 layers were random (Fig. 9b). Compared to the HT morphology on HDG substrate in our previous study [12], the cerium cation addition changed considerably both morphology and size of HT nanosheets at the same pH solution. It can be found from the EDS (Table 2) and EDS maps (Fig. 10a, c, and e), the original HT layers mainly contained O, Al, Zn, and Ce elements, and their contents were distributed differently among the analyzed regions. The solution pH also influenced the HT layer compositions (Table 2). The O and Al concentrations were higher than those of the bare substrate, confirming the growth of HT layers. Moreover, the Al contents of HT-12 and HT-13 samples were higher than that of HT-11 sample, demonstrating the larger amount of HT crystals precipitated at solution pH 12 and 13. The Ce concentration of HT-12 layer was around 6.0–6.4 wt%, which was higher than those of the HT-11 and HT-13 layers. The previous studies found that the Ce^{3+} and Ce^{4+} ionic radii are bigger than Zn^{2+} and Al^{3+} ones, so the Ce content significantly affected the crystallization of HT [23,42]. Therefore, the HT-12 morphology was much different from the HT-11 and HT-13 ones.

Fig. 11. presents the morphology of all ZnAlCe HT layers after 168 h exposure to 0.1 M NaCl. The corrosion products on surface of HDG and HT-11 samples had microporous structures after exposure to the corrosion media. From EDS results, the appearance of Cl element and a larger O content were observed on the surface of bare substrate and HT-11 samples after 168 h exposure to 0.1 M NaCl solution, which indicated the formation of simonkolleite and ZnO as corrosion products [12]. These results were suitable for the XRD and XPS results. Several significant microcracks on the surface of HT-12 sample can be observed after

168 h (Fig. 11c). Wang et al. indicated that the cerium oxides/hydroxides precipitates can be easily broken and induce some microcracks on surface after exposure to NaCl solution [43], therefore, the cracks on HT-12 surface were related to the formation of self-repairing cerium oxides/hydroxides film. Besides, the EDS and EDS map results also indicated that the Ce content varied from region to region after 168 h, confirming the uneven precipitation of cerium oxide/hydroxide layer on the surface of HT-12 layer. The SEM result suggested the integrity and stability of HT-13 layer after 168 h of exposure to NaCl (Fig. 11d). However, the precipitation of corrosion products was observed with the formation of cracks due to the inhomogeneous internal stress on the surface of this sample. The Zn, Al, Ce, C and O elements were found on the surface of all HT layers after exposure to NaCl (Table. 2), however, the Ce and Al contents were lower compared to the original ones, confirming the partial destruction of HT nanoplates. There was no strong difference in the Al content of HT-12 and HT-13 layers, which was strongly higher than HT-11 one. In contrast, the Ce content of HT-12 was by far highest than for the other pH values, indicating that the large amount of cerium cations was also existing in HT-12 network after exposure to NaCl. Besides, the O content of all the HT layers was higher after 168 h of exposure to NaCl, confirming that the oxygen-containing products such as metals oxides/hydroxides and simonkolleite are formed on the HT surfaces. The trace amount of Cl element can be detected on the surface of HT-12 and HT-13 samples, which was related to the capture of Cl^- ions in the HT interlayer [11,12].

3.2. Corrosion protection of ZnAlCe-HT layers

3.2.1. OCP monitoring

The OCP of HDG substrate and all ZnAlCe-HT layers exposure to 0.1 M NaCl solution is shown in Fig. 12. The OCP values of all HT layers were higher than that of bare substrate, confirming that these HT layers provided much more anodic protection than cathodic one during

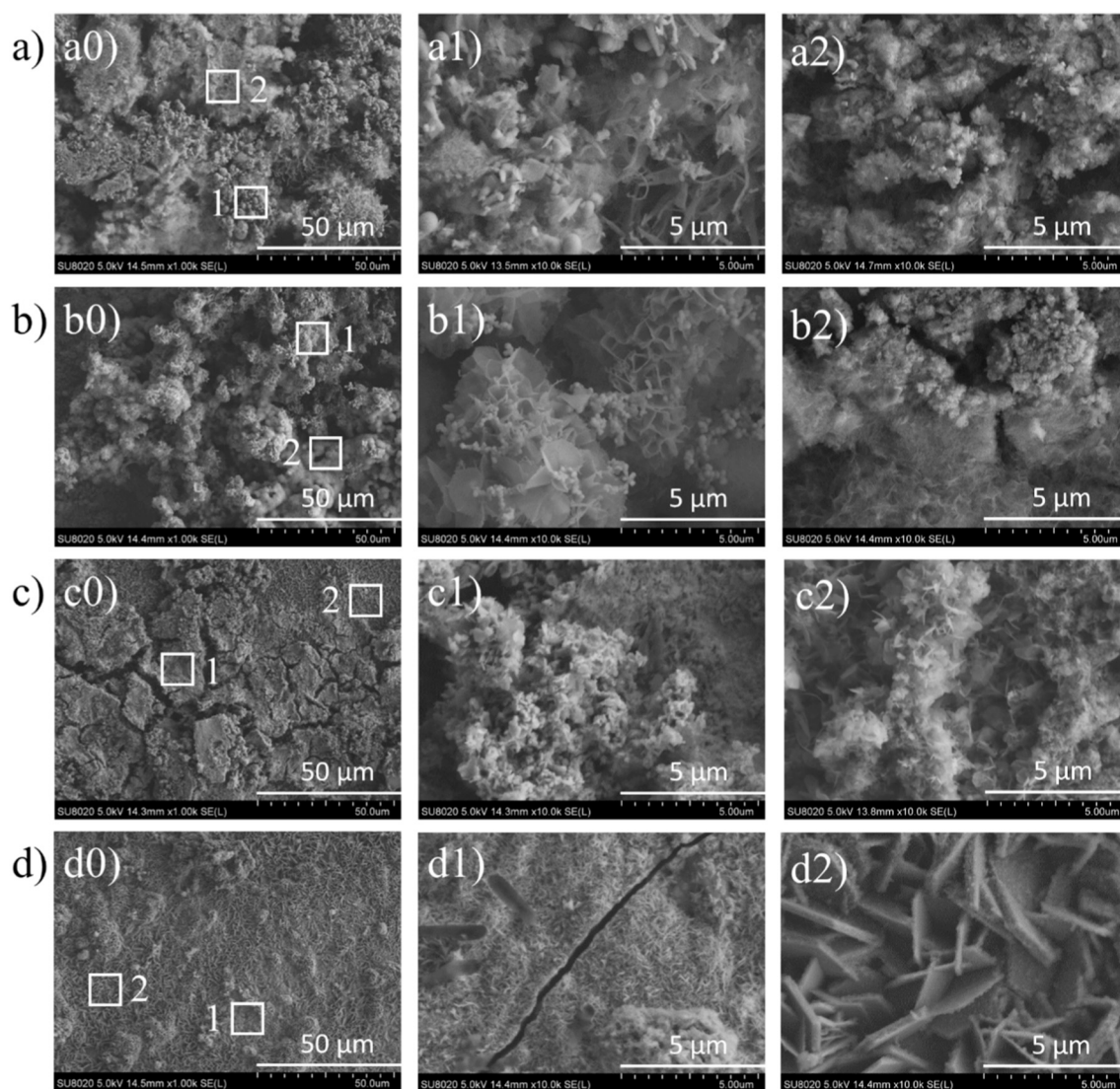


Fig. 11. SEM images of top surface of bare HDG substrate (a), HT-11 (b), HT-12 (c), and HT-13 (d) samples after 168 h exposure to 0.1 M NaCl.

exposure time. In addition, the HT-12 OCP values were more positive than those of other two samples. The OCP values of HT-11 and HT-13 samples were around -1.03 V versus Ag/AgCl. The HT-12 OCP values had a slight increase during exposure period and these values were about -0.98 V versus Ag/AgCl after 168 h.

3.2.2. Polarization curves

Fig. 13. shows the polarization curves of bare substrate and samples with ZnAlCe-HT layers after 24 h and 168 h exposure to 0.1 M NaCl. Previous studies have shown that localized corrosion can occur on zinc and its alloy coatings [2,44], moreover, it can also be observed inhomogeneity and porosity of all HT layer surfaces (Fig. 9). In contrast, the Tafel method has been applicable only for obtaining an average uniform corrosion rate when the charge transfer is the limiting step which is not the case in NaCl neutral medium [45]. In addition, the scan rate of 0.2 mV s^{-1} may result in current deviations that could lead to inaccurate corrosion current density measurements [46]. Therefore, the polarization curves were used to qualitatively evaluate the corrosion protection ability of all HT layers. Compared to bare substrate, the anodic and cathodic current densities of all the Ce-doped HT layers reduced gradually at whatever the pH condition of the precursor baths after 24 h immersion, indicating that the corrosion resistance of HDG substrates enhanced significantly with HT layers. The current density of

HT-12 sample was lower than those of two other HT samples. However, these pH values impacted closely to the current densities of HT layers as well as their corrosion resistance. Similar to our previous studies in the absence of cerium cations [11,12], the development of Ce-doped HT layers also provoked a positive shift of the corrosion potential, indicating that their HT layers had a more obvious impact on the anodic process than on the cathodic one after 24 h. The current densities of all HT layers were also significantly lower than that of bare substrate after 168 h exposure to NaCl. Like after 24 h exposure, the HT-13 current densities were not much different from HT-11 one. The HT-12 current densities continued to decrease and were significantly lower than HT-11 and HT-13 ones. In the case of HT-12 and HT-13 samples, it can be observed a plateau on the anodic branch during exposure time, which was probably attributed to their growth of HT layers acting as barrier as well as causing passivation on HDG substrates [47].

3.2.3. EIS analysis

EIS was employed to study the corrosion protection behavior of Ce-doped HT layers during 168 h exposure to 0.1 M NaCl solution (Figs. 14 and 15). For the case of bare substrate, the impedance diagrams showed two-time constants after 2 h, 72 h, and 168 h exposure to 0.1 M NaCl, thus the electrochemical equivalent circuit (EEC) in Fig. 16.a was applied to fit the EIS results: R_s was related to the solution resistance, R_{f1}

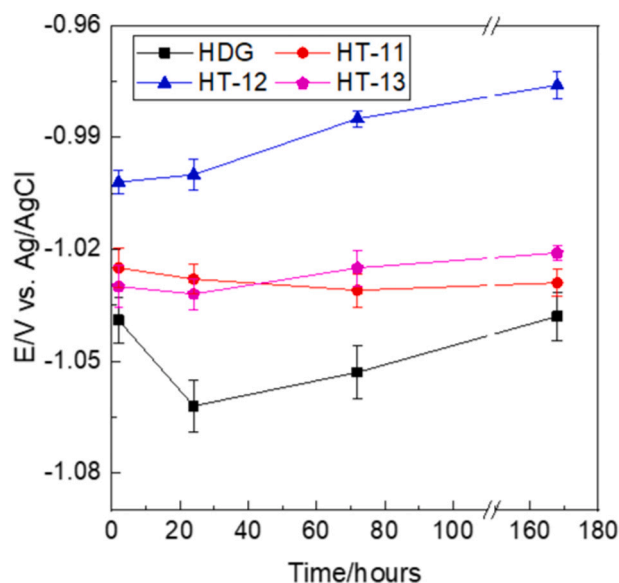


Fig. 12. OCP of bare HDG substrate, HT-11, HT-12, and HT-13 samples during exposure period.

and CPE_{f1} were related to the corrosion product layer, and R_p and CPE_{dl} corresponded to the double layer [12]. However, it can be seen a single time constant after 24 h, thus the EEC in Fig. 16.b was suitable for this EIS result [12]. Three-time constants were observed in the impedance diagrams of all the HT layer samples, thus the EEC in Fig. 16.c was employed to fitting EIS results: R_s , R_{f1} , R_{f2} , and R_p were related to solution resistance, oxide layer resistance, hydrotalcite layer resistance, and charge transfer resistance, respectively; CPE_{f1} , CPE_{f2} , and CPE_{dl} were related to oxide capacitance, hydrotalcite capacitance, and double layer capacitance, respectively [11,12]. For all the samples, the capacitive loop was not a perfect semicircle during exposure time, which may be due to the heterogeneity and porosity of sample surface (Figs. 9 and 11), thus the classical capacitance (C) was turned into a constant phase element (CPE) [12]. The results of EIS fitting were shown in Table 3.

The R_p values of bare substrate were significantly reduced from 1184 to 401 $\Omega\cdot\text{cm}^2$ after 168 h (Table 3 and Fig. 17). The microporous structure of the corrosion product layer on bare substrate (Fig. 11.a) can

be detrimental to corrosion resistance because it allows to the Cl^- aggressive anions to penetrate the layer and attack the underlying fresh zinc alloy surface. It can be noted that higher R_p values and $|Z|$ modulus at low frequencies (around 10 mHz) were reached for all HT layers compared to bare substrate (Fig. 15 and Fig. 17), claiming the improvement of corrosion resistance of HT layers. The R_p and $|Z|$ 10 mHz values of HT-12 layers were significantly higher than those of HT-11 and HT-13 ones (Fig. 17). However, the R_p and $|Z|$ 10 mHz values of HT-11 and HT-13 layers were slightly lower than that of HT layer (HT-HDG) without addition of Ce on same HDG substrate at pH 12 obtained in our previous research after the first 24 h of exposure time [12], confirming that the HT-11 and HT 13 layers did not present any enhancement in the anti-corrosion protection compared to the results for the HT-HDG. In contrast, the HT-12 layer, prepared in a similar pH condition to the HT-HDG layer, showed significant corrosion improvement for 24 h. Initially, the HT-11 R_{oxide} and R_{HT} values, which were related to the barrier properties of oxide and HT layers, were 142 and 2518 $\Omega\cdot\text{cm}^2$, respectively, and were lower than those of HT-HDG sample after 2 h of immersion. The less amount of HT crystals deposited on the surface can cause this undesirable change in the anti-corrosion properties of these oxide and HT layers (Figs. 8 and 9). This reduction in barrier properties negatively affected the inhibition of ions at the interface [28], thus the HT-11 R_p value was 5464 $\Omega\cdot\text{cm}^2$, which was also lower than that of HT-HDG. In the case of HT-13 sample after 2 h, the R_{oxide} and R_{HT} values were 162 and 4761 $\Omega\cdot\text{cm}^2$, respectively, which was not considerably different from those of HT-HDG. However, the HT-13 R_p value was also slightly lower than that of HT-HDG after 2 h. Moreover, the HT-13 CPE_{dl} value, which depended on the heterogeneities, porosity, and roughness of the electrode surface [12,27], was higher than that of HT-HDG. The decrease in HT-13 R_p value and increase in HT-13 CPE_{dl} value confirmed the reduction of corrosion protection of the HT-13 layer compared to HT-HDG layer. The porous structure of zinc alloy top coating after immersion in the precursor bath with high pH condition can be the main reason of ineffectiveness of HT layer (Fig. 8). After 2 h of exposure, the HT-12 sample showed significant barrier properties (R_{oxide} , R_{HT} , and R_p) compared to HT-HDG sample, moreover, the HT-12 CPE values were lower than HT-HDG ones (Table 3). They indicated that the partial replacement of Al by Ce into HT lamellar layer at pH value 12 presented a considerable enhancement in corrosion resistance of HT-12 sample.

During 168 h exposure to 0.1 M NaCl solution, the HT-11 R_{HT} and CPE_{HT} values did not vary significantly, while the reduction of R_{HT} values and the gradual increase in CPE_{HT} values were seen in the HT-13

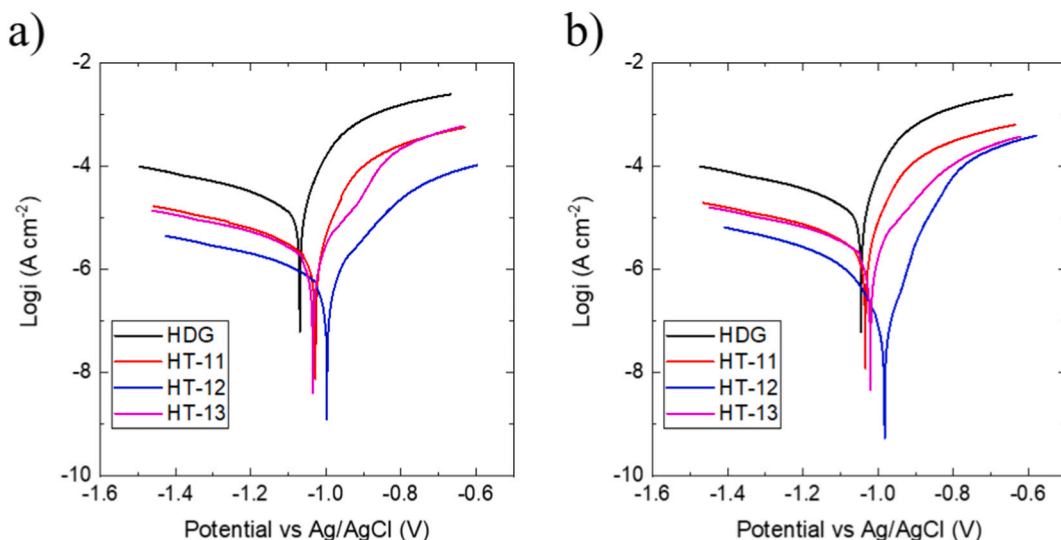


Fig. 13. Polarization curves of bare HDG substrate, HT-11, HT-12, and HT-13 samples after 24 h (a) and 168 h (b) exposure to 0.1 M NaCl.

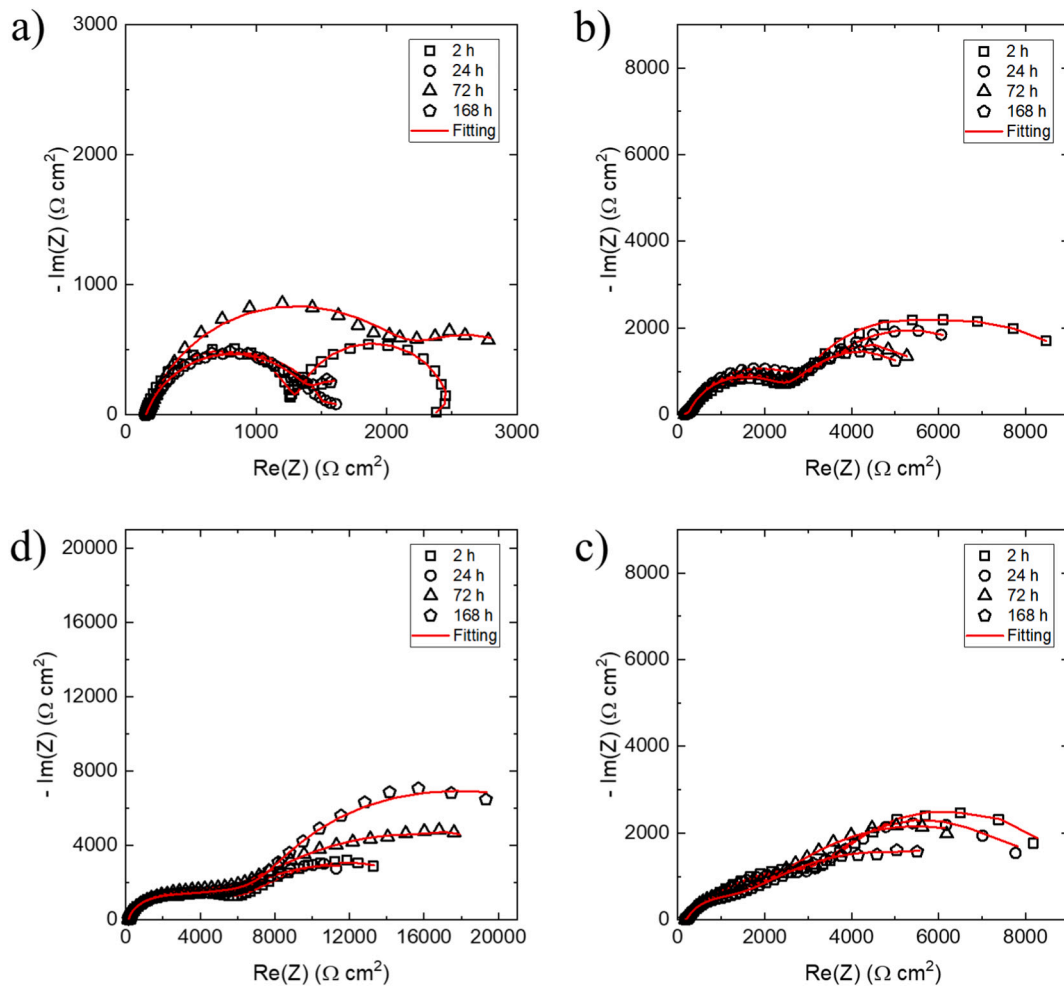
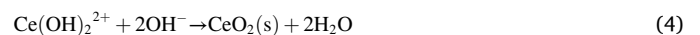
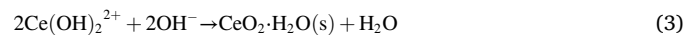
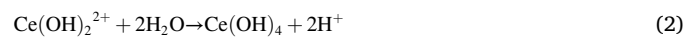
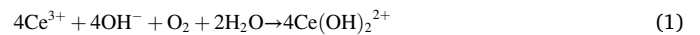


Fig. 14. Nyquist plots of bare HDG substrate (a), HT-11 (b), HT-12 (c), and HT-13 (d) samples during 168 h exposure to 0.1 M NaCl.

sample (Table 3). However, the HT-13 R_p values were slightly higher than HT-11 ones in the whole exposure time, confirming that the barrier property of HT-13 layer was slightly improved due to a larger amount of HT formed on HDG surface (Fig. 17). The decrease in R_p values and the increase in CPE_{dl} of both HT-11 and HT-13 samples after 168 h (Table 3), were due to the penetration of ions through these HT layers and the increase in electrochemical activity at the interface between surface of substrate and HT layer [48]. The corrosion protection of these HT samples did not remain long-time stable possibly due to the porous structure of upper HT layers and their microcracks (Fig. 11). In contrast, the HT-12 R_{HT} values rose slightly and the HT-12 CPE_{HT} values decreased slowly after 168 h (Table 3), indicating that the structure of HT-12 layer was more stable than those of the other two HT layers during 168 h of exposure to the corrosive solution. The previous studies confirmed that the Ce content in HT network further improved the initial anti-corrosion and durability after exposure to electrolyte for longer time [28]. Therefore, this higher stability was related to the dense morphology of initial HT-12 layer and the larger amount of Ce in HT lamellar layer (Fig. 9 and Table 2). Notice that the HT-12 R_p values rose with increase in exposure time, and this increase was two orders of magnitude after 168 h (Table 3). Besides, the HT-12 CPE_{dl} values were also stabilized in the surveyed period (Table 3). The significant improved anti-corrosion properties of HT-12 can be attributed to the dissolution of cerium cations from the HT network into the electrolyte solution, and then the precipitation of cerium oxides/hydroxides at cathodic regions [23,27].

4. Formation mechanism and anti-corrosion mechanism of ZnAlCe-HT layers

In this research, the ZnAlCe-HT conversion layers on HDG substrate were prepared by “in-situ” growth method using the same procedure as our previous study [12]. However, the Zn, Al, and Ce nitrates with a molar ratio of 3:4:1 were used in the precursor baths with a pH varying in a range from 11 to 13. The ionic radius of Ce^{3+} is considerably larger than those of Zn^{2+} and Al^{3+} , thus the Ce^{3+} intercalation into the ZnAl-HT network was very unlikely [32,42]. The precursor baths with high pH values (above 10) facilitated the oxidation of trivalent cerium to tetravalent cerium (Eqs. (1) and (2)) [23]. The ionic radius of Ce^{4+} was slightly larger than Zn^{2+} and Al^{3+} , hence these cations were easier to interleave into the HT network [42]. However, the cerium oxides can also be formed (Eqs. (3) and (4)) when the pH value of the solution increased to 12.5 [23,49]. The XRD, XPS, and EDS results confirmed the intercalation of Ce^{3+} and Ce^{4+} cations inside ZnAl-HT network.



In alkaline solutions, the Zn^{2+} and Al^{3+} exist in aqueous media by forming stable $Zn(OH)_3^{-}$ and $Al(OH)_4^{-}$ species (Eqs. (5) and (6)),

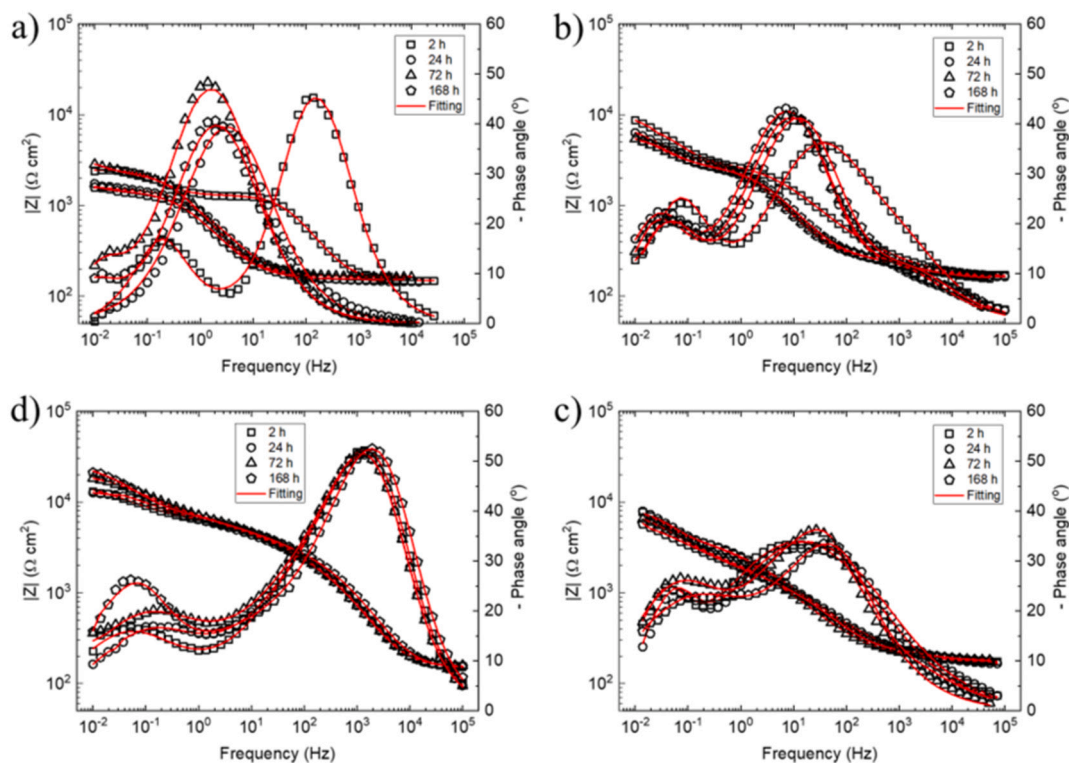


Fig. 15. Bode plots of bare HDG substrate (a), HT-11 (b), HT-12 (c), and HT-13 (d) samples during 168 h exposure to 0.1 M NaCl.

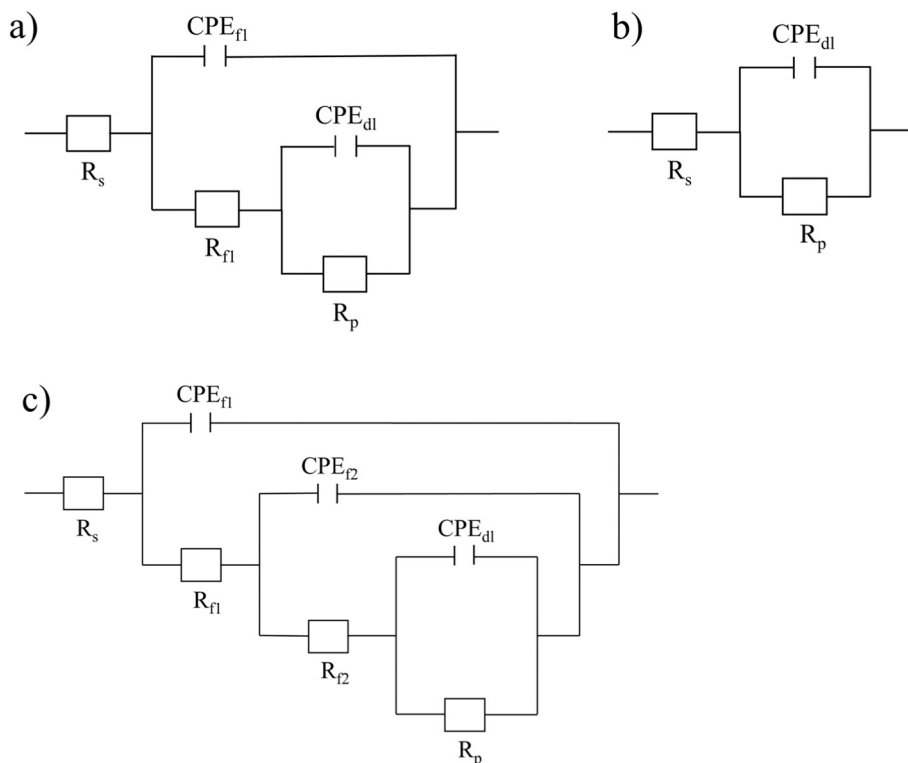


Fig. 16. EEC for the EIS data fitting of bare HDG substrate and HT-11, HT-12, and HT-13 samples.

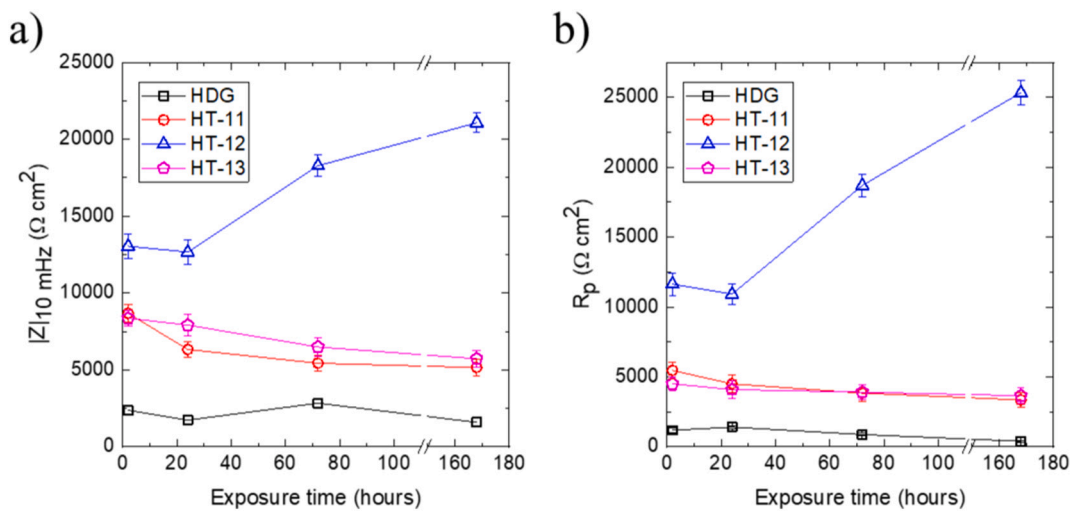
however, the concentration of $\text{Zn}(\text{OH})_3^-$ and $\text{Al}(\text{OH})_4^-$ depends on the pH solutions [6]. Zinc and aluminum are highly active metals in alkaline solutions, thus Zn^{2+} and Al^{3+} can be provided by the dissolution of the top coating of HDG substrate (Eqs. (7) and (8)) [6,12]. However, when

the pH solutions were high (above 12.6), the dissolution of Zn occurs under Eqs. (9) and (10) reactions [6]. This was the main reason explaining the characteristic peaks of ZnO on the HT-13 XRD (Fig. 2.a). Besides, the CO_3^{2-} anions were formed by CO_2 dissolution in the high pH

Table 3

Fitting parameters from EIS results for bare HDG substrate, HT-11, HT-12, and HT-13 during 168 h exposure to 0.1 M NaCl.

Sample	Exposure time (h)	CPE _{dl} (Ω ⁻¹ .s ⁿ .cm ⁻²)	n ₁	R ₁ (Ω.cm ²)	CPE _{dl} (Ω ⁻¹ .s ⁿ .cm ⁻²)	n ₂	R ₂ (Ω.cm ²)	CPE _{dl} (Ω ⁻¹ .s ⁿ .cm ⁻²)	n	R _p (Ω.cm ²)	Z _{10mHz} (Ω.cm ²)
HDG	2	5.66E-06	0.89	1167	—	—	—	9.89E-04	0.94	1184	2378
HDG	24	—	—	—	—	—	—	2.31E-04	0.76	1409	1738
HDG	72	2.58E-04	0.82	2241	—	—	—	1.51E-03	0.9	877	2841
HDG	168	3.18E-04	0.78	1329	—	—	—	4.78E-03	0.81	401	1589
HT-11	2	2.05E-05	0.65	142	1.62E-05	0.69	2518	1.02E-03	0.90	5464	8680
HT-11	24	3.44E-05	0.63	165	3.62E-05	0.81	2775	1.50E-03	0.85	4507	6336
HT-11	72	4.05E-05	0.64	164	8.41E-05	0.81	2656	1.66E-03	0.84	3844	5440
HT-11	168	6.42E-05	0.64	154	1.63E-04	0.81	2581	3.20E-03	0.83	3355	5160
HT-12	2	5.17E-06	0.88	1684	1.65E-05	0.55	4926	2.89E-04	0.73	11,640	13,049
HT-12	24	5.71E-06	0.88	1609	2.02E-05	0.52	5033	1.74E-04	0.71	10,920	12,664
HT-12	72	5.94E-06	0.88	1630	1.84E-05	0.53	5152	1.27E-04	0.82	18,700	18,282
HT-12	168	3.30E-06	0.90	1709	4.45E-05	0.55	5370	1.37E-04	0.90	25,340	21,078
HT-13	2	5.72E-05	0.53	162	2.29E-05	0.54	4761	1.63E-03	0.90	4505	8364
HT-13	24	6.95E-05	0.52	178	3.48E-05	0.53	4576	3.15E-03	0.90	4092	7918
HT-13	72	9.31E-05	0.59	341	6.39E-05	0.62	3870	4.26E-03	0.92	3908	6496
HT-13	168	1.02E-04	0.60	309	8.16E-05	0.60	3184	5.27E-03	0.87	3658	5726

**Fig. 17.** The values $|Z|_{10 \text{ mHz}}$ (a) and R_p (b) of HDG substrate and HT-11, HT-12, and HT-13 samples during exposure time.

solutions (Eq. (11)) [11]. The synthesis of the Ce-doped ZnAl-HT layers can be formed via Eq. (12). The concentration of $\text{Zn}(\text{OH})_3^-$ and $\text{Al}(\text{OH})_4^-$ present in the lower pH solution (about 11) was lower [6], therefore, it can be observed a less amount of HT crystals deposited on HDG surface (Fig. 2, 8, and 9). The concentrations of main species such as $\text{Zn}(\text{OH})_3^-$ and $\text{Al}(\text{OH})_4^-$ were large enough to form and deposit the HT building blocks on HDG substrate at pH 12 [11,12]. Besides, pH 12 was favorable for the formation of initial ZnO crystals, which were a conditioner surface leading to denser HT crystals [6]. The increase in pH solution to higher value (about 13) facilitated the dissolution of zinc coating of substrate and ZnO formation, which affect the porous of top coating of substrate as well as the microstructure and morphology of the HT layer [6]. The characteristic results also confirmed that the pH value of precursor bath at 12 was the favorable conditions for the nucleation and deposition of HT crystals as well as the intercalation of cerium cations into HT layers.

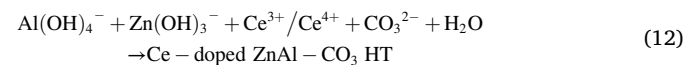
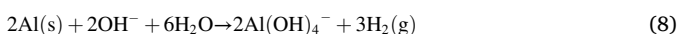
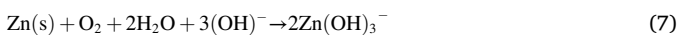


Fig. 18. presents the schematic of the Ce-doped ZnAl-HT layers anti-corrosion mechanism in 0.1 M NaCl solution. The dense HT layers played the physical barrier coatings, which avoided exposing the surface of HDG substrate to Cl^- ions of corrosive media, thus enhancing the anti-corrosion of substrate (Fig. 18.a) [12]. In addition, the HT layer with higher Ce concentration (HT-12 layer) can block its nano-pores, therefore, they prevented the penetration of Cl^- ions into the HT layer [42]. Moreover, the HT sheets were ion-exchangeable, thus Cl^- ions were trapped and restricted to move in the HT layer, which can delay the degradation of HT layer as well as substrate (Fig. 18.b) [22,23]. When the Cl^- ions infiltrated HT layers and continued attacking the fresh zinc alloy coating under HT layers, the corrosion process generated corrosion products with a porous and loose structure such as zinc oxides/hydroxides or simonkolleite, which caused the defective areas and cracks of HT layers [2,12]. The Zn^{2+} and Al^{3+} were released due to partial breakdown of HT layer [11,12]. Besides, the cerium cations from

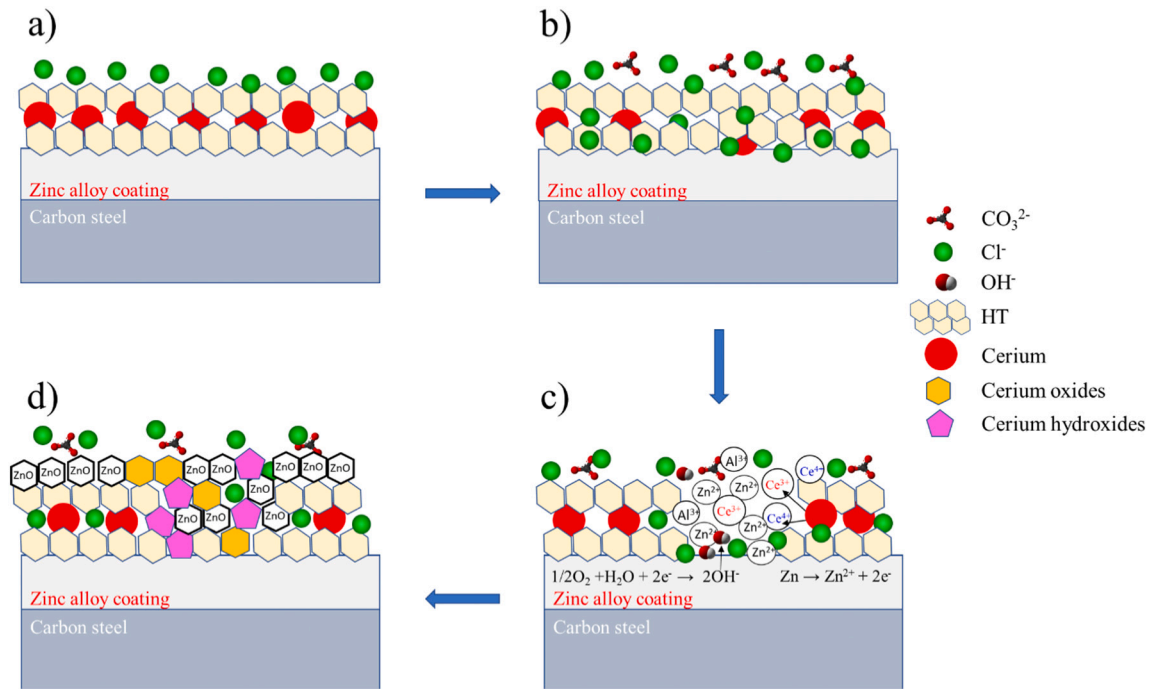


Fig. 18. Corrosion protection mechanism of ZnAlCe HT layers. The HT layers played physical barrier coatings (a); “nano-trap” of Cl^- ions (b); release of zinc, aluminum, and cerium cations in the degraded area of HT layers (c); and self-repairing metal oxides/hydroxides layer (d).

defective HT areas were released and entered the electrolyte solution during exposure period (Fig. 18.c). In the corrosion process, the OH^- species, which were formed at cathodic region due to oxygen reduction reactions, led to increase in local pH values at surface (Eq. (13)) [2,44]. According to the solubility product of zinc hydroxide, aluminum hydroxide, trivalent and tetravalent cerium hydroxide (1.2×10^{-17} , 1.3×10^{-33} , 1.6×10^{-20} and 2.0×10^{-48} at 10–20 °C), Ce^{4+} , Ce^{3+} , and Al^{3+} ions can preferentially convert to form hydroxides earlier than Zn^{2+} due to the reaction with OH^- ions. $\text{Al}(\text{OH})_3$, which was deposited on surface of samples, continued to react with Cl^- ions to form aluminum compound containing chloride and entered the solution [50]. Besides, small amount of $\text{Al}(\text{OH})_3$ was transformed into aluminum oxide due to a dehydration reaction, which was confirmed by the present Al—O bonds in XPS results [50]. Ce^{3+} and Ce^{4+} ions migrated to corrosion defects at cathodic regions and reacted with OH^- anions promoting the formation of cerium oxides/hydroxides (Eqs. (13)–(19)) [21,51]. Thus, the reprecipitation of cerium cations formed oxides/hydroxides layer, which deposited in the defected regions and surface of HT layers (Fig. 18.d) [23,42]. The cerium oxides/hydroxides deposition was able to demonstrate the self-healing ability of HT layers containing Ce. Moreover, the cerium oxides/hydroxides layer was also responsible for the formation of a protective coating [23]. These cerium compounds can reduce the oxygen reduction reaction rate and the electrochemical activity of metal. Therefore, the Ce, added to HT structures, acted as a cathodic inhibitor and enhanced the anti-corrosion of the HDG substrate. Zn^{2+} ions also reacted with OH^- ions resulting in self-healing $\text{Zn}(\text{OH})_2$ and eventually ZnO in these degraded areas at the later stage (Eqs. (20) and (21)) [11,12].



5. Conclusions

Ce-doped ZnAl-HT layers were developed on the surface of HDG substrate at the pH range from 11 to 13. However, the pH values of precursor baths impacted the HT crystal nucleation and the deposition of HT crystals on surface of substrates as well as the intercalation of cerium inside HT layer. The microstructure of the deposited HT layer was heterogeneous at pH 11. A large amount of dense HT crystals was deposited on HDG substrate at pH 13, however, a significant degradation of the top zinc coating and a larger amount of ZnO were observed. A low amount of cerium cations intercalated inside HT network at pH 11 and 13 was observed. In contrast, the pH value of precursor bath at 12 was the most suitable condition for HT layer formation as well as cerium cations intercalation into HT network. All the HT layers significantly enhanced the anti-corrosion properties of HDG substrate during 168 h exposure to 0.1 M NaCl solution. The electrochemical results also suggested that the HT-12 showed comparatively better corrosion resistance than the other two HT layers. In addition, the intercalation of cerium inside HT-12 layer showed a significant improvement of the corrosion properties compared to HT layer, which was prepared in a similar pH condition on HDG substrate [12]. The Ce-doped HT layers acted as the physical barrier coatings and “nano-trap” of Cl^- ions. Especially, the release of cerium cations from HT layers can reacted with OH^- at cathodic region, which promoted the self-repairing oxides/hydroxides layers in the degraded areas and reduced inhibited oxygen reduction reaction.

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

The data will be available under request to the corresponding author.

Acknowledgments

The authors would like to thank ArcelorMittal for providing the metallic substrate and Sebastien Colmant from Metallurgy Department for his help to prepare 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 l'expertise environnementale du centre de compétences en protection contre la corrosion et en électrochimie), and the Vietnam Academy of Science and Technology under grant number TDVLT.04/21-23.

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