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Full Length Article

# Reducing damage extent of epoxy coating on magnesium substrate by Zr-enhanced PEO coating as an effective pretreatment

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#### Abstract

This research was undertaken to study the effect of Zr-enhanced plasma electrolytic oxidation (PEO) as a pretreatment on the corrosion performance of epoxy coating applied on Magnesium in 3.5 wt% NaCl solution. The parameters of delamination index along with coating damage index were extracted through electrochemical impedance spectroscopy (EIS) tests to determine how Zr may affect the corrosion protection of duplex PEO/epoxy coated samples. Pull-off adhesion tests were also accomplished to form a better understanding of Zr-enhanced PEO coating' function. According to the obtained results, the presence of Zr can reduce the damage to the coating system by almost twice.

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Keywords: Magnesium; EIS; Pretreatment; PEO; Epoxy; Zirconyl nitrate.

### 1. Introduction

Magnesium and its alloys are commonplace in many industrial applications owing to their high strength-to-weight ratio as well as other worthwhile properties. Widespread usage of Magnesium has been somehow limited because of its low corrosion resistance and high chemical reactivity. A nonprotective surface layer consisting of Mg(OH)<sub>2</sub> and MgO<sub>2</sub> will form on the Mg surface while it is exposed to the air [1–3]. This surface layer is unstable in corrosive environments such as NaCl solutions, due to the presence of Cl<sup>-</sup> ions. Mg alloys are also susceptible to localized corrosion as due to the existence of secondary phases and intermetallic compounds, which can bring about severe corrosion in natural aqueous solutions [4].

Various coatings have been applied on Mg and its alloys to improve their corrosion resistance [5-8]. The application

of an organic coating is among the most prevalent methods to enhance the corrosion resistance of Mg and its alloys [9]. In other word, organic coatings have attracted the attention of many researchers due to their striking chemical resistance and superior protective properties [10-15]. These coatings can be used as a final coating layer in different coating systems on Mg. The presence of a non-protective layer on the surface of Mg will cause the adhesion strength of organic coating to fall dramatically during the time of immersion in a corrosive medium. [16]. Therefore, organic coatings are highly likely to delaminate from the substrate when they are exposed to harsh corrosive environments for a long time. Hence, a sharp drop in the corrosion resistance of the organic coating can be seen because of an increasing delamination area [17]. Various strategies have been taken to enhance the corrosion resistance, stability, and the durability of the organic coating throughout the whole period of plunging in corrosive media [18-21]. Some scholars used appropriate additives, selfhealing properties developed by hybrid silane organic coating and appropriate surface preparation methods [10,12,22]. As was mentioned, surface preparation is a common method to

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boost the adhesion strength of organic coatings to the substrate. Various pretreatments, such as conversion coatings and silane layers, have been applied on Mg to increase the adhesion strength and durability of epoxy coatings, as well as to postpone their delamination in severe corrosive media [23-25]. Plasma electrolytic oxidation (PEO) as an electrochemical surface treatment can be operated as a pretreatment for light metals like Mg, Al, and Ti alloys to improve the corrosion resistance and the adhesion strength of the polymer coating [26,27]. The formation mechanism of PEO coating comprise both outward growth (towards the electrolyte) and inward growth (toward the Mg substrate) which may contribute to the higher adhesion strength of the top layer to the substrate [28]. Meanwhile, PEO coating has a porous structure due to electrical discharges occurring throughout the coating process and these porosities act as pathways for the penetration of corrosive media into the coating system and causing lower corrosion performance[29]. However, pore sealing was introduced as a viable strategy to tackle with that problem. Having said that, applying epoxy layer as a top coat on PEO pretreatment will contribute to higher corrosion protection properties of PEO coating due to filling the pores. Furthermore, the presence of these pores in the PEO coating structure causes the mechanical interlocking between the epoxy coating and oxide layer [30-32]. In other word, PEO pretreatment enhances the adhesion strength of epoxy layer to the PEO coating, and the epoxy layer improves the corrosion performance of PEO coating by filling a fraction of its pores. As a result, a duplex PEO/epoxy coating system with higher corrosion resistance compared to monolayer epoxy coating was applied on Mg [21,22,33]. A summary of the previous studies on corrosion properties of duplex PEO/organic coating systems is presented in Table 1.

Moreover, the corrosion properties of the duplex coating system will also deteriorate after prolonged immersion time, as the corrosive medium will penetrate the interface of epoxy coating and Mg substrate. When the corrosive medium reaches the epoxy/substrate interface, epoxy bonds will be gradually decomposed due to the increase in the concentration of hydroxyl ions produced in cathodic reactions [34,35]. The formation of corrosion products beneath the epoxy coating at longer exposure times will also lead to even higher rate of epoxy delamination [36]. In recent studies, appropriate additives have been utilized in the composition of PEO coating to improve the corrosion resistance of duplex PEO/epoxy coating at longer period of exposure. Due to the porous structure of the PEO coating, it can be used as a reservoir for various additives such as inhibitors, and thus, the presence of some elements such as La, Ce, and Zr into the pores of PEO coating may contribute to the formation of coatings with higher densities and lower diffusion pathways for the corrosive media [38-40].

A variety of additives have been used within the PEO electrolyte, and their effects have been studied on the morphology, chemical composition, and corrosion properties of either monolayer PEO coatings or duplex PEO/epoxy coatings [41–45]. The majority of these additives improved the

corrosion resistance of coating systems, especially when used at their optimal concentration. Adding these additives to the electrolyte of the PEO coating has led to the formation of the oxide coating with pores smaller in size. Some of the Zr compounds, such as  $ZrO_2$  and  $K_2ZrF_6$ , have been also used as an additive in the PEO electrolyte and resulted in the noticeable enhancement of corrosion resistance of the PEO coating in comparison with other additives [38, 46-48].

In similar studies, adding different salts containing Zr in the PEO electrolyte resulted in the formation of  $ZrO_2$  in PEO coating thereby higher corrosion resistance than PEO coating without Zr, with lower solubility of  $ZrO_2$  compared to MgO in NaCl solution [49–51]. In another study, zirconyl nitrate was used as an additive in the sol-gel coating process on mild steel. PEO coatings containing Zr showed higher corrosion performance compared to PEO coating without Zr, due to the presence of a Zirconium oxide which is more stable than MgO [52].

In this study, Zr-enhanced PEO coating was employed as a pretreatment of epoxy coating applied on commercial Mg. Various concentrations of zirconyl nitrate were added to the PEO electrolyte, and then their effects were investigated on the corrosion protection performance of samples, both PEO and Duplex PEO/epoxy coatings. It is worth noting that the weight percentage of Zr in the composition of oxide coating was higher than other additives such as Cerium and Lanthanum considering the primitive consumption concentration of zirconyl nitrate and the other additives in the electrolyte of PEO. Furthermore, the inductively coupled plasma-optical emission spectrometer (ICP-OES) test was conducted to investigate the release of Zr<sup>4+</sup>in the corrosive solution. The adhesion strength of epoxy coating on PEO pretreatment was considerably improved with the addition of zirconyl nitrate to the PEO electrolyte. According to the description provided and as a research innovation, complete investigation has been done to ascertain how PEO pretreatment formed in the presence of zirconyl nitrate could increase the corrosion performance of epoxy coating. In this route, two parameters of coating damage extent and coating delamination index were identified for different duplex PEO/epoxy coating as well as monolayer epoxy coating at different immersion times. The results showed a fall of roughly 50% in these parameters for Duplex-6Zr compared to the monolayer epoxy coating.

# 2. Experimental procedure

#### 2.1. Sample preparation

Commercial grade Magnesium (99.1% wt. Mg, 0.3% wt. Al, 0.15% wt. Zn, 0.24% wt. Mn, 0.2% wt. Si, 0.001% wt. Fe, 0.0005% wt. Ni) served as the substrate to eliminate the effect of alloying elements on the final results and maintain the simplicity of the system. First, the specimens were cut in dimensions of  $4 \times 2.5 \times 0.2$  cm<sup>3</sup> and then they were abraded with sandpapers (#600 to 3000) to reach a roughness of R<sub>a</sub><0.5 µm. Afterward, the prepared samples were washed with de-ionized water and were dried.

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#### Table 1

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Summary of previous studies in which properties of duplex PEO/organic coating system have been studied.

Substrate	Coating system	Electrolyte of PEO process	Polymer layer	Thickness (µm) (PEO/polymer layer)	Results	Ref.
AZ31	PEO/silane/epoxy	Na <sub>3</sub> PO <sub>4</sub> +KOH+Ce(NO <sub>3</sub> ) <sub>3</sub> •5H2O	Ероху	(13,15)	Higher corrosion resistance due to a silane layer between PEO and	[25]
AZ31	PEO (with inhibitor)/epoxy	Na <sub>3</sub> PO <sub>4</sub> +KOH+CeO <sub>2</sub>	Ероху	(12–15,30)	epoxy coatings. CNPs additives in PEO coating used to higher corrosion resistance and higher adhesion strength of duplex PEO/epoxy coating.	[29]
AZ31	PEO/epoxy(with inhibitor)	NaAlO <sub>2</sub> + NaOH	Epoxy doped with CeNaX	(Not mentioned/20)	Good self-healing ability of epoxy resin doped with CeNaX and coated on PEO coated AZ31 against corrosion.	[18]
AZ91D	PEO/polymer	Na <sub>2</sub> SiO <sub>3</sub> +KOH+C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	Polyurethane resin+BaSO4	(14,92)	Good protection of Mg alloys against corrosion and tribological wear by the aid of applying B-coating on the surface of PEO pretreatment on Mg.	[11]
AZ31	PEO/BTESPT/Epo	Na <sub>2</sub> SiO <sub>3</sub> +KOH xy	Ероху	(7,25)	Promoted corrosion protection property of epoxy coating on PEO coated AZ31 by formation of a thin BTESP silane film on the substrate.	[21]
AZ31	PEO/polymer	Na <sub>2</sub> SiO <sub>3</sub> +KOH	polypropylene	(not mentioned)	High corrosion resistance of PEO coated Mg due to pore filling by PP coating thereby reducing the diffusion path (PEO coating's porosities).	[19]
AZ91D	PEO/Epoxy	Na2SiO3+Na3PO4+Na2CO3	Mg-rich primer(MRP)	(6130)	PEO coating significantly caused to increase the lifetime of MRP.	[43]
ZE41	PEO/hybrid	Na2SiO3+NaOH+KF	Epoxy+EDTA +APTES	(\$2,10)	Considerable improvement in the corrosion protection of ZE41 alloy by sealing the anodic layer with the hybrid epoxy-silane coating and stronger mechanical inter-locking due to better morphology of PEO coating in presence of polyethylene oxide.	[17]
AZ31	PEO/polymer	Na <sub>2</sub> SiO <sub>3</sub> +KOH	Poly (ether imide) Ultem 1000	(12,25)	Superior corrosion resistance of duplex PEO/ polymer coating on AZ31 substrate at long term immersion without appearing the signs of corrosion attack at the surface of substrate.	[34]
ZK30	PEO/hybrid (with inhibitor)	Na <sub>3</sub> PO <sub>4</sub> +NaOH+KF+Al(OH) <sub>3</sub>	TiO <sub>2</sub> +GPTMS	(3,4)	Great adhesion strength of polymer coating to the PEO coating and higher corrosion resistance of complex coating on Mg substrate due to that PEO coating acted as a reservoir for the inhibitor and then formation of a less soluble passive layer on the surface of substrate	[44]

### 2.2. PEO coating process

PEO coating was applied on the Mg samples using a highvoltage power supply (600 V, 2.5A, 750 W) at a constant current density of 0.1 A/cm<sup>2</sup>. The coating process continued for 10 min after sparks showed up. DC current mode was employed to eliminate the influence of pulse parameters on the results, such as frequency and duty cycle, and to keep the system as simple as possible. PEO coating process was conducted in a stainless-steel chamber which acted as the cathode while the Magnesium specimens acted as the anode. A brass rod with a hole on it was used for hanging the samples in the solution. Besides, an alkaline phosphate based solution containing 5 g/l Na<sub>3</sub>PO<sub>4</sub> and 2 g/l KOH was used as the electrolyte of the PEO coating process, with different concentrations (0, 0.1, 0.6 g/l) of zirconyl nitrate (pure analytical grade). All these consumable materials were purchased from Merck Co. The electrolyte was continuously stirred throughout the PEO coating process, and the temperature of the electrolyte was kept constant at 25 °C using a cooling system.

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At the end of the process, samples were washed with deionized water and then dried. For the ease of documentation, all PEO coated samples were coded as PEO-0Zr, PEO-1Zr, and PEO-6Zr in the case of 0, 0.1, and 0.6 g/l zirconyl nitrate in the PEO electrolyte, respectively. The thickness of PEO coatings was measured through a portable thickness gauge (Q nix 8500, Germany).

### 2.3. Epoxy coating

The epoxy coating was formed, first blending the epoxy resin (Silikopon EF) and the hardener (3-Aminopropyltriethoxysilane, 98%) as a curing agent with a weight ratio of 80:20 for 10 min. The mixture's bubbles were removed by putting it in an ultrasonic bath for 30 min. At the next stage, the epoxy coating was applied as a top coat through dip-coating method. It is worth noting that another Mg sample without PEO pretreatment was also polished with 600, 800, 1200, 1500 emery paper and then degreased by acetone, for the sake of comparison. Next, this prepared Mg sample and all of the PEO coated samples were dipped into the prepared mixture for 10 s and then were stored for 7 days at room temperature in the clean room to complete the curing stage of the epoxy coating. Finally, samples were placed in an oven and heated at 120 °C for 1 hour to ensure the completion of the epoxy coating curing process. The thickness of final epoxy coatings was measured through the portable thickness gauge too, which remained roughly 40  $\pm$  2  $\mu$ m. The duplex coated samples containing 0, 0.1 and 0.6 g/l zirconvl nitrate in the PEO electrolyte were respectively coded as Duplex-0Zr, Duplex-1Zr and Duplex-6Zr.

# 2.4. Characterization

## 2.4.1. Surface characterization

The top surface and the cross-section morphologies of the monolayer PEO coated samples with and without Zr were evaluated by scanning electron microscope (SEM) (FEI ESEM QUANTA 200, 25 kV). Furthermore, the crosssection of the samples was evaluated by energy dispersive spectroscopy (EDS) (EDAX EDS Silicon Drift 2017), as well as an elemental map and linear scan analyses in the case of all samples. Before the morphological analysis, all specimens were cut slowly in dimension of 1 cm<sup>2</sup> by a low speed diamond saw and then they were mounted on a cold mount epoxy resin. In the next stage, they were polished via emery papers (#600 to 3000) followed by a process of polishing via suspension solution containing alumina colloidal particles for 30 min.

In the meanwhile, the surface free energy of monolayer PEO coated samples were calculated with the static contact angle of a distilled water droplet on the surface of samples using an OCA 15 plus type contact angle measuring system. For this purpose, a small droplet of distilled water  $(3-4 \ \mu l)$  was poured on the PEO surface, and after 10 s the shape of

the droplet was captured by a Canon digital camera. Measurements were then carried out at the temperature and humidity of  $25 \pm 2$  °C and  $30 \pm 5\%$ , respectively. The contact angles were calculated using Image J software.

# 2.4.2. EIS measurements

The corrosion properties of PEO coated and PEO/Epoxy coated samples with and without Zr were studied by EIS test (ASTM G106) equipped with an EC lab biological SP300 device. The conventional three-electrode cell containing a saturated calomel electrode (SCE) as a reference electrode, a platinum foil as a counter electrode and the sample as the working electrode was used in this test. The cell was placed in a faraday cage to reduce the amount of noise throughout the test time frame. The EIS test was done on the PEO coated samples by immersing them in 0.5 wt.% NaCl, and the test was run at different immersion times up to 7 days. Furthermore, the duplex PEO/epoxy coated samples were immersed in 3.5 NaCl for 40 days. After 2 days of open circuit potential (OCP) stabilization, the EIS test was performed and repeated at different times until the 40th day. The exposed surface area of samples to the corrosive solution was 0.785 cm<sup>2</sup>, and the temperature of the NaCl solution was  $24 \pm 2$  °C. In addition, the frequency range was kept at  $10^5$  to  $10^{-2}$  Hz using the voltage range of  $\pm 10$  mV (vs. SCE / sat KCl). Each test was repeated at least three times to ensure both the repeatability of the test as well as the reliability of the results. In the case of PEO coated samples, the data of EIS spectra were fitted by Zsim software to discover the associated values with equivalent circuit elements. Moreover, the top view of exposed surfaces of monolayer epoxy coated sample, as well as all PEO/epoxy coated samples were studied in terms of corrosion effects using an optical microscope.

# 2.5. Pull-off adhesion test

The pull-off adhesion test in dry and wet environments was carried out to investigate the adhesion strength of epoxy coatings on PEO pretreatment. The dimension of samples was  $3 \times 3 \text{ cm}^2$  in both wet and dry adhesion tests. Prior to the wet adhesion tests, the duplex PEO/epoxy coating samples were exposed to the atomized 5 wt.% NaCl solution (pH 7.0, temperature 40 °C) for 72 h in a salt spray container. Aluminum dollies with 2 cm diameter were glued on the epoxy surface by deploying a double-sided Araldite 2015 glue. The samples were then left at the room temperature for one day to ensure the complete curing of the adhesive. The Posi-testpull-off adhesion tester (Defelsko) was utilized to module the adhesion strength of the epoxy coating on the PEO coating. Before all the adhesion tests, the surface of the duplex coating around the dollies was eroded to remove the bonding between the epoxy coating beneath the dolly from the part which was out of the circle. To start the pull-off test, the dollies were pulled out of the surface of the samples at a constant speed of 5 mm/min in a direction perpendicular to the coating. The test was kept on until the dollies were fully detached from

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the surface of the samples. All tests were repeated three times to ascertain the reliability of the results.

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### 2.6. ICP-OES test

ICP test was performed to investigate the release of  $Zr^{4+}$ ions from PEO coating in a 3.5 wt.% NaCl solution. For this purpose, two reference electrolytes and one unknown electrolyte were provided. For preparing reference electrolytes, 5 g/l Na<sub>3</sub>PO<sub>4</sub> and 2 g/l KOH, as well as particular concertation of ZrO(NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O for each electrolyte were solved in distilled water to reach the Zr concentrations of 100 and 50 ppm. Moreover, for the preparation of the unknown electrolyte, the PEO coating with the dimension of  $3 \times 3 \times 0.2$ cm<sup>3</sup> was completely shaved from the Mg surface, and all the shaved coating powder was poured into a 100 ml 3.5 wt.% NaCl solution. The unknown electrolyte was stirred continuously for 3 days, and each day 3 ml of this electrolyte was evaluated through ICP test. Finally, Zr ion concentration in the unknown electrolyte was calculated by fitting an appropriate curve on 3 values related to Zr intensity for both reference electrolytes and water (Zr concentration = 0 ppm).

### 3. Results and discussion

First, all PEO coated samples were examined in terms of morphology, chemical composition, and corrosion protection performance to find how pouring zirconyl nitrate in phosphate-based electrolyte would impact the mentioned properties of the coatings.

### 3.1. PEO coating characterization

### 3.1.1. Surface characterization

The top surface and cross-section SEM micrographs of PEO coated samples as well as EDS results obtained from the cross-section of the coatings, are presented in Fig. 1. As can be observed in top surface images, the overall morphology of all PEO coatings contains pores and cracks. However, the number and size of these pores are different for each coating. The pores and cracks were generated due to gas evolution in the discharge channels and thermal stress caused by quick solidification of the molten substance, respectively [53,54]. The PEO coating process takes place at voltages higher than the voltage where sparks begin to appear on the Mg surface. Then, the substrate and oxide layer partially melts and the molten substance is ejected into the cool electrolyte due to the high energy generation of electric discharge. There might be some elements originated from PEO electrolyte inside the quenched erupted molten oxide which can get involved in the reactions taken place in discharge channels [55]. It is worth noting that the composition of the electrolyte has a prominent effect on the intensity of sparks as well as the size of the pores. As a result, the electrolyte's chemical composition has a significant role in the final composition and even the structure of PEO coating. Looking to details in Fig 1. a, d and g, it is axiomatic that adding zirconyl nitrate to the PEO



Fig. 1. Surface and cross-section SEM images along with EDS results associated with the selected part of PEO coated samples. (a, b, c) PEO-0Zr; (d, e, f) PEO-1Zr; (g, h, i) PEO-6Zr.

electrolyte has reduced the average pore size. Moreover, the pores seem to be filled in the presence of zirconyl nitrate additive, and this is even more obvious in the case of PEO-6Zr. Another series of top surface images at lower magnification were also taken for all the samples and presented in Fig. S1. These images also indicate that the pores seem to be filled in the case of the Zr-enhanced PEO coatings. Filling the pores can further affirm that Zr has participated in coating formation reactions which occurred within the electrical discharge channels. Besides, the surface area of pores in PEO coatings had been evaluated through image J software and the results were some 18%, 15% and 9% for PEO-0Zr, PEO-1Zr and PEO-6Zr, respectively. These results demonstrated the positive role of zirconyl nitrate in improving the morphology of PEO coating. It should be noted that higher concentrations of zirconyl nitrate, were also added to the electrolyte of PEO coating. However, the associated coating wasn't of the proper quality for further investigation. Based on previous researches, excessive presence of the additive in the PEO electrolyte solution (more than an optimum amount) causes a decrease in the conductivity of the solution as well as disrupting the ignition of the PEO process, which ends up with an undesirable coating [56,57].

According to the cross-section images, the general crosssection morphology of all the samples is roughly equal. Based on SEM results and thickness gauge measurements, the thicknesses of PEO coatings were  $10\pm1$ ,  $12\pm1$  and  $16\pm1$  µm for PEO-0Zr, PEO-1Zr and PEO-6Zr, respectively. Indeed, PEO coating which formed without adding zirconyl nitrate in the electrolyte had the lowest thickness however, the thickness of Zr-enhanced PEO coatings were higher. It is worth noting that the most influential factor on PEO coating properties, such as its thickness, is the chemical composition of the electrolyte

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Fig. 2. EDS map analysis as well as line scan result related to PEO-6Zr sample.

[58]. Therefore, additives can help fabricate coatings with a higher thickness and oxide growth rate and enable the entry of ions into the discharge channel by increasing the intensity of sparks [59,60].

According to the EDS results, the PEO coating has Mg, Na, O, Al and P in its composition when there is no zirconyl nitrate added to the electrolyte and there were all these elements along with Zr in the case of Zr-enhanced PEO coatings. Regarding the weight percentages, Mg showed the highest figure which is due to formation of PEO coating mainly from molten Mg. It is also axiomatic that the weight percentage of Zr was increased by adding higher concentration of zirconyl nitrate in the PEO electrolyte. Such an increasing trend has also been reported in similar studies [47,61]. The remarkable point was the weight percentage of Zr in the composition of oxide coating, which was higher than the other elements such as cerium and lanthanum considering the primary consumable concentrations of the aforementioned additives [37,62].

Elemental mapping accompanied by line scan analysis were carried out for PEO-6Zr and the results are shown in Fig. 2. The elements of Mg, O, Na, P, Al, and Zr are exist in the coating, and as can be observed from the mapping result, Zr was uniformly distributed all over the PEO coating. The results of line scan analysis also confirmed that Zr distributed uniformly in the PEO coating. Fig. S2 and Fig. S3 also illustrate the results of the elemental map and line scan analyses in the case of PEO-0Zr and PEO-1Zr, respectively.

#### 3.1.2. EIS measurements

The EIS test was carried out to investigate the effect of zirconyl nitrate on the corrosion protection performance of all PEO coated samples in 0.5 wt.% NaCl solution over a week. The Bode-modulus and Bode-phase diagrams extracted from EIS tests are shown in Fig. 3. The EIS tests were re-

peated 3 times to ensure the authenticity of the results and the error bars were calculated by averaging the three values. Moreover, the equivalent circuits contained two or three time constants in the presence or absence of the inductor Fig. 4. Two time constants were dedicated to PEO coating due to its structure that contained an outer porous layer and an inner dense layer. The equivalent circuits include  $R_s$ ,  $R_o$ ,  $CPE_o$ ,  $R_i$ ,  $CPE_i$ ,  $R_{ct}$ ,  $CPE_{dl}$ ,  $R_l$  and L which are defined as solution resistance, resistance and constant phase element of the outer porous layer, resistance and constant phase element of double layer, respectively. Moreover,  $R_l$  is the resistance of localized corrosion with an inductance (L).

The corresponding values of the defined parameters at different times of exposure are given in Table 2. These values were obtained by averaging values out of three performed measurements. Two time constants at higher frequencies are related to the outer and inner layers of PEO coating, and the time constant at lower frequencies is attributed to the electrochemical activities on the surface of the Mg substrate. The resistance of the outer layer was not significant due to its porous nature and has not remained constant as seen in the Bode-modulus. For all the samples, the time constant of the double-layer appeared only after 1 hour, proving that the PEO coating was unable to efficiently hamper the diffusion of corrosive solution even at early stages, so the corrosive solution electrolyte had reached the surface of the Mg substrate [63]. Corrosive ions, water, and oxygen molecules began penetrating the PEO coating mainly through its pores which act as diffusion pathways for these corrosive agents [64,65]. The values of  $R_o$  and  $R_i$  showed a radical decrease until 24 h. These values were increased at 72 h maybe because of the barrier effect of MgO and Zr-based compounds. At longer period of time, though, the corrosive agents pene-



Fig. 3. Bode-modulus and Bode-phase plots of (a) PEO-0Zr; (b) PEO-1Zr; (c) PEO-6Zr, exposed to 0.5 wt.% NaCl solution for 1 week.



Fig. 4. Equivalent circuits were used to fit the EIS data with (a), (b) at shorter time of immersion (c), (d) at higher time of immersion. All PEO coated samples were plunged in 0.5 wt.% NaCl solution for 1 week.

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#### Table 2

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Extracted electrochemical parameters by equalization of impedance data with appropriate equivalent circuits for PEO coated samples, at various immersion times of exposure in 0.5 wt% NaCl solution; each test repeated at least 3 times to check the reliability of results.

	Time(h)	$R_o^a(\Omega.cm^2)$	CPEO		$R_i{}^a(\Omega.cm^2)$	CPEi		$R_{ct}{}^a(\Omega.cm^2)$	CPE <sub>dl</sub>		$R_L^a(\Omega.cm^2)$
sample			$\overline{Y_o{}^b(\Omega^{-1}~cm^{-2}~S^n)}$	n <sup>c</sup>		$\overline{Y_o{}^b(\Omega^{-1}~cm^{-2}~S^n)}$	n <sup>c</sup>		$\overline{Y_o{}^b(\Omega^{-1}~cm^{-2}~S^n)}$	n <sup>c</sup>	
PEO-0Zr	1	112	$5.23 \times 10^{-6}$	0.85	959	$2.23 \times 10^{-7}$	0.89	59,000	$1.08 \times 10^{-6}$	0.89	14,850
	24				206	$3.40 \times 10^{-7}$	0.84	11,510	$6.18 \times 10^{-6}$	0.9	1245
	72	290	$1.50 \times 10^{-6}$	0.78	439	$2.50 \times 10^{-7}$	0.79	7906	$2.50 \times 10^{-6}$	0.88	2475
	120				230	$4.20 \times 10^{-7}$	0.86	5400	$5.30 \times 10^{-6}$	0.93	1860
	168	40	$1.10 \times 10^{-6}$	0.86	87	$3.10 \times 10^{-6}$	0.78	4669	$6.20 \times 10^{-6}$	0.9	
PEO-1Zr	1	190	$2.50 \times 10^{-7}$	0.82	1120	$3.20 \times 10^{-6}$	0.88	62,450	$2.10 \times 10^{-6}$	0.87	
	24	110	$4.30 \times 10^{-6}$	0.78	180	$2.60 \times 10^{-7}$	0.79	21,000	$3.40 \times 10^{-6}$	0.83	8760
	72	340	$3.20 \times 10^{-6}$	0.84	590	$6.70 \times 10^{-6}$	0.89	12,765	$8.60 \times 10^{-6}$	0.9	6800
	120				450	$1.30 \times 10^{-7}$	0.85	9650	$4.10 \times 10^{-6}$	0.78	5140
	168	65	$6.30 \times 10^{-6}$	0.76	160	$4.70 \times 10^{-6}$	0.75	3400	$1.20 \times 10^{-6}$	0.84	3263
PEO-6Zr	1	260	$3.20 \times 10^{-6}$	0.89	1200	$3.50 \times 10^{-7}$	0.87	67,000	$4.20 \times 10^{-6}$	0.9	16,780
	24				410	$1.50 \times 10^{-6}$	0.82	23,600	$3.80 \times 10^{-6}$	0.88	
	72	410	$6.50 \times 10^{-7}$	0.8	740	$4.80 \times 10^{-7}$	0.78	15,400	$2.10 \times 10^{-6}$	0.84	9500
	120	210	$9.10 \times 10^{-6}$	0.79	520	$3.80 \times 10^{-6}$	0.86	11,000	$6.70 \times 10^{-5}$	0.79	7634
	168	95	$7.30 \times 10^{-6}$	0.86	210	$7.80 \times 10^{-6}$	0.89	5600	$5.40 \times 10^{-5}$	0.83	4370

 $^a$  The standard deviation ranges for  $R_o,\,R_i,\,R_{ct}$  and  $R_L$  values are between 1.7% and 3.9%.

<sup>b</sup> The standard deviation range for  $Y_0$  values is between 1.1% and 4.3%.

<sup>c</sup> The standard deviation range for n values is between 0.5% and 1.5%.

trate more thereby showing a downward trend once again at 168 h.

The impedance modulus values at 10 mHz frequency  $(|Z|_{0.01 \text{ Hz}})$ , as well as the capacitive response region (where the slop of the Bode-modulus plot is -1) start to decrease due to the penetration of the corrosive solution into the PEO coating [45]. However, the drops in both  $|Z|_{0.01 \text{ Hz}}$  and capacitive response region were not similar for all the PEO coated samples, they were much lower in the case of PEO-6Zr in comparison with the other samples. The  $|Z|_{0.01 \text{ Hz}}$  for PEO-0Zr was decreased by about two orders of magnitude after 1 week, whereas this drop was even twice lower in the case of PEO-6Zr over the same period. Furthermore, the frequency ranges of capacitive response became shorter for all samples passing the immersion time, whereas the PEO-6Zr sample exhibited capacitive response at wider frequency range than the other samples during the entire immersion process. In conclusion, adding zirconyl nitrate to the electrolyte of PEO coating caused to enhance the corrosion performance of PEO coating on Mg substrate. Furthermore, in the case of a few PEO coated samples, the positive phase angles at low frequencies of the Bode-phase diagram as well as the drop in impedance modulus values at low frequencies in the Bodemodulus diagrams indicate the initiation of local corrosion on the Mg substrate [32,41]. Therefore, an inductor element (L) was added to the equivalent circuit to demonstrate the occurrence of localized corrosion on Mg specimens.

For further insight into the subject, variations of  $|Z|_{0.01 \text{ Hz}}$  versus immersion time were extracted from Bode-modulus plots for all PEO coated samples and shown in Fig. 5. It can be seen that the PEO-6Zr sample has the highest impedance modulus and the lowest drop compared to the other samples across the time frame. In addition, the higher density and thickness of PEO-6Zr proved to be the effective factors in



Fig. 5. Variation of impedance modulus value at 10 mHz versus immersion time for PEO coated samples with and without Zr, immersed in 0.5 wt.% NaCl solution for 1week.

its higher corrosion resistance. Moreover, Zhuang et al. [60], used  $K_2ZrF_6$  in the electrolyte of PEO coating and XRD results proved the presence of  $ZrO_2$  in PEO coating. There are other similar studies in which adding Zirconium containing salts to the electrolyte of PEO coating contributed to the presence of  $ZrO_2$  in the coating [44,49,51,61]. Nevertheless, Zirconium oxide is more likely to form since it has higher stability than Magnesium oxide. In this concern, HSC chemistry 6 software was deployed to ensure whether  $ZrO_2$  is more likely to form than MgO. The associated results are shown in Fig. 6. As can be seen,  $\Delta G$  values for MgO are much more than those for  $ZrO_2$ . Therefore,  $ZrO_2$  is more likely

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Fig. 6. Thermodynamic calculations associated with two possible reactions during the immersion period by HSC software.

to form than MgO. For further investigation, the solubility of these oxides were taken into account. The solubility of MgO at room temperature is 0.0068 g/l [66], however, it is almost  $10^{-7}$  for ZrO<sub>2</sub> at the same temperature [67], which is much lower. These solubility statistics also show that Zr has a higher tendency to form an oxide than Mg.

On the other hand, ICP test was employed after the first, second, and third days of exposure to check whether  $Zr^{4+}$  is likely to originate from the PEO coating in the NaCl solution. For this purpose, the concentration of Zr ion was measured daily up to the third day. The results indicated a 17.3 ppm  $Zr^{4+}$  in the corrosive solution after 1 day which was increased to 34.6 ppm on the second day, and 33.7 ppm on the third day. The concentration of Zr on the last two days had been almost equal. Zirconyl nitrate was added to the electrolyte of PEO coating as an anodic inhibitor. Concerning whether zirconyl nitrate is an anodic inhibitor or not, a majority of nitrates are anodic corrosion inhibitors [68]. However, in some research, zirconyl nitrate has been used as an inhibitor [69–



Fig. 7. Bode-modulus and Bode-phase plots of (a) monolayer (epoxy) (b) Duplex-0Zr (c) Duplex-1Zr (d) Duplex-6Zr at different time of immersion in 3.5 wt.% NaCl solution for 40 days.

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Fig. 8. (a) Variation of  $|Z|_{0.01Hz}$ , (b)  $\Theta_{10kHz}$  and (c)  $f_b$  values versus immersion time for monolayer epoxy coated sample and duplex PEO/epoxy coated samples with and without Zr, immersed in 3.5 wt.% NaCl solution for up to 40 days.

71], and its anodic inhibitory effect was also proved [53]. According to the ICP results and due to the composition of the PEO electrolyte solution, it seems that the  $Zr^{4+}$  released from the unstable compounds such as zirconium phosphate formed during the PEO process.

# 3.2. Duplex PEO/epoxy coating

The microstructure of Duplex-6Zr sample at two different magnifications is shown in Fig. S4. It seems that the epoxy layer entered into the porosities of PEO coating and caused mechanical interlocking between PEO coating and the epoxy layer.

### 3.2.1. EIS measurements

The EIS test was carried out on the monolayer epoxy coated sample as well as duplex epoxy/PEO coated samples

with and without Zr in 3.5 wt.% NaCl solution for up to 40 days, to investigate the effect of Zr-enhanced PEO coating as a pretreatment for epoxy coating applied on Mg substrate. Bode-modulus and Bode-phase diagrams for all tested samples at different immersion times are shown in Fig. 7.

Researchers often acquire beneficial information regarding the coating delamination extent as well as the coating barrier performance, which can be compared across all samples by studying impedance modulus at frequency of 0.01 Hz ( $|Z|_{0.01 \text{ Hz}}$ ) and negative phase angle at frequency of 10 kHz ( $\Theta_{10\text{kHz}}$ ), respectively [68–70]. Furthermore, there is another helpful criterion known as breakdown frequency ( $f_b$ ) that is associated with the coating delamination area and is defined as the frequency related to the phase angle of  $-45^{\circ}$  [71]. This parameter decreases by the diffusion of corrosive solution into the duplex coating system [72,73]. Therefore, variation in  $|Z|_{0.01 \text{ Hz}}$ ,  $\Theta_{10\text{kHz}}$  and  $f_b$  versus immersion time were

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Fig. 9. (a) Bode-modulus diagram related to duplex PEO/epoxy coated at a certain time of immersion in 3.5 wt.% NaCl solution; an extrapolated line with slope of -1 on impedance values at high frequencies associated with capacitive region;  $Z_1$  and  $Z_2$  are values of  $|Z|_{0.01 \text{ Hz}}$  related to undamaged coating and damaged coating, respectively, (b) the area under the extrapolated line (A<sub>1</sub>), (c) the area under Bode-modulus diagram (A<sub>2</sub>), both two areas were measured at selected range of frequency ( $-1 \le \log F \le 4$ ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

drawn out from Bode-modulus at different immersion times and presented in Fig. 8. The  $|Z|_{0.01 \text{ Hz}}$  is first decreased by the penetration of the corrosive solution into the coating system during the immersion time [74]. However, different coating systems show different changes in  $|Z|_{0.01 \text{ Hz}}$  over the immersion time. Duplex coated samples, particularly Duplex-6Zr, exhibited higher  $|Z|_{0.01 \text{ Hz}}$  and lower reduction in this parameter due to the higher resistance against the corrosive medium penetration in comparison with monolayer epoxy coated sample. As can be seen from the Bode-modulus, lower penetration of corrosive agents leads to the appearance of capacitive response at a longer range of frequencies, as Duplex-6Zr had the lowest reduction in the frequency range of the capacitive response region in comparison with others. Moreover, with the immersion time progression, the frequency range related to capacitive response was shifted to lower frequency values. However, this shift was still lower in the case of Duplex-1Zr and Duplex-6Zr samples compared to Duplex-0Zr and monolayer epoxy coating. The values of the mentioned parameters were also presented in Table S1.

Yet another point of interest was that the maximum phase angle became less durable throughout the immersion time due to the penetration of corrosive medium, whereas it showed more durability in the case of duplex coatings that had Zrenhanced PEO pretreatments, especially Duplex-6Zr sample. In addition, changes in  $f_b$  values versus immersion time proved the positive impact of Zr-enhanced PEO pretreatment on the dwindling delamination area of epoxy coating on the bottom layer (PEO coating in the case of the duplex coated sample, and substrate in the case of monolayer epoxy coated sample) owing to the lower  $f_b$  values in the case of Zrenhanced PEO/epoxy coating samples, namely the Duplex6Zr sample in collation with monolayer epoxy coating and Duplex-0Zr samples.

Ramamurthy et al. [75] introduced two methods for assessing the portion of damage at the polymer/substrate interface. Two equations were reported to calculate the extent of coating delamination as well as coating damage extent at specific times during immersion. In this study, these two parameters were investigated for monolayer epoxy coated samples and duplex PEO/epoxy coated samples using the Bode-modulus diagrams on the 21th and 40th days. As can be observed in Fig. 9(a), first a line with a slope of -1 was extrapolated on the impedance values related to the capacitive region and then the impedance modulus value associated with a frequency of 0.1 Hz (log f = -1) was extracted from the equation of the extrapolated line and defined as |Z| for undamaged coating  $(Z_1)$ . Furthermore,  $Z_2$  was defined as |Z| for damage coating and was exploited from the Bode-modulus at 0.1 Hz. Subsequently, the coating delamination index  $(D_1)$  was calculated according to the Eq. (1).

$$D_1(\%) = 100 \times \left(\frac{Z_1 - Z_2}{Z_1}\right)_{0.1H_z} \tag{1}$$

Coating damage index (D<sub>2</sub>) was also calculated through Eq. (2), in which A<sub>1</sub> and A<sub>2</sub> (Fig. 9(b)& 9 (c)) are the area under the extrapolated line and the area under the Bode-modulus diagram inside the selected frequency range  $(-1 \le \log f \le 4)$ , respectively. The Bode-modulus diagrams and extrapolated lines in Fig. 9(b) and 9 (c) are the same as those seen in Fig. 9(a).

$$D_2(\%) = 100 \times \left(1 - \frac{A_2}{A_1}\right)$$
(2)

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# 10 8 6 4 Monolayer Duplex-0Zr Duplex-1Zr Duplex-6Zr

Fig. 10. Values of (a) Coating delamination index and (b) coating damage index associated with monolayer epoxy coated sample as well as three duplex PEO/epoxy coated samples after 21 and 40 days of immersion in 3.5 wt.% NaCl solution; the error bar values declared the data variation range by the average value of triplicates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

 $D_1$  and  $D_2$  were also derived for monolayer epoxy coated sample and duplex PEO/epoxy coated samples after 21 and 40 days of immersion in 3.5 wt.% NaCl solution. Finally, all the measured values (D<sub>1</sub> and D<sub>2</sub>) related to the 21st and 40th days of immersion in the case of different samples are shown in Fig. 10. In regard with the results, duplex coated samples with Zr-enhanced PEO pretreatment demonstrated a lower coating delamination index and coating damage index in comparison with monolayer epoxy coated sample and Duplex-0Zr sample for both the 21st and 40th days of immersion. Zr-enhanced PEO pretreatment was able to increase the performance of duplex PEO/epoxy coated sample during longer immersion times in 3.5 wt.% NaCl solution. Besides, the EDS analysis was carried out for duplex PEO/epoxy coatings with and without Zr after 40 days of immersion in 3.5 wt.% NaCl and the obtained results showed 3.7 and 2.4 wt.% Zr in the case of PEO-6Zr and PEO-1Zr, respectively.

#### 3.2.2. Surface characterization after longtime immersion

The optical microscope images of monolayer epoxy coated sample together with duplex PEO/epoxy coated samples after 40 days of immersion in 3.5 wt.% NaCl solution were studied to assess the appearance of samples in terms of corrosion at the end of the timeline, associated images are shown in Fig. S5. Monolayer epoxy coated samples had the highest volume of corrosion attack, whereas the volume of corrosion attack was remarkably lower in the case of duplex coated samples with Zr-enhanced PEO coating as a pretreatment. It is worth noting that the corrosion regions of Duplex-6Zr (Fig. S5. (d)) might not been detectable by the optical smicroscope.

In conclusion, PEO pretreatment had a significant impact on the corrosion performance of the epoxy coating. The addition of zirconyl nitrate to the PEO electrolyte resulted in the higher capability of PEO coating to improve the corrosion performance of epoxy coating in comparison with the PEO coating without Zr. Duplex coated samples with Zr-enhanced PEO preparation had lower volume of corrosion attack than Duplex-0Zr and monolayer epoxy due to their higher thicknesses and densities (smaller pore size and lower surface area of pores). Furthermore, based on the mechanism of PEO process, ZrO<sub>2</sub>, which is more stable than MgO, is likely to form during the coating process.

### 3.2.3. pull-off adhesion test

The adhesion strength of the epoxy coating to the layer beneath is a vital factor in the corrosion protection performance of epoxy coated samples in NaCl solution in the long immersion term. On the other hand, corrosion reactions will be activated when the corrosive media reach the interface of epoxy and substrate. Corrosion products and hydroxyl ions are inevitably produced as a result of the corrosion reactions. Increasing the pH values will cause gradual bonding decomposition in the epoxy coating. Hence, both corrosion products and bonding decomposition will contribute to a noticeable drop in the adhesion strength of the epoxy coating to the Mg substrate. Since the PEO coating was applied as a pretreatment, interfacial bonds between PEO coating and epoxy coating had a substantial influence on the performance of PEO coating [76]. The addition of zirconyl nitrate to the PEO electrolyte will affect the interfacial bonding with epoxy coating as a top coat. The outputs of the adhesion tests, which are displayed in Fig. 11, indicate that the dry adhesion strength of all the duplex coated samples were roughly equal, whereas the results of the wet adhesion strengths tests showed substantial differences. According to the images associated with the dry adhesion test, it seems that Zr-enhanced PEO coating has led to a slight increase in the adhesion strength of the epoxy coating due to the higher cohesive failure (higher surface area of remained epoxy coating) in comparison with PEO pretreatment without Zr. The average surface area of pores in PEO coatings had been evaluated through image J software and the results were 18%, 15% and 9% for PEO-0Zr, PEO-1Zr and PEO-6Zr, respectively. Zr-enhanced PEO coatings, specially PEO-6Zr, illustrated larger effective surface area (lower surface area of pores) which led to stronger physical and me-

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Fig. 11. Dry and wet adhesion strength diagrams of different duplex PEO/epoxy coating, values of adhesion loss and surface view of duplex coated samples after the adhesion test in dry and wet conditions.

chanical interlocking between the substrate and the coating. Therefore, the larger effective surface area in the case of Zrenhanced PEO coatings played a significant role in improving the adhesion strength. Contact angle test was also carried out on monolayer PEO coated samples to investigate the effect of zirconyl nitrate on the surface free energy of the PEO coatings which affect the adhesion strength of the epoxy coating to the substrate [77].

Surface free energy  $(\gamma_{sv})$  and work of adhesion (W<sub>A</sub>) values were obtained with the aid of Neumann's and Young's equations [78].

$$W_A = 2(\gamma_{l\nu}, \gamma_{s\nu})^{1/2} exp\left[-\beta(\gamma l\nu - \gamma s\nu)^2\right]$$
(3)

$$W_A = \gamma_{l\nu} (1 + \cos\theta) \tag{4}$$

In which  $\Theta$  is the contact angle of water,  $\gamma_{\rm lv}$  is the surface tension of water,  $\gamma_{\rm sv}$  is the surface free energy of the PEO coating and  $\beta$  is 0.0001247  $\pm$  0.000010 (mJ/m<sup>2</sup>)<sup>2</sup>.

According to Fig. 12, Zr-enhanced PEO coatings had a lower contact angle and a higher surface free energy in comparison with PEO coating without Zr. This can be ascribed to the morphology of Zr-enhanced PEO coatings which had smaller pores as well as lower surface fraction of pores compared to PEO coating without Zr. That is to say, lower propor-



Fig. 12. Contact angle and surface free energy of PEO coated samples.

tion of pores alongside with smaller pore size resulted from adding zirconyl nitrate to the electrolyte of PEO coating, has led to lower contact angle as well as higher wetting ability in comparison with the PEO coating without Zr [79]. Accordingly, the dry adhesion strength of epoxy coating underwent a small increase in the presence of Zr-enhanced PEO pretreat-

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Fig. 13. Schematic of corrosion stages for duplex PEO/epoxy coating system immersed in 3.5 wt.% NaCl solution over the time, (a) without Zr-based compound; (b) with Zr-based compound.

ment owing to the higher surface free energy in comparison with PEO pretreatment without Zr. Besides, another reason for the superior adhesion strength of the epoxy coating to the Zr-enhanced PEO coating may be the formation of stronger interfacial bonds between coating and substrate.

The adhesion loss values were also measured through Eq. (5). According to the results, the adhesion loss value is the lowest in the case of the Duplex-6Zr sample and is the highest in the case of the Duplex-0Zr sample.

$$Adhesion loss(\%) = \frac{\text{Dry adhesion strength} - \text{Wet adhesion strength}}{\text{Dry adhesion strength}}$$
(5)

Improving wet adhesion strength of epoxy coating and thus reducing the adhesion loss in the presence of zirconyl nitrate may be the result of lower epoxy delamination in the case of duplex Zr-enhanced PEO/epoxy coatings. Epoxy delamination in wet conditions can occur due to the increase in pH values. Therefore, the rate of hydrolysis of bonds between PEO and epoxy coatings will increase accompanied with higher amount of corrosion products. However, in the case of Zr-enhanced PEO coatings, the presence of Zirconium oxide in PEO coating and formation of  $ZrO_2$  on the anodic regions contributed to both lower extent of MgO and hydrolysis rate [52,69,80].

# 3.2.4. Schematic of the corrosion process of the PEO/epoxy coating system

The schematic of various stages of the corrosion process is presented over the immersion time in a 3.5 wt.% NaCl solution for Duplex PEO/epoxy coating without Zr (Fig. 13(a)) and with Zr (Fig. 13(b)). The positive effect of PEO pretreatment containing Zr on increasing the corrosion resistance of duplex PEO/epoxy coated samples over the immersion time is demonstrated by comparing the corrosion stages associated with duplex coated samples containing PEO pretreatment with and without Zr. Zr was able to lower the number of unstable corrosion products (MgO) due to a higher tendency to form an insoluble oxide. ZrO<sub>2</sub> is more stable than MgO, so the coating containing Zr shows higher corrosion properties. This insoluble oxide can also act as a diffusion barrier, effectively

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decreasing the diffusion rate of the corrosive media within the coating system. As a result, duplex PEO/epoxy coated samples with Zr have higher corrosion resistance in the 3.5 wt.% NaCl solution throughout the immersion time, compared to the Duplex-0Zr.

### 4. Conclusion

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- In this study, PEO coating containing Zr-based compounds had been applied on Mg substrate as a pretreatment to improve the corrosion protection properties along with adhesion strength of duplex PEO/epoxy coating.
- Zr-enhanced PEO coatings showed a better morphology, pores seemed to be filled and the coating had a lower surface fraction of pores compared to PEO coatings without Zr.
- The corrosion performance of duplex coated samples improved in the case of those including Zr-enhanced PEO coating, mainly due to a better morphology and the presence of  $ZrO_2$  in the PEO coating.
- Duplex coated samples with Zr-enhanced PEO pretreatment showed both lower delamination index and coating damage index at longer immersion period compared to monolayer epoxy coated sample and Duplex-0Zr.
- The adhesion strength of epoxy coating to the PEO coating improved in the presence of Zr due to larger effective surface area (lower surface area of pores) as well as higher surface free energy obtained for Zr-enhanced PEO coatings compared to PEO coating without Zr. The delamination rate of epoxy coating in wet adhesion test also decreased due to the formation of ZrO<sub>2</sub>.

### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jma.2022.05. 018.

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