

Article

Investigation of Protective Performance of a Mg-Rich Primer Containing Aluminum Tri-Polyphosphate on AZ91D Magnesium Alloy in Simulated Acid Rain

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Abstract: Mg-rich primer (MRP) containing aluminum tri-polyphosphate functions via a galvanic mechanism to protect AZ91D alloy from corrosion in the 3 wt % NaCl solution. However, its protective performance can be strongly affected by the testing environment. Therefore, it is important to investigate the performance of the primer on magnesium alloys in an acid rain environment. In the present study, the protective performance of MRP with or without aluminum tri-polyphosphate was investigated via open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), scanning electronic microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) in the simulated acid rain. Compared to the primer without aluminum tri-polyphosphate, the MRP containing aluminum tri-polyphosphate pigments exhibited better protective performance in the simulated acid rain condition. In the initial stage, the acidic condition prompted the aluminum tri-polyphosphate pigments to release phosphates and H⁺ to form magnesium phosphates on Mg particles, retarding their consumption rate. The Mg-rich primer with aluminum tri-polyphosphate can provide cathodic protection to AZ91D alloy for about 49 days in the simulated acid rain solution. Simultaneously, the corrosion products of Mg particles, magnesium oxides and phosphates, precipitated on the Mg particles and improved the stability of the primer. In addition, a protective film, consisting of magnesium oxides and phosphates, formed on the AZ91D substrate. Consequently, all these factors contributed to the long cathodic protection and improved corrosion resistance of MRP containing aluminum tri-polyphosphate in the simulated acid rain.

Keywords: magnesium alloy; acid rain; corrosion; Mg-rich primer; EIS; XPS

1. Introduction

Magnesium alloys are among the potential candidates for applications in aerospace, automobile and communication fields, etc., due to their properties of high specific strength, low density, good machinability and low elastic modulus [1,2]. However, the widespread applications of Mg alloys are limited by their poor corrosion resistance, which is mainly attributed to their high reacting activity [3,4]. Therefore, in recent years it has been a hot research issue to enhance the corrosion resistance of Mg alloys by surface engineering technology. Generally, organic coatings have better corrosion resistance than chemical conversion coatings [5,6]. Compared to the protective coatings prepared via anodic

oxidation [7,8], vapor deposition [9,10] and electroplating [11,12], organic coatings have the advantages of good resistance, simple process, low cost and good adaptability [13].

Recently, a magnesium-rich primer (MRP) providing cathodic protection to AZ91D Mg alloy has been developed [14,15]. Song et al. deduced and verified that the corrosion rate of Mg alloys could be slowed down sufficiently when they were cathodically polarized by ~30 mV [16]. Since Mg alloys usually contain Al, Zn and other alloying elements, their corrosion potentials are higher than that of pure magnesium [17]. On the basis of above principle, MRP was developed by adding pure magnesium particles with diameters of 10–20 μm to epoxy coatings [14,15,18–21]. The AZ91D alloy could be cathodically polarized by the MRP and the protective performance of the epoxy coatings for the substrate was significantly strengthened by Mg particles [14,15]. MRP provides protection to the AZ91D alloy by a three-stage mechanism [15]. Firstly, the barrier effect of MRP is observed on the AZ91D substrate; meanwhile, the permeated water activates the Mg particles in the primer gradually. Secondly, the anodic dissolution of Mg particles makes the AZ91D alloy cathodically protected. Lastly, $\text{Mg}(\text{OH})_2$ precipitates in MRP, improving the barrier effect to some extent. Nevertheless, Mg particles are of high chemical reactivity and the corrosion products accumulate rapidly around Mg particles, leading to the rapid failure of the cathodic protection [14,15]. Besides, the barrier effect of MRP on Mg alloys is not as satisfactory as that of Zn-rich primer on steels because of the relatively loose structure of $\text{Mg}(\text{OH})_2$ [14,15,19–23]. The performance of MRP on Al alloys or Mg alloys has been improved by a number of measures [19,24–27]. ZnO particles were added into MRP to reduce the dissolution rate of Mg particles and improve the physical crosslink density of the epoxy matrix, leading to the decrease of defects and the increase of the barrier property and adhesion for the primer on AZ91D alloy [25]. Pathak et al. employed the carbonation of Mg particles to enhance the corrosion resistance of MRP on A2024 aluminum alloy and the carbonization-treated MRP performed better than the untreated MRP [26]. Wang et al. investigated the effects of Mg particle phosphatization on the protective properties of MRP on Al alloy and reported that the phosphatizing surface treatment could not only improve the coating barrier effect but also decrease the corrosion rate of the Al substrate [27]. Aluminum tri-polyphosphate was added to the MRP on AZ91D alloys to improve its protective properties in marine environments [19]. Aluminum tri-polyphosphate could change the composition of the Mg corrosion products to form an insoluble complex, enhancing the cathodic and barrier effect of MRP on AZ91D alloy [19].

In recent years, as atmospheric pollution has become more and more serious, the worldwide acid rain problem is one of the most important environmental factors causing corrosion [28–31]. In fact, acid rain resistance is important for most of Mg components in practical service for automobile, military and telecommunication applications [32]. Cui et al. suggested that the addition of NH_4NO_3 in NaCl solution increased the corrosion rate of AZ31 alloy and contributed to the formation of a cracked and loose corrosion product layer [33]. In addition to the aggressive ions in acid rain, the decreasing pH could accelerate the corrosion of magnesium alloy [34]. Even though the protective performance of coatings for magnesium alloys has been investigated in neutral NaCl solution [3,35–37], we found via literature searches that only one study addressed the corrosion behavior of a coating on magnesium alloy in acid rain [38]. In combination with hydrothermal treatment and magnetron sputtering, Wu et al. produced super-hydrophobic surfaces on magnesium alloys, improving corrosion protection in H_2SO_4 solution [38]. Moreover, the testing environment can strongly affect the assessment of the efficiency and durability of MRP [39,40]. Battocchi et al. reported that the dilute Harrison solution caused the increase of the electromotive force for the cathodic protection of aluminum alloys by MRP but reduced the cathodic protection time [39]. In addition, the Mg-dissolution reactions increased with the pH changes according to the Pourbaix diagram [41]. Hence, the mechanism of deterioration of protective coatings for outdoor exposure under acid rain conditions should be investigated to strengthen their practical applications. In this paper, we investigated the protective behavior of MRP with or without aluminum tri-polyphosphate on AZ91D magnesium alloy in simulated acid rain.

2. Materials and Methods

2.1. Materials

The substrate sheets were AZ91D alloys, supplied by Yingkou Galaxy Magnesium Aluminum Co., Ltd., Liaoning, China. The chemical compositions are shown in Table 1. The film-forming material was a two-component commercial epoxy varnish (KFH-01) supplied by Shijiazhuang Golden Fish Paint Company, Shijiazhuang, China. The γ -glycidoxy propyl trimethoxy silane (γ -GPS) coupling agent was supplied by Beijing Antepuna Trade Co., Ltd., Beijing, China. The average diameter of pure Mg particles (99.9%) was 20 μm ; they were produced by Qinhuangdao Taiji Nano Products Co., Ltd., Qinhuangdao, China. The modified aluminum tri-polyphosphate was a commercial-grade anticorrosion pigment obtained from Shanghai Yipin Pigments Co., Ltd., Shanghai, China. According to datasheets, the trademark of the pigment is SAP-1.

Table 1. Nominal composition (wt %) of AZ91D magnesium alloy.

Al	Mn	Zn	Fe	Si	Ni	Cu	Mg
9.4	0.23	0.82	0.005	0.01	0.002	0.02	remainder

2.2. Sample Preparation

The commercial AZ91D alloy sheets were cut into small samples with dimensions of 50 mm $\times$ 50 mm $\times$ 3 mm. Prior to being coated, the AZ91D samples were ground to 240 grit with SiC abrasive paper, rinsed with deionized water, degreased with ethanol and acetone in turn, then blown dry with cold air. MRP was prepared by adding pure Mg particles at a content level of 50% *w/w*, with respect to the dry primer weight, into the epoxy varnish. SAP-MRP was composed of 40% *w/w* Mg particles and 10% *w/w* aluminum tri-polyphosphate pigments. In those primers, the γ -GPS addition was 1% *w/w* with respect to the pigment weight. After the pigments and γ -GPS were added in the epoxy component, they were stirred and dispersed by high-speed agitation equipment for 10 min. Next, the curing component was added into the epoxy paint and well stirred. The manual brushing method was used to prepare the primers on AZ91D substrates. The coated samples were cured for a week at room temperature. The dry primer's thickness was $130 \pm 10 \mu\text{m}$, measured with a digital thickness gauge TT230.

2.3. SEM

A Hitachi S4700 field emission scanning electron microscope (SEM, Hitachi, Tokyo, Japan) was employed to observe the surface morphology of AZ91D alloy, MRP and SAP-MRP. The accelerating voltage of the field emission source was 20 kV. The samples were coated with gold before being tested.

2.4. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was conducted with an ESCALAB 250 instrument (Thermo Fisher Scientific, Waltham, Massachusetts, USA) to evaluate the chemical states of the elements in the AZ91D alloy underneath SAP-MRP. A monochromatized Al K line (1486 eV) was used as the excitation source. All the binding energy values were calibrated based on the C 1s peak at 285 eV. The narrow scan spectra were fitted with XPSPEAK 4.1 software.

2.5. Electrochemical Measurements

The tested solution was simulated acid rain. The simulated acid rain was prepared by diluting the mixture of H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, MgSO_4 , $\text{Ca}(\text{NO}_3)_2$ and HNO_3 with deionized water to reach a pH of 4.0. The chemical composition of the simulated acid rain corresponds to the components of acid rain in southern China shown in Table 2 [42,43].

A CS300 electrochemical system (Corrtest, Wuhan, China) was used to measure the potentiodynamic polarization plots of the AZ91D alloy as well as the MRP and SAP-MRP coated samples in the simulated acid rain solution. A saturated calomel electrode (SCE) was the reference

electrode, a Pt electrode was the counter electrode and the working electrode area was 1 cm². For the AZ91D substrate, after 10 min of immersion in the tested solution the potentiodynamic polarization was performed from −200 mV (relative to the OCP) to the anodic direction with a rate of 0.2 mV/s. For the MRP and SAP-MRP coated samples, after 2 days of immersion in the tested solution the potentiodynamic polarization was performed with a rate of 1 mV/s.

Table 2. Chemical composition (M) of the simulated acid rain.

SO ₄ ^{2−}	NO ₃ [−]	Mg ²⁺	NH ₄ ⁺	Ca ²⁺
0.1	0.015	0.002	0.002	0.001

Electrochemical impedance spectroscopy (EIS) measurements were conducted in the simulated acid rain solution using an electrochemical workstation (PARSTAT 2273, AMETEK, Oak Ridge, Tennessee, USA). The frequency range was 100 kHz to 10 mHz and the sinusoidal amplitude was 10 mV. The coated samples were working electrodes with 10 cm² of working area. Similarly, an SCE was used as the reference and Pt mesh was selected as the counter electrode. The fitting of the impedance spectra was carried out with ZSimpWin software. Before the EIS tests, open circuit potential (OCP) measurements were conducted for 30 min to ensure that the potential reached a steady state.

3. Results

3.1. OCP Measurements

Figure 1 displays the variations of the OCPs for AZ91D as well as the MRP and SAP-MRP samples with immersion time in the simulated acid rain solution. The E_{OCP} for the AZ91D alloy substrate in simulated acid rain solution was about −1.3 V vs. the SCE (Figure 1a). After 4 h of immersion, the E_{OCP} of the MRP coated sample was below −1.3 V vs. the SCE (Figure 1b,c), indicating that the MRP could protect the AZ91D alloy cathodically. After 14 days of immersion, the E_{OCP} was above −1.3 V vs. the SCE, implying that the cathodic protection failed. After 332 days of immersion, the E_{OCP} reduced to −1.3 V vs. the SCE, implying the failure of the MRP. The E_{OCP} of the SAP-MRP coated sample was below −1.3 V vs. the SCE during the immersion time from 4 h to 49 days, showing that aluminum tri-polyphosphate addition could strengthen the cathodic protection effect significantly. In the following immersion process, the E_{OCP} values fluctuated in the range of −0.8 to −1.1 V vs. the SCE, illustrating that the protective properties of SAP-MRP remained stable without conspicuous deterioration.

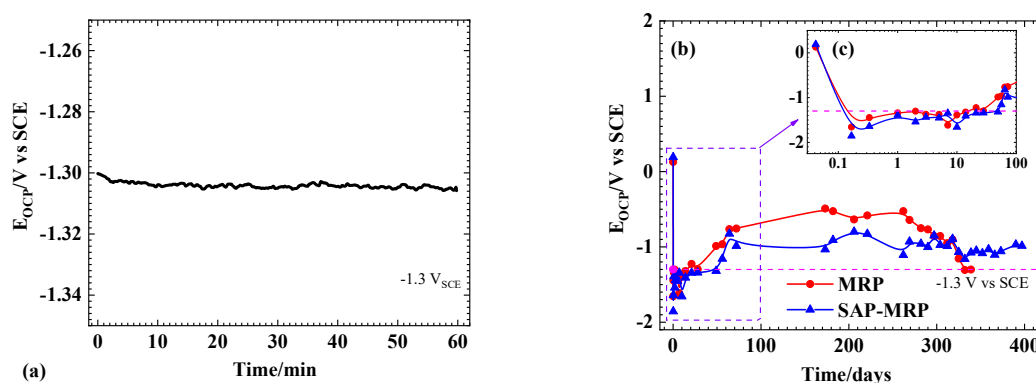


Figure 1. The variations of the open circuit potentials for AZ91D alloy (a) and Mg-rich primer (MRP) and SAP-MRP samples (b) with immersion time in the simulated acid rain solution; (c) partial enlargement of the MRP and SAP-MRP samples during the immersion time from 1 h to 100 days.

3.2. Polarization Measurement

Figure 2 shows the polarization plots for AZ91D alloy as well as the MRP and SAP-MRP coated alloys in the simulated acid rain solution. Table 3 shows the related parameters obtained from Figure 2 by

the extrapolation of the Tafel line. The corrosion rate of AZ91D was approximately $1.37 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$ and the corrosion potential was about -1.32 V vs. the SCE. For the MRP sample, the corrosion rate was about $1.18 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$ and the corrosion potential was about -1.46 V vs. the SCE, about 140 mV lower than that of AZ91D, suggesting that the MRP50 could cathodically polarize AZ91D alloy. For the SAP-MRP sample, the corrosion potential was about -1.43 V vs. the SCE, about 110 mV lower than that of bare AZ91D alloy, indicating the cathodic protection of SP-MRP on the substrate. The corrosion rate of the SAP-MRP coated sample was about $1.32 \times 10^{-9} \text{ A}\cdot\text{cm}^{-2}$. Similar to the polarization results in NaCl solution [15,19], the MRP with or without aluminum tri-polyphosphate could cathodically polarize the AZ91D substrate for about 100 mV. According to our previous calculation, the anodic dissolution reaction of the AZ91D substrate could be reduced to 6.60% [15].

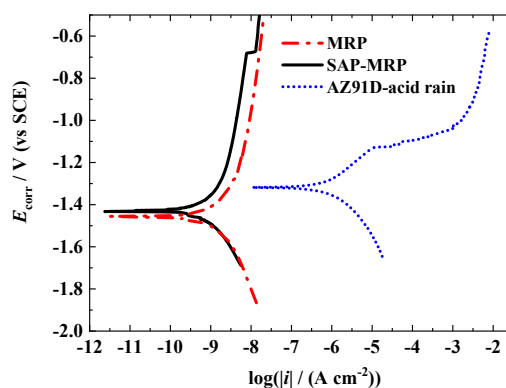


Figure 2. Polarization plots for AZ91D alloy as well as the MRP and SAP-MRP coated alloys in the simulated acid rain solution.

Table 3. The related parameters of the polarization plots for AZ91D alloy as well as the MRP and SAP-MRP coated samples in the simulated acid rain.

Sample	E_{corr} (V vs. SCE)	i_{corr} (A cm^{-2})	β_a (mV/decade)	β_c (mV/decade)
AZ91D	−1.3185	1.3793×10^{-6}	256.30	238.45
MRP	−1.4589	1.1817×10^{-9}	456.32	366.95
SAP-MRP	−1.4301	1.3192×10^{-9}	566.02	360.21

3.3. EIS Measurement

Figure 3 presents the EIS spectra of MRP-coated and SAP-MRP-coated samples after immersion in the simulated acid rain solution for different periods of time. In the initial 1 h of immersion, a line nearly perpendicular to the x -axis could be observed in the Nyquist plot of MRP (Figure 3a); the $|Z|_{0.01 \text{ Hz}}$ (the impedance modulus at 0.01 Hz) value was higher than 10^{11} cm^2 (Figure 3b) and the phase angles in the full range of tested frequency were lower than -80° (Figure 3c), indicating that the primer showed a good barrier property. After 1 day of immersion, the radius of the capacitive loop decreased (Figure 3a), the $|Z|_{0.01 \text{ Hz}}$ value of MRP dropped by one order of magnitude (Figure 3b) and the values of the phase angle increased, due to the gradual permeation of the electrolyte into the primer and the activation of the Mg particles [14,18]. As the immersion time was prolonged, the radius of the capacitive loop and the $|Z|_{0.01 \text{ Hz}}$ of MRP showed an increase while the phase angles decreased. The phenomenon is ascribed to formation of the corrosion products of the Mg particles in MRP, providing barrier protection to some extent [14,15,19]. Nevertheless, after immersion from 72 to 297 days, the EIS of MRP almost remained the same and the $|Z|_{0.01 \text{ Hz}}$ value declined slowly, reflecting that the protective performance of the MRP persisted without remarkable deterioration. After 325 days of immersion, the Nyquist plot showed several time constants, the phase angle at 0.01 Hz approached 0° , $|Z|_{0.01 \text{ Hz}}$ began to decrease severely due to deterioration of MRP and afterwards it approached $1 \text{ G}\Omega \text{ cm}^2$ following immersion for 339 days. Meanwhile, some blisters were observed, indicating MRP failure.

For SAP-MRP coated samples, the EIS results were similar to those of the MRP coated samples in the initial immersion stage (Figure 3d–f). However, after 397 days of immersion, the Nyquist plot still showed one capacitive loop (Figure 3d); moreover, the $|Z|_{0.01 \text{ Hz}}$ value for the SAP-MRP coated samples was $14 \text{ G}\Omega \text{ cm}^2$ and they increased even higher ($23 \text{ G}\Omega \text{ cm}^2$) (Figure 3e). The phase angle at 0.01 Hz was near 20° . All these phenomena demonstrate that the SAP-MRP still provides good protective properties to AZ91D. However, the aluminum tri-polyphosphate could strengthen the stability of MRP in the simulated acid rain.

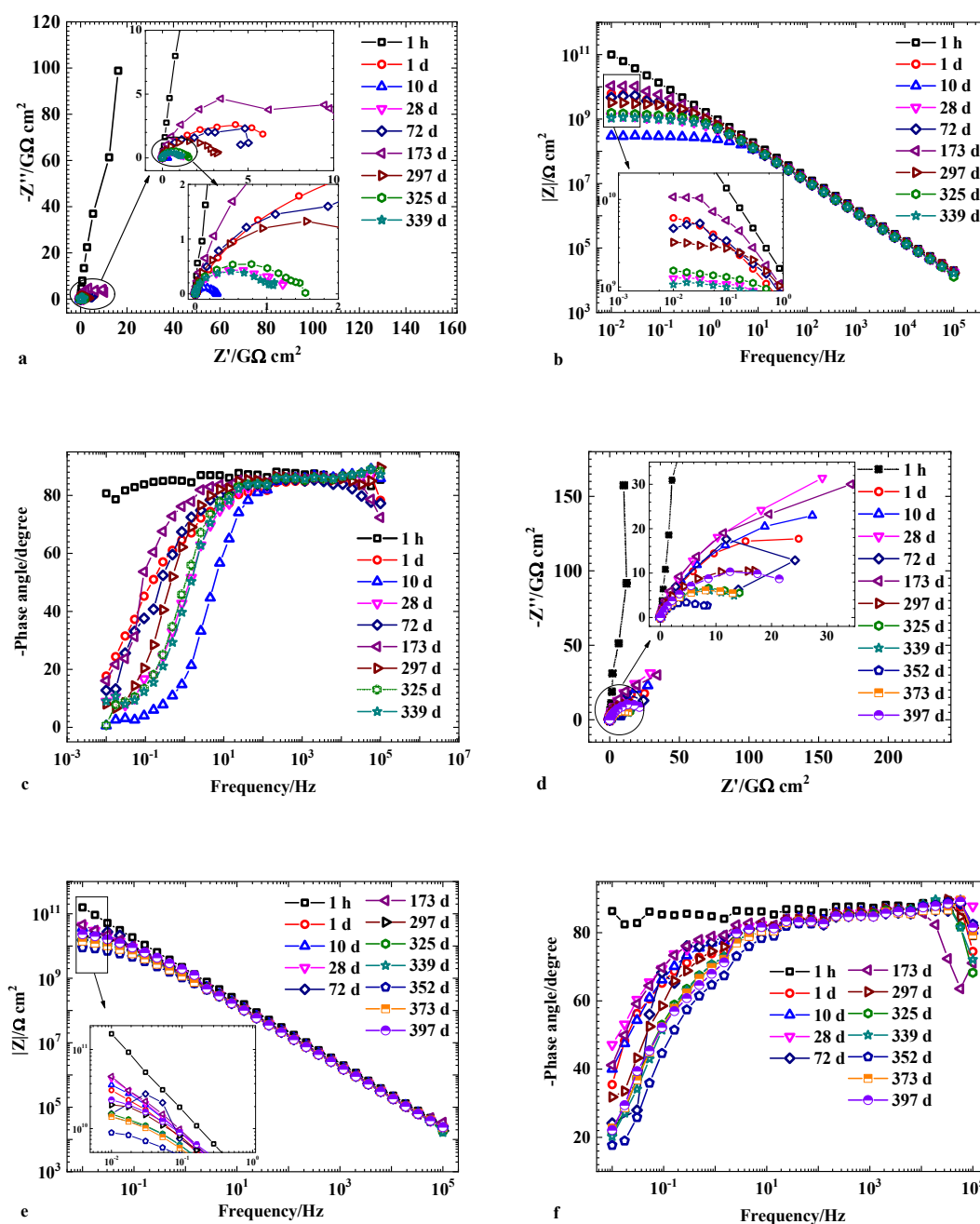


Figure 3. Electrochemical impedance spectroscopy (EIS) spectra of MRP and SAP-MRP samples after immersion in the simulated acid rain solution for different days: (a) Nyquist plots of MRP; (b,c) Bode plots of MRP; (d) Nyquist plots of SAP-MRP; (e,f) Bode plots of SAP-MRP.

Figure 4 shows the changes of $|Z|_{0.01 \text{ Hz}}$ values with various immersion times in the simulated acid rain solution. In the initial immersion, both $|Z|_{0.01 \text{ Hz}}$ values for the MRP and the SAP-MRP coated

samples dropped dramatically because of the electrolyte permeation into the primers and the activation of Mg particles [14,15,19]. Next, the $|Z|_{0.01 \text{ Hz}}$ values of the MRP began to rise, which is attributed to the precipitation corrosion products of Mg particles in the primer, leading to the improvement of the barrier effect. After 282 days of immersion, the $|Z|_{0.01 \text{ Hz}}$ values of the MRP started to decline due to the deterioration of the coating. For the SAP-MRP coated sample, the $|Z|_{0.01 \text{ Hz}}$ values also showed a small rise after the initial decrease and then fluctuated around $10 \text{ G}\Omega \text{ cm}^2$. In addition, the $|Z|_{0.01 \text{ Hz}}$ values of the SAP-MRP coated samples were always higher than those of the MRP samples at the immersion time of 397 days, suggesting the improvement of the coating performance by aluminum tri-polyphosphate addition.

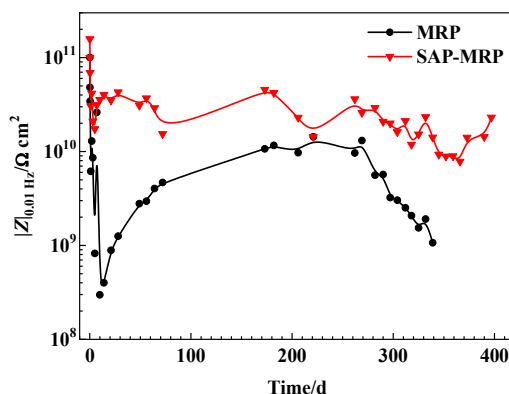


Figure 4. The variations of $|Z|_{0.01 \text{ Hz}}$ values with immersion time in the simulated acid rain solution.

The electrical equivalent circuits (EECs) in Figure 5 were employed to fit the EIS spectra. For the purpose of obtaining accurate results, the capacitive responses were fitted by the constant phase elements (CPE), Q , whose impedance is defined as:

$$Z_Q = \frac{1}{Y_0(2\pi f)^n} \quad (1)$$

in which Y_0 is the CPE constant, $j = \sqrt{-1}$, f is the frequency (Hz), $n = \alpha/(\pi/2)$ and α is the phase angle of the CPE (radians).

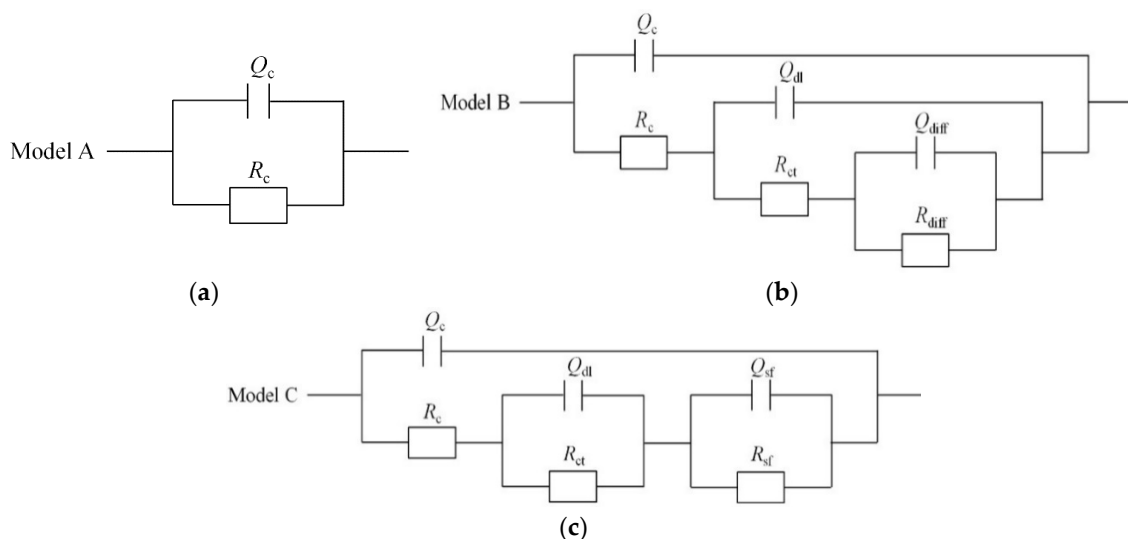


Figure 5. Electrical equivalent circuits (EECs) used to fit the EIS spectra: (a) initial stage, (b) stable stage and (c) late stage.

The EECs (Figure 5) were adopted to fit the EIS spectra of MRP on AZ91D alloys in previous studies [14,15,18,19]. Here, Q_c and R_c are the coating capacitance and coating resistance, respectively. Q_{dl} and R_{ct} are the double layer capacitance and the charge-transfer resistance of the Mg particles in the primers, respectively. The diffusion processes caused by the presence of corrosion products of Mg particles can be expressed using Z_{diff} , which is composed of the capacitance Q_{diff} in parallel to the resistance R_{diff} [14,18,19,44,45]. When the substrate began to corrode, another time constant ($R_{sf}C_{sf}$) was caused by the lateral diffusion of the electrolyte at the substrate/coating interface [46–48]. Since a corrosion product film would form on the substrate, C_{sf} and R_{sf} represent the film capacitance and the film resistance, respectively [45,49]. For the MRP coated samples, good fitting results were obtained using Model A in the immersion period of 1 h to 1 day, Model B in the immersion period of 2 to 318 days and Model C in the immersion period of 325 to 339 days. For the SAP-MRP coated samples, good fitting results were obtained using Model A in the immersion period of 1 h to 2 days, Model B in the immersion period of 3 to 345 days and Model C in the immersion period of 352 to 397 days. Table 4 shows the examples of the fitting values for the elements of each circuit with the error of the elements and chi factor.

Table 4. Examples of the fitting values for the elements of each circuit with the error of the elements and chi factor.

Samples	MRP			SAP-MRP		
Immersion Time	1 h	10 Days	339 Days	1 h	10 Days	373 Days
Q_c ($\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$)	1.27×10^{-10}	1.73×10^{-10}	1.84×10^{-10}	9.01×10^{-11}	1.27×10^{-10}	1.50×10^{-10}
error (%)	1.684	0.7086	0.6032	1.172	0.9542	0.9875
n_c	0.96743	0.95634	0.9565	0.96844	0.95032	0.9409
error (%)	0.2293	0.1261	0.6987	0.1677	0.1513	0.2241
R_c ($\Omega \cdot \text{cm}^2$)	5.79×10^{11}	2.32×10^8	8.40×10^8	2.29×10^{12}	5.68×10^9	3.38×10^9
error	3.384	3.631	2.414	3.572	2.134	1.397
Q_{dl} ($\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2}$)	—	1.63×10^{-9}	3.08×10^{-9}	—	4.69×10^{-11}	2.33×10^{-10}
error (%)	—	3.161	2.834	—	2.271	3.946
n_{dl}	—	0.93551	0.95069	—	0.94445	0.93198
error (%)	—	2.926	1.021	—	0.3079	1.239
R_{ct} ($\Omega \cdot \text{cm}^2$)	—	3.68×10^7	1.90×10^8	—	2.01×10^{10}	3.31×10^9
error (%)	—	0.2583	1.184	—	1.831	4.641
Q_{diff}/Q_{sf} ($\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2}$)	—	2.28×10^{-8}	3.74×10^{-8}	—	2.23×10^{-10}	3.68×10^{-10}
error (%)	—	2.285	1.544	—	2.888	3.504
n_{diff}/n_{sf}	—	0.82824	0.74574	—	0.83679	0.76716
error (%)	—	2.075	1.527	—	2.186	4.347
R_{diff}/R_{sf} ($\Omega \cdot \text{cm}^2$)	—	3.08×10^7	1.49×10^9	—	3.39×10^{10}	1.11×10^{10}
error (%)	—	2.502	3.898	—	1.463	1.741

Figure 6 presents the changes of R_c and R_{ct} for different primers. R_c is often used to characterize the number of pores or capillary channels through which the electrolyte penetrates into coatings [49,50]. In general, R_c decreases with prolonging immersion time due to the electrolyte permeation. It can be observed from Figure 5a that the R_c values for both the coatings decreased sharply in the initial immersion time and then showed an increase. This phenomenon might be explained by the initial electrolyte permeation and the subsequent precipitation of corrosion products in the coatings. In the whole immersion process, the R_c values of the SAP-MRP were higher than those of the MRP, indicating that the addition of aluminum tri-polyphosphate could enhance the coating stability in longer immersion periods.

R_{ct} is utilized to characterize the electrochemical reaction activity of Mg particles in the primers and the interface stability between Mg particles and the binder [14,22]. Initially, a thin layer of Mg oxide covers the Mg particle. As electrolyte permeates into the primers, the oxide film is dissolved and more Mg particles become exposed, leading to the decline of R_{ct} values. Subsequently, the R_{ct} values of the MRP coated samples showed an increase because of the accumulation of Mg corrosion products. As the immersion time was prolonged, MRP deteriorated gradually and the number of

microdefects increased in the coatings. Hence, more electrolytes filled in the coating, leading to the sharp decrease of R_{ct} values. Nevertheless, for the SAP-MRP coated samples, the R_{ct} values increased in the initial immersion, indicating that the corrosion products on the Mg particles were compact. Therefore, the aluminum tri-polyphosphate addition could reduce the corrosion rate of Mg particles in the simulated rain.

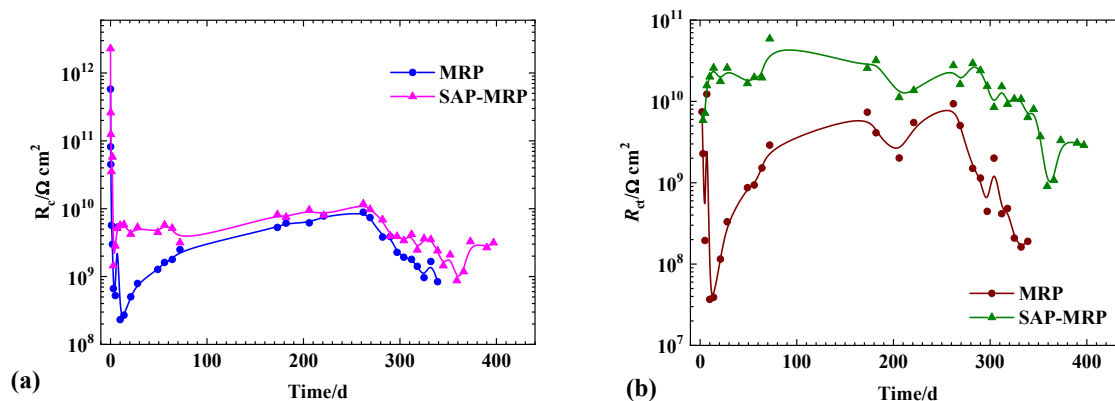


Figure 6. The changes of the obtained impedance parameters with time: (a) coating resistance, R_c ; (b) charge-transfer resistance R_{ct} .

Figure 7 displays the changes of R_{sf} and Q_{sf} at the substrate/SAP-MRP interface in the simulated acid rain solution. The R_{sf} values presented an increasing trend with the immersion time. Since R_{sf} is the resistance of the corrosion product film, the increase of R_{sf} occurs due to the enhancement of the barrier effect of the film on the AZ91D substrate. Hence, it can be inferred that a protective film may form on the substrate, leading to the decreasing corrosion rate of the AZ91D substrate [19]. The variation trend of Q_{sf} showed a decrease, which may be attributed to the deposition of the protective film on the substrate surface [19]. From the changes of the Q_{sf} values, it also can be inferred that a protective film may reduce the corrosion rate of the AZ91D during the immersion test.

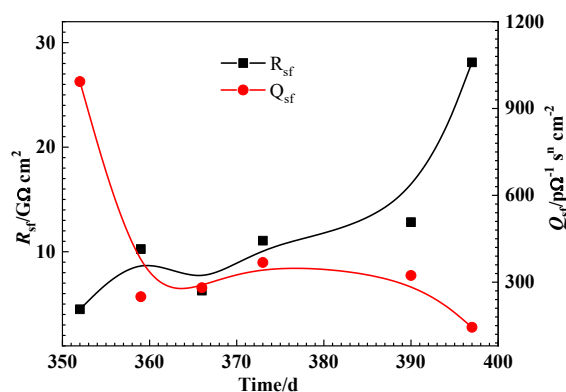


Figure 7. The changes of R_{sf} and Q_{sf} at the substrate/primer interface for the SAP-MRP coated samples as a function of immersion time in the simulated acid rain solution.

3.4. SEM Observation

Figure 8 presents the surface morphology for MRP and SAP-MRP coated samples before and after exposure to the simulated acid rain solution. It can be observed that the resins cover Mg particles to form the MRP on AZ91D alloy (Figure 8a). After 339 days of immersion, the dissolution of Mg particles led to the formation of micropores on the MRP surface [14] (Figure 8b). For SAR-MRP, it can be observed that Mg particles and aluminum tri-polyphosphate pigments were evenly distributed in the resins (Figure 8c). Nevertheless, the surface of the SAP-MRP was more compact with only small

flaws after 397 days of immersion (Figure 8d). This phenomenon could be explained by the fact that the corrosion products of Mg particles are compact and stable in the SAP-MRP.

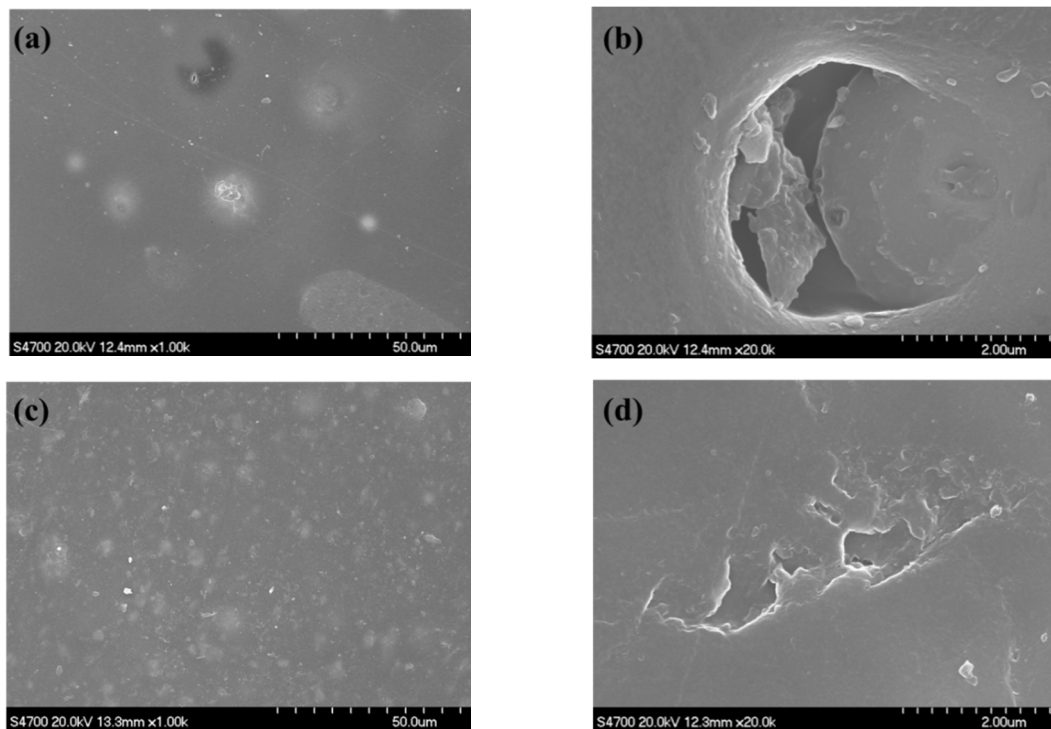


Figure 8. Surface morphology for MRP and SAP-MRP before and after exposure to the simulated acid rain solution: (a) surface of MRP before immersion, (b) surface of MRP after 339 days of immersion, (c) surface of SAP-MRP before immersion, (d) surface of SAP-MRP after 397 days of immersion.

Figure 9 displays the surface morphologies of the substrates underneath the MRP and SAP-MRP coatings after immersion in the simulated acid rain solution. It can be observed that a film with a needle-like structure existed on the substrate underneath the MRP after 339 days of immersion in the simulated acid rain (Figure 9a). The film was mainly composed of $\text{Mg}(\text{OH})_2$ and MgO and was several nanometers thick [19,51]. For the substrate underneath the SAP-MRP, a compact layer was observed after 397 days of immersion (Figure 9b).

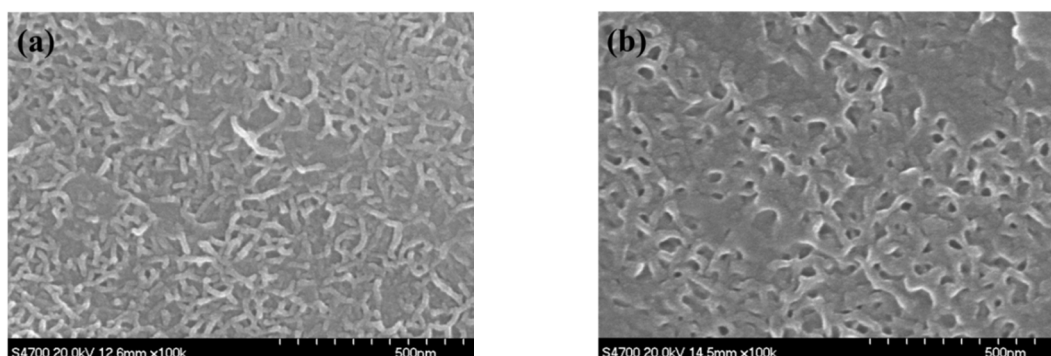


Figure 9. SEM images of the substrate surface underneath (a) MRP after 339 days of immersion in the simulated acid rain solution and (b) SAP-MRP after 397 days of immersion in the simulated acid rain solution.

3.5. XPS Analysis

XPS was utilized to characterize the chemical state of the AZ91D alloy substrate underneath the SAP-MRP after 397 days of exposure in the simulated acid rain. The binding energy value of P $2p_{3/2}$ (Figure 10a) was consistent with that of the aluminum tri-polyphosphate powder [19], suggesting that the film contained phosphates. The O 1s spectra could be divided into three main peaks at 531.30, 532.40 and 532.6 eV in Figure 10b, in turn attributed to $\text{Mg}(\text{OH})_2$ [52], MgO [52] and metaphosphate ($\text{P}-\text{O}-\text{P}$, $\text{P}-\text{O}-\text{Mg}$) [52,53]. The Mg 1s peak (Figure 10c) was deconvoluted into three peaks at 1302.8, 1303.7 and 1304.6 eV, attributed to the existence of Mg [54], magnesium oxides [55] and $\text{Mg}-\text{PO}_y$ [19], respectively. According to the above data, it can be inferred that magnesium oxides and phosphates are the main compositions of the film on the AZ91D alloy substrate underneath the SAP-MRP. The XPS spectra of bare AZ91D alloy before exposure were analyzed in our previous study [19]. The XPS data indicate that the oxide film on the surface of bare AZ91D alloy was composed of mainly $\text{Mg}(\text{OH})_2$ and MgO [19]. Hence, the formation of phosphate film is attributed to the addition of the aluminum tri-polyphosphate pigments in the primer.

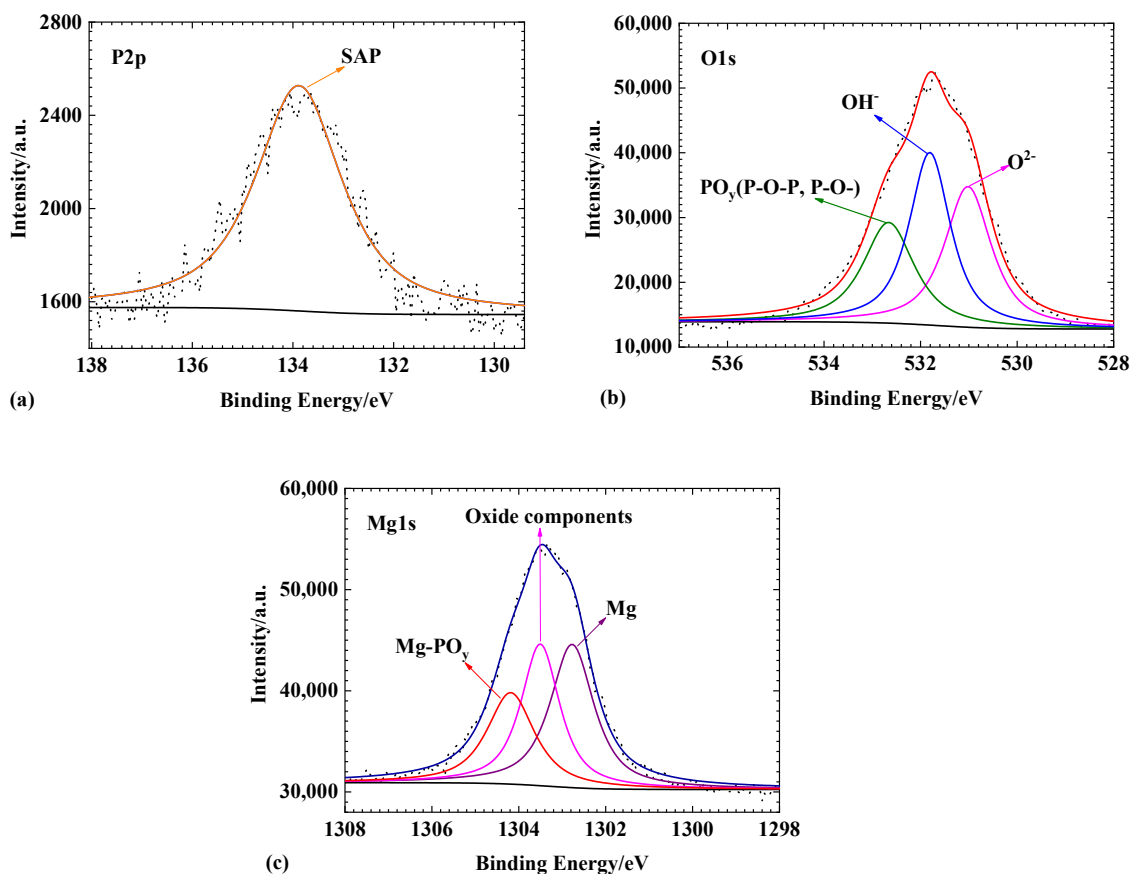


Figure 10. X-ray photoelectron spectroscopy (XPS) survey spectra of the substrate surface underneath SAP-MRP after 339 days of immersion in the simulated acid rain solution: (a) P $2p$, (b) O 1s and (c) Mg 1s.

4. Discussion

In our previous papers, the protective mechanism of MRP on AZ91D alloy was investigated in 3 wt % NaCl solution [14,15,19]. On the one hand, pure Mg particles could provide cathodic protection to AZ91D alloy. On the other hand, MRP could serve as a barrier coating against corrosive species. The main differences between the 3 wt % NaCl solution and the simulated acid rain solution are the pH values and the corrosive ions. The protection mechanism of MRP on AZ91D alloy in the simulated

acid rain is illustrated in Figure 11a,c,e. Originally, the Mg particles were covered with an oxide layer which formed naturally in air. As the electrolyte permeated into the MRP, the oxide film dissolved and the Mg particles were reactivated, leading to the formation of the electrical contact between the Mg particles and AZ91D alloy. Therefore, the activated Mg particles provided cathodic protection to the AZ91D substrate in the initial stage, as proven by the OCP results (Figure 1b). With the prolongation of the immersion time, the corrosion product of Mg particles, $\text{Mg}(\text{OH})_2$, precipitated in MRP [14] and blocked the electrolyte permeation to some extent, as supported by the variations of $|Z|_{0.01 \text{ Hz}}$ values in Figure 4. A large accumulation of $\text{Mg}(\text{OH})_2$ around Mg particles made the cathodic protection fail and caused the MRP to enter a stable stage. However, $\text{Mg}(\text{OH})_2$ can only precipitate at a pH value higher than 10.5 [14,15]. Therefore, the precipitation of $\text{Mg}(\text{OH})_2$ in the simulated acid rain was slower than that in 3 wt % NaCl solution, which could lead to the extension of the cathodic protection time from 7 [19] to 14 days (Figure 1b). Additionally, the dissolution of Mg corrosion products on the surface of MRP resulted in pores, as shown in Figure 8. Next, the MRP began to degrade and much electrolyte permeated into MRP along the defects resulting from the dissolution of $\text{Mg}(\text{OH})_2$, as demonstrated by the decrease of the R_c value (Figure 6a). As more and more electrolyte entered into the MRP, the $\text{Mg}(\text{OH})_2$ in MRP was dissolved partly and a greater proportion of fresh surface was exposed to the electrolyte, leading to the decrease of the R_{ct} value (Figure 5b). With the increase of the microdefects, MRP failed after 332 days of immersion.

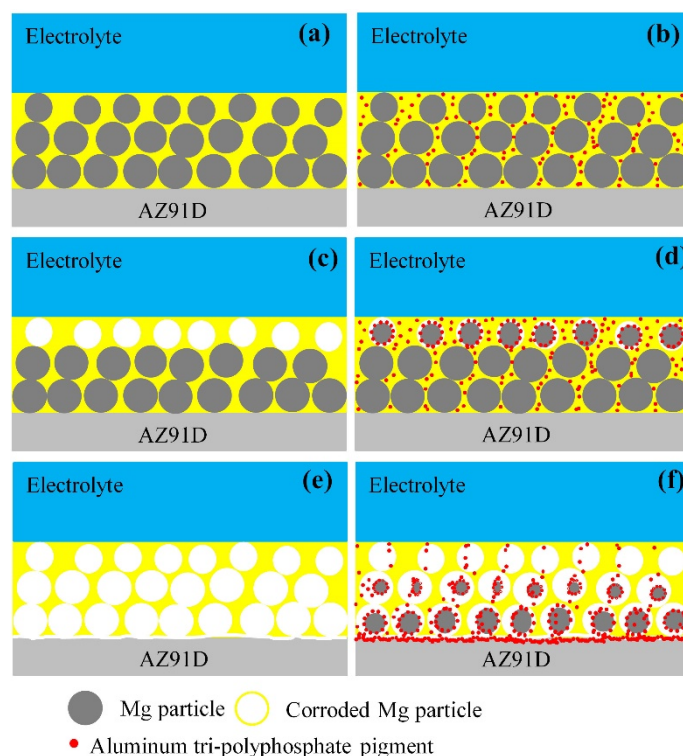


Figure 11. Schematic diagrams illustrating the mechanisms of MRP and SAP-MRP samples in the simulated acid rain solution: (a) MRP in the initial stage; (b) SAP-MRP in the initial stage; (c) MRP in the stable stage; (d) SAP-MRP in the stable stage; (e) MRP in the late stage; (f) SAP-MRP in the late stage.

The improvement mechanism of aluminum tri-polyphosphate for MRP mainly includes the following three aspects [19]: firstly, the deposition of $\text{Mg}(\text{OH})_2$ is slowed down by the pH buffering effect of aluminum tri-polyphosphate, prolonging the cathodic protection of MRP; secondly, the corrosion products, consisting of magnesium phosphates and oxides, form in MRP to enhance the stability of the primer; and lastly, a protective film composed of magnesium phosphates and oxides

forms on the AZ91D alloy substrate, which improves the barrier effect of the coating. The protection mechanism of SAP-MRP on AZ91D alloy in the simulated acid rain is illustrated in Figure 11b,d,f. Once the SAP-MRP sample was exposed in the simulated rain solution, the aluminum tri-polyphosphate pigments released phosphates and H^+ . It is reported that the magnesium phosphates begin to form at pH 4.5 [56]. Then, the consumption rate of Mg particles would be reduced by the magnesium phosphates on their surface, which could greatly increase the cathodic protection time, as proven by OCP results in Figure 1b. In addition, the solubility of aluminum tri-polyphosphate was higher in the simulated acid rain (pH = 4) than in the 3 wt % NaCl solution (pH = 7) [14]. The SAP-MRP could provide cathodic protection to AZ91D alloy for about 30 days in the 3.5% NaCl solution, while MRP could provide cathodic protection to AZ91D alloy for 49 days in the simulated acid rain solution. Next, the corrosion products of Mg particles formed in the coatings. Since the XPS results showed that the protective film on the substrate underneath the SAP-MRP mainly consisted of magnesium oxides and phosphates, the corrosion products of Mg particles in SAP-MRP also included magnesium phosphates, leading to the high R_{ct} values (Figure 6b). Moreover, the SEM observations also indicated that aluminum tri-polyphosphate pigment prevents Mg particles from dissolving in the simulated acid rain (Figure 8e). Therefore, the protective properties of SAP-MRP are more stable than those of MRP in long immersion processes. Furthermore, a protective film forms on the substrate surface underneath SAP-MRP, which enhances the protective performance of the primer. Above all, the aluminum tri-polyphosphate pigments could improve the protective behavior of MRP in the simulated acid rain as follows: by retarding the corrosion rate of Mg particles to prolong their cathodic protection; by making corrosion products of Mg particles more compact to improve the primer stability; and by producing a film on the substrate to strengthen the primer's protective performance.

5. Conclusions

The protective performance of MRP in simulated acid rain was greatly improved by the addition of aluminum tri-polyphosphate pigments. The improvement mechanism of aluminum tri-polyphosphate pigments for MRP in the simulated rain solution is illustrated as follows. In the initial stage, the aluminum tri-polyphosphate pigments release phosphates and H^+ to form magnesium phosphates on Mg particles, prolonging the cathodic protection to 49 days. Meanwhile, the products of Mg particles, magnesium oxides and phosphates, precipitate on the Mg particles and improve the primer stability. Finally, a protective film forms on the AZ91D substrate, further enhancing the primer's protective performance.

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