Influence of Zn and Mg Alloying on the Corrosion Resistance Properties of Al Coating Applied by Arc Thermal Spray Process in Simulated Weather Solution

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Abstract

In this study, Al–Zn and Al–Mg coatings were deposited on steel substrates by an arc thermal spray process. X-ray diffraction and scanning electron microscopy were used to characterize the deposited coatings and corrosion products. Open circuit potential (OCP), electrochemical impedance spectroscopy, and potentiodynamic studies were used to assess the corrosion characteristics of these coatings after exposure according to the Society of Automotive Engineers (SAE) J2334 solution of varying durations. This solution simulates an industrial environment and contains chloride and carbonate ions that induce corrosion of the deposited coatings. However, the Al–Mg alloy coating maintained an OCP of approximately -0.911 V versus Ag/AgCl in the SAE J2334 solution even after 792 h of exposure. This indicates that it protects the steel sacrificially, whereas the Al–Zn coating provides only barrier-type protection through the deposition of corrosion products. The Al–Mg coating acts as a self-healing coating and provides protection by forming $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ (Al–Mg layered double hydroxides). $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ has interlocking characteristics with a morphology of plate-like nanostructures and an ion-exchange ability that can improve the corrosion resistance properties of the coating. The presence of Zn in the corrosion products of the Al–Zn coating allows dissolution, but, at the same time, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ are formed and act to reduce the corrosion rate.

Keywords Self-healing coating · Corrosion · Arc thermal spray · Electrochemical impedance spectroscopy

1 Introduction

The protection of steel structures from corrosion in aggressive environments is an issue of great concern for the entire world. Corrosion of structural steel and alloys results in mechanical properties loss affecting the structural integrity of infrastructure and bridges, as well as the

durability of structures. In addition, increased industrialization has caused a significant increase in the corrosion of steel structures, resulting in economic losses worldwide. Industrially polluted environments contain aggressive acidic ions such as Cl^- , CO_3^{2-} , and SO_4^{2-} that depend on industrial effluents and cause the failure of structures. These aggressive ions are responsible for the corrosion of industrially exposed metallic components. Therefore, it is necessary to protect steel structures by employing various protective methods. These protective methods can include utilization of epoxy coating, cathodic protection, metal plating, or aluminization. A number of different coating processes, including hot dip galvanizing, sol–gel methods, electroplating, and thermal spraying, are all used for application.

Al, Zn, and Mg are anodic in nature and thus can be used as coating materials to protect steel from corrosion in aggressive environments. Gudić et al. [1] and Khireche et al. [2] have noted that Al has versatile applications owing to its wide use in construction, metallurgy, and

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mechanical engineering and its standard reversible potential. However, the formation of Al_2O_3 on pure Al surface makes Al unsuitable for cathodic protection in sea water [3]. Therefore, to increase the activity of Al, additional metallic elements such as Cu, Mn, Si, Mg, Zn, and Sn are used [2]. The less active elements like Cu, Mn, and Si can enhance the active potential of Al, while the active elements like Zn and Mg can decrease the potential.

Bessone et al. [4] determined that the addition of Zn or Sn to an Al matrix activates the pitting potential in a more anodic direction in weakly acidic chloride solutions, allowing its use as a coating material for steel. Therefore, a variety of active metallic elements are being used to enhance the corrosion resistance properties of Al.

The effects of alloying elements on the corrosion resistance properties of coatings have been investigated by Panossian et al. [5] and Baker et al. [6], who determined that alloying Al and Zn in coatings enhances the corrosion resistance properties of steel substrates in certain environments. The addition of up to 1 wt% Mg to Zn coatings moderately improves corrosion resistance [7, 8]. However, the use of 3 wt% Mg with Al in galvanized coatings significantly increases corrosion resistance and is available commercially in Japan and Europe [9–16].

The corrosion resistance properties of Al alloying in Zn coatings are improved as a result of the formation of layered double hydroxides (LDH) at the cathode that act as a barrier for oxygen reduction reactions [10, 12, 16].

The use of an Al and Zn alloy coating provides advantageous corrosion resistance effects over the use of Al or Zn individually in certain atmospheres [17, 18].

Among the available coating processes, application of an arc thermal spray coating is relatively simple and has been applied to both freshly erected and rusted steel surfaces for more than 50 years with minimal drawbacks [19–22]. Varacalle et al. [23] used grit blasting media to assess the adhesion of Al and Al–Zn coatings applied by this process. They found that these coatings resisted corrosion for more than 20 years in a variety of aggressive environments as a result of their improved bonding strength with the steel substrates [23]. The arc thermal spray process requires several steps for the deposition of a coating. In this process, twin wires (these may be either the same or different metals) are fed into a gun, where an electric arc melts the tips of the wires. The molten droplets are then accelerated in a gas stream and deposited onto the substrate to be coated, resulting in thin lamellar particles that adhere to the surface after solidifying at atmospheric temperature [20, 24]. As a result of this sudden cooling at atmospheric temperature, the deposited coating can exhibit defects or pores as well as shrinkage [21, 25–31]. The deposited coating is generally thicker and composed of larger grain sizes than those deposited by other processes

owing to the multiple steps in the deposition process. During deposition, pores, defects, splats, and rough surfaces are formed in the coating. This coating does not allow for the formation of an intermetallic layer, which is found in coatings deposited by hot dip galvanization, and the adhesion is largely mechanical. The formation of defects and pores is an inherent property of the arc thermal spray coating process, and, while it cannot be avoided completely, it can be minimized through application of a variety of pore sealing agents [32–34].

The arc thermal spray coating process is currently used to protect cars and other vehicles from corrosion by applying Al, Zn, or other anodic metals. However, these vehicles are moving objects in the open atmosphere and they encounter a large amount of industrial pollutants, particularly the Cl^- , CO_3^{2-} and SO_4^{2-} ions that lead to deterioration. Most studies have performed corrosion tests in either mobile or stationary conditions. However, these are not cost effective and can require a large amount of time. An alternative to performing these tests is to perform accelerated tests in a laboratory by simulating the weathering environment, providing realistic results comparable to those obtained in actual weathering conditions. These tests can consist of salt sprays, intermittent cycles of salt and humidity, elevated humidity and temperature conditions, and drying. However, they are not as realistic as natural weathering conditions and do not provide a precise ranking of materials [35]. Therefore, these tests have been excluded and are not being considered for natural weathering tests [36–41]. Moreover, in recent years, car producers have begun to use different procedures to determine the ability of the protective coating to protect against deterioration. For instance, the Volvo Car Corporation employs test standard VCS 1027,149, while Renault uses test ECC1 D17 2028. American producers use a test developed by the Society of Automotive Engineers (SAE), SAE J2334, and German producers use test VDA621-415 [35].

The literature shows that there are few studies regarding the effects of Zn and Mg alloying in Al coatings on corrosion resistance during long exposure periods in industrially polluted solutions containing Cl^- and CO_3^{2-} ions. In this study, Zn and Mg were used as alloying elements in an Al coating deposited by an arc thermal spray process. An industrially polluted environment containing aggressive ions was simulated by dissolving sodium and calcium salts in distilled water, and the corrosion resistance performance of Al–Zn and Al–Mg coatings was assessed during prolonged exposure periods.

2 Materials and Methods

2.1 Coating Process

A carbon steel coupon with dimensions of 80 mm × 60 mm × 1 mm containing C = 0.240, Mn = 0.950, Si = 0.260, S = 0.008, P = 0.016, Cu = 0.020, Cr = 0.040 and Fe = balance (wt%) was used for deposition. The steel coupon was pickled in 10% HCl (V/V), washed with distilled water, dried, and grit-blasted with a mixture of 0.7 and 0.8 mm steel balls to roughen the surface for proper adhesion of the coating. The diameter of the Al, Zn, and Al–Mg wires for the arc thermal spray was 1.6 mm. For the deposition of Al–Mg coatings, twin wires of an alloy of 95 wt% Al and 5 wt% Mg were used. In contrast, to deposit the Al–Zn coating, two dissimilar wires of Al and Zn were used, resulting in the formation of an Al–Zn pseudo alloy coating rather than a true alloy [42].

The typical deposition parameters for the coatings used in this study have been described elsewhere, and the setup maintains a distance of 20 cm between the steel substrate and the spray gun at an air pressure of 6 bars [43–45]. During the spraying process, the voltage and current were maintained at 30 V and 200 mA, respectively.

The average thickness of each coating was approximately 100 µm (± 5 µm) and was measured at three different locations using a nondestructive Elcometer 456 (Tokyo, Japan). The bond strength of the deposited coating was measured according to test method KS F4716 for four consecutive samples [46]. An area of 16 cm² was selected for the bond strength measurements, exceeding the area size recommended in the standard method [46].

2.2 Characterization of Coatings and Corrosion Products

The morphology of the coatings and corrosion products was carried out with a scanning electron microscope (SEM, Philips XL 30, North Billerica, MA, USA) operated at 15 kV.

The X-ray diffraction (XRD, Philips X'Pert-MPD, EA Almelo, Netherland) analyses of the coatings and corrosion products were performed using CuK_α radiation (λ = 1.54059 Å) generated at 40 kV and 100 mA. The XRD data were scanned from 10°–90° at a rate of 0.5°/min.

2.3 Electrochemical Analysis

Electrochemical analysis of the deposited coatings was performed in SAE (Society of Automotive Engineers) J2334 solution [25, 47–52]. This solution was prepared by

dissolving analytical grade salts of NaCl (0.5 wt%), CaCl₂ (0.1 wt%), and NaHCO₃ (0.075 wt%) in distilled water with a pH of 9.17 at 25 °C (± 1 °C). Before beginning the experiments, the coating was stored in the SAE J2334 solution and the potential was stabilized with a potentiostat. The electrochemical analyses were performed with a three-electrode system, where the deposited coating acts as the working electrode, a platinum wire acts as the counter electrode, and silver-silver chloride (Ag/AgCl) is used as the reference electrode. The sample area on the working electrode was 0.78 cm², and it was fixed for all samples.

Electrochemical impedance spectroscopy (EIS) analyses were conducted by changing the frequency of a 10 mV sinusoidal voltage from 100 kHz to 0.01 Hz. DC polarization analyses were performed at a scan rate of 1 mV/s from −0.4 V to +0.8 V versus Ag/AgCl [53]. The potentiostat was a VersaSTAT (Princeton Applied Research, Oak Ridge, TN, USA), and data analysis was carried out with Metrohm Autolab Nova 1.10 software by fitting the experimental data to a constant phase element (CPE) model. All electrochemical analyses were performed in triplicate at 25 °C (± 1 °C) for consistency.

3 Results and Discussion

3.1 Characterization of Coatings

Characterization of the deposited coatings was carried out with several different techniques. After the coatings were deposited with an arc thermal spray process, the bond strength was measured, and the results are given in Table 1. These results indicate that the bond strength of the Al–Mg coating is 1.3 times greater than that of the Al–Zn coating. As previously reported, the addition of Mg to Al coatings influences the mechanical properties when deposited by an arc thermal spray process [54, 55].

It is well known that the morphology of coatings deposited by arc thermal spraying suffer from the occurrence of defects and pores on the top surface, which has been previously characterized [21, 25–31]. The Al–Zn coating, as shown in Fig. 1a, contains larger particles and

Table 1 Bond strengths (MPa) of coatings deposited by an arc thermal spray process

Coating ID	Sample no.				Average
	1	2	3	4	
Al–Zn	4.00	3.99	3.80	3.92	3.93
Al–Mg	5.48	4.86	4.78	4.97	5.02

Fig. 1 SEM images of deposited **a** Al-Zn, **b** Al-Mg coatings

has broad and elongated cracks on the surface. On the other hand, the Al-Mg coating shown in Fig. 1b exhibits a regular plate-like morphology with fine cracks on the top surface, which may be responsible for its enhanced bond strength compared to the Al-Zn coating.

The XRD spectra of the deposited coatings shown in Fig. 2 indicate that the Al-Mg coating consists solely of an Al phase, while the Al-Zn coating exhibits both Al and Zn both phases. For the Al-Mg coating, the Mg phase is not observed owing to limitations of the XRD technique. The content of Mg is very small and thus cannot be detected by the instrument.

3.2 OCP with Varying Exposure Periods

Results of the OCP measurements for the deposited coatings carried out in the SAE J2334 solution with varying

Fig. 2 XRD spectra of the deposited coatings

exposure periods are shown in Fig. 3. The active OCP of both types of coating during initial exposure in the SAE J2334 solution may be attributed either to the presence of aggressive ions (i.e., Cl^- and CO_3^{2-}) or to the preferential dissolution of the more anodic components of the coatings.

3.2.1 OCP of the Al-Zn Coating

The OCP of the Al-Zn coating for the first 120 h of exposure was active. However, as the exposure period increased beyond 216 h, the OCP shifted in the noble direction until reaching steady-state, as shown in Fig. 3. The Al-Zn coatings provided sacrificial protection to steel for the first 120 h of exposure, but it exhibited a noble potential after this period. This is due to the deposition of corrosion products on the coating surface that inhibits the penetration of the solution to the surface. This is indicated by the observation that after 216 h of exposure, the Al-Zn coatings become passive and provide a barrier-type protection rather than a cathodic protection to the steel.

The shifting of the OCP in the noble direction is a result of the formation of oxide passive film, as indicated by the Pourbaix diagram [56]. Muller and Galvele [57] noted a Zn content of more than 5 wt% or less than 0.9 wt% in Al does not provide sacrificial protection. Therefore, the OCP for the Al-Zn coating reflects the formation of oxide films on the coating during the period from 216 to 792 h of exposure.

3.2.2 OCP of the Al-Mg Coating

One interesting feature of the OCP plots in Fig. 3 is that the Al-Mg coating exhibits a more positive (noble) potential than the Al-Zn coating for the first 2 h of exposure (shown

Fig. 3 OCP of coatings measured in SAE J2334 solution with varying exposure periods

by arrow in Fig. 3). This may be due to the presence of a very small oxide layer, which cannot be identified by XRD. This small oxide film may act as a barrier to the penetration of solution during the initial 2-h period of exposure. However, after 2 h of exposure, this film began to dissolve. The active OCP of the Al-Mg coating is a result of the greater dissolution and more anodic nature of Mg ($Mg = -2.380$ V vs. standard hydrogen electrode (SHE) at 25°C). This result suggests that the Al-Mg coating is preferentially dissolved over the Al-Zn coating in this solution and maintains a potential of approximately -1.00 V versus Ag/AgCl after 2 h of exposure. This potential indicates that the coating has characteristics that would provide sacrificial protection for the steel. It has been reported that a coating that maintains a standard electrode potential of less than -0.870 V versus Ag/AgCl can provide cathodic protection to steel [55]. Figure 3 demonstrates that only the Al-Mg coating maintained an OCP of -0.926 V to -0.911 V versus Ag/AgCl at 216 and 792 h of exposure, respectively.

The OCP is steady from 216 to 792 h of exposure for both deposited coatings. A slight fluctuation in OCP was observed for both coatings owing to transient processes during the period from 216 to 792 h of exposure. During this period, passive oxide films were formed. However, these films may be porous as a result of pores, defects, or cracks in the coating surface, which allows the ingress of Cl^- and CO_3^{2-} ions through perturbation of the passive film and initiates pit formation. At the same time, some pits are re-passivated and form complex compounds.

3.3 EIS Analyses

EIS analyses of the coatings at their OCP after varying exposure periods in the SAE J2334 solution are shown in Figs. 4, 5, 6 and 7. The Nyquist plots for the coatings after 1 h of exposure are shown in Fig. 4a and illustrate that the coatings exhibit two depressed semicircle capacitive loops, indicating the corrosion process is associated with two time constants at different frequencies. The high-frequency capacitive loops are attributed to charge transfer with the surface film of the coatings [58–60], while the low-frequency loops are a result of double-layer capacitance at the coating–solution interface [61]. The Al-Zn coating is under a more active dissolution condition than the Al-Mg coating owing to its surface morphology, and this disparity can be seen from the dimensions of the Nyquist plots. However, Zn is the more active element than Al in the Al-Zn coating, and preferentially dissolves. This coating had a larger particle size and thus a greater number of cracks formed, as shown in Fig. 1. In contrast, the Al-Mg coating has a larger dimension in the Nyquist plots than the Al-Zn coatings as a result of the formation of a very small protective oxide layer and a plate-like morphology that inhibits solution penetration. During the initial phase of corrosion, morphology of the coating is the most important factor for controlling the deterioration of materials.

The Bode log modulus-frequency plots for the coatings after 1 h of exposure are shown in Fig. 4b. The impedance values measured at a low frequency (i.e., 0.01 Hz) are an indication of the total polarization resistance of the coating.

Fig. 4 EIS analyses of samples after 1 h of exposure in SAE J2334 solution: **a** Nyquist, **b** Bode log modulus–frequency, **c** Bode phase–frequency plots

Fig. 5 EIS analysis of samples after 24 h of exposure in SAE J2334 solution: **a** Nyquist, **b** Bode log modulus–frequency, **c** Bode phase–frequency plots

Fig. 6 EIS analyses of samples after 216 h of exposure in SAE J2334 solution: **a** Nyquist, **b** Bode log modulus–frequency, **c** Bode phase–frequency plots

Fig. 7 EIS analyses of samples after 792 h of exposure in SAE J2334 solution: **a** Nyquist, **b** Bode log modulus–frequency, **c** Bode phase–frequency plots

The Al–Mg coating exhibits a higher impedance than the Al–Zn coating. This suggests that alloying Al with 5 wt% Mg significantly influences the corrosion resistance properties of a coating deposited by arc thermal spraying in an aggressive solution, in spite of the addition of pure Zn.

The Bode phase-frequency plots for the coatings after 1 h of exposure are shown in Fig. 4c. The coated samples exhibit two maxima in different frequency ranges. The lower-frequency maxima are due to the coating-solution interface, while the middle range maxima are attributed to the coating capacitance. The Al–Mg coating shifted one maximum near -43° at 0.02 Hz owing to a reaction occurring at the coating-solution interface, and another near -36° at 40 Hz resulting from the coating capacitance. The shifting of the phase maximum to a higher angle at 0.02 Hz indicates resistance to reaction at the coating-solution interface. The Al–Zn coating shows a shift in the maximum at -25° for the same frequency, suggesting that this coating is susceptible to corrosion owing to the presence of more defects that can lead to galvanic or crevice corrosion.

As the exposure periods of the coatings in solution increase, the dimensions of the Nyquist plots also increase, as shown in Fig. 5, compared to the plots for 1 h of exposure as a result of the barrier type of protection provided by corrosion products and the passive film formed during the initial period of exposure. Initially, the coatings exhibit defects that allow significant solution penetration during the first 24 h of exposure, leading to corrosion. However, at the same time, the deposition of corrosion products as a passive film also occurs, resulting in an increase in resistance to corrosion. The corrosion reactions on an active surface area of the coatings have occurred and formed corrosion products. These corrosion products are deposited on the coating surface and correspond to the formation of an additional small semicircular capacitive loop at low frequency in the Nyquist plots for the coatings after 24 h of exposure, as shown in Fig. 5a. A complete semicircle loop in the high- to middle-frequency range results from coverage of the active surface area by corrosion products. Therefore, the dimension of this semicircular capacitive loop is greater than that observed after 1 h of exposure. The semicircular loop at the lower frequency is a result of resistance from the corrosion products and is much higher than that after 1 h of exposure. After 24 h of exposure in an aggressive solution, the defective coating may be dissolved, while uniform corrosion products have formed, causing resistance to penetration of the solution at the coating surface. The trend in the size of the Nyquist plots for both coatings at 24 h of exposure is identical, but the absolute sizes are greater than those after 1 h of exposure. These results suggest that corrosion products are more protective than the coating.

The impedance values of the coatings after 24 h of exposure are shown in Fig. 5b. The trend in the impedance is the same as that observed after 1 h of exposure (i.e., the Al–Mg is higher than the Al–Zn coating), but the values are greater because the corrosion products significantly reduce the active surface area and are compact, adherent, and uniformly deposited. The gradual increase in impedance values of the coatings indicates that corrosion phenomena in arc thermal deposited coatings are largely controlled by the nature of the corrosion products formed.

The Al–Mg coating exhibits higher values than the Al–Zn coating. This suggests that Mg plays a major role in controlling corrosion of the coating and acts as a self-healing coating in the aggressive solution. It was suggested by Lester et al. [62] that addition of 5 wt% Mg in Al alloy can significantly improve the corrosion resistance properties of a coating. Zn also has a positive effect on the corrosion resistance properties in the Al–Zn coating, which can be attributed to its preferential dissolution to form a protective passive oxide film.

The disappearance of the maxima at lower frequency and shift toward the middle-frequency range in Fig. 5c indicates that the capacitance of the Al–Mg coating is modified by the corrosion process [63]. This may be due to the dissolution of the coating and formation of corrosion products over time. The maximum at -57° shifted around 2 Hz for the Al–Mg coating, while the Al–Zn maximum at -39° and 50 Hz illustrates the protective properties of the corrosion products.

As the exposure periods of the coatings increase to 216 and 792 h in the SAE J2334 solution, the nature and orientation of the Nyquist plots change compared to those for the previous exposure periods. This is due to the continuous exposure of coatings in aggressive solution causing corrosion of the coatings and simultaneous deposition of corrosion products on the surface. EIS analysis plots for samples after 216 and 792 h of exposure are shown in Figs. 6 and 7, respectively. The Nyquist plots for the coatings after 216 and 792 h of exposure are shown in Figs. 6a and 7a, respectively. The presence of one half semicircular loop with a greater size indicates that the corrosion products have completely covered the surface of the coating and are blocking the pores and defects. Therefore, the sizes of the Nyquist plots are increased compared to those for shorter exposure periods and are directly proportional to corrosion resistance [64].

The impedance plots for the samples after 216 and 792 h of exposure are plotted in Figs. 6b and 7b, respectively. The impedance values increased gradually with the exposure period. However, even after much longer exposure durations, the coatings still exhibit high resistance to corrosion as a result of the formation of adherent, uniform, and sparingly soluble corrosion products that inhibit the

penetration of aggressive ions. The impedance of the Al–Mg coating after 216 and 792 h of exposure is significantly greater than for shorter exposure periods. Mg and Zn are more electronegative elements than Al and thus preferentially dissolve to form corrosion products that fill the pores and defects in the coating, resulting in higher corrosion resistance.

The surface area covered by corrosion products increased during the exposure periods for the Al–Mg coating. As a result, the phase angle maxima shifted toward higher angles (i.e., -70° and -75° for 216 and 792 h, respectively) for broader frequency ranges compared to those for the Al–Zn coating. This broader frequency range indicates that the coating exhibits higher corrosion resistance, as shown in Figs. 6c and 7c. These results indicate that the corrosion products on the Al–Mg coating after 792 h of exposure are homogenous, uniform, and have less defects than the deposited coating.

The electrochemical data were extracted after fitting the EIS plots to a suitable electrical equivalent circuit (EEC) for the exposure periods. The EEC of the coatings after 1 and 24 h of exposure is shown in Fig. 8a. This EEC consists of two equivalent circuits in series, and R_s , R_{pore} , and CPE represent the solution resistance, polarization resistance, and constant phase element, respectively. CPE₁ is the pseudo double-layer capacitance. The EEC also contains the charge transfer resistance (R_{ct}), which is associated with the metal oxide–solution interface. CPE₂ refers to the second capacitor loop at lower frequencies and is attributed to the formation or diffusion of the corrosion product/oxide/passive film on the coating surface.

Fig. 8 EEC models for coatings exposed in SAE J2334 solution after **a** 1–24 h, **b** 216–792 h of exposure

The CPE originates as a result of surface roughness, heterogeneity, electrode porosity, slow adsorption reactions, non-uniform potential, and current distribution [65–67]. The CPE can be described by the following equation:

$$Z_{\text{CPE}(\omega)} = [Y(i\omega)^n]^{-1}, \quad (1)$$

where Y is the magnitude of the CPE, i is the imaginary number, $\omega = 2\pi f$ and represents the angular frequency (rad/s, f is frequency in Hz), and n is an exponential term corresponding to the depression degree in the impedance spectrum. On the basis of n values obtained from fitting the EIS plots to a suitable EEC, the CPE can be determined. $n = 0, 1, -1$ or 0.5 corresponds to pure resistance, pure capacitance, pure inductance, or Warburg impedance, respectively [2, 68–70]. The EEC model for samples after 216–792 h of exposure is shown in Fig. 8b [68–72].

The electrochemical data for fitting the EIS plots to suitable EEC are summarized in Table 2. As the exposure periods increased, R_{pore} and R_{ct} also increased gradually. However, the Al–Mg coating exhibits an abrupt increase in these values from 216 to 792 h of exposure, possibly due to the compact, adherent, and stable nature of the corrosion products formed.

It has been previously reported that the Mg in an Al coating acts as a self-healing element to enhance the corrosion resistance at prolonged exposure durations [62]. With longer exposure periods, the capacitive response of the coatings, as well as the corrosion products, decreases, as can be seen from Table 2, where Y_1 and Y_2 decrease with exposure owing to the decrease in defects in the coating and the increase in deposition of uniform and homogenous corrosion products, respectively. Therefore, the n values trend toward 0.9, suggesting that the corrosion products are homogenous, uniform, and regular [73, 74]. This observation is more pronounced for the Al–Mg coating. Table 2 indicates that the R_{ct} value is greater than R_{pore} , suggesting that the corrosion products of the coatings are more stable and protective than the coating itself. Therefore, this suggests that prolonged exposure of these coatings in the aggressive solution is controlled by the nature of corrosion products. The R_s value increases continuously for both coatings as a result of the increase in R_{pore} .

3.4 Potentiodynamic Analyses After 792 h of Exposure

The potentiodynamic plots for the coatings after 792 h of exposure in SAE J2334 solution are shown in Fig. 9. The Al–Zn coating exhibits more cathodic current than the Al–Mg coating as a result of the oxygen reduction reaction at the cathodic site. The corrosion potential of the Al–Zn

Table 2 Electrochemical parameters extracted after fitting EIS data to suitable EEC for varying exposure periods

Time (h)	Sample ID	R_s (Ω cm ²)	R_{pore} (Ω cm ²)	CPE_1		R_{ct} (Ω cm ²)	CPE_2	
				Y_1 (1×10^{-4}) (Ω^{-1} cm ⁻² s ⁿ)	n_1		Y_2 (1×10^{-4}) (Ω^{-1} cm ⁻² s ⁿ)	n_2
1	Al-Zn	63.47	251.01	2.46		0.63	462.91	87.96
	Al-Mg	78.93	431.46	2.15		0.71	5499	8.12
24	Al-Zn	65.61	659.58	2.11		0.73	679.1	66.79
	Al-Mg	85.11	785.8	2.02		0.74	5560.0	5.52
216	Al-Zn	66.21	1230.2	1.94		0.75	3816.2	42.02
	Al-Mg	87.56	11,728.0	0.84		0.81	16,789.0	2.93
792	Al-Zn	81.84	1293.11	1.15		0.79	4789.7	40.53
	Al-Mg	60.00	18,515	0.47		0.85	27,129.0	1.19

Fig. 9 Potentiodynamic plots for samples after 792 h of exposure in SAE J2334 solution

coating shifted in the direction of the cathodic site owing to deposition of corrosion products on the coating and defects that block the active site, whereas for the Al-Mg coating it exhibited a higher value.

These results suggest that the Al-Zn coating is under active dissolution. The Al-Zn coating shows a limiting current density (I_{lim}) due to the deposition of corrosion products that act as mass transfer resistance during anodic scanning. Moreover, the Al-Zn coating exhibits pitting potential (E_{pit}) during anodic scanning that can be attributed to the removal of loosely bound oxides and the localized attack of Cl^- ions on defects in the coating or passive film. The Al-Mg coating exhibits an active corrosion potential (E_{corr}) and less cathodic and anodic current than the Al-Zn coating. The cathodic plots reveal the occurrence of an oxygen reduction reaction rather than a hydrogen evolution reaction. The oxides formed during exposure in the solution are reduced and deposited on the coating surface, resulting in higher resistance to corrosion. The anodic current gradually increases during anodic

scanning, indicating that the corrosion products are adherent, compact, stable, and less porous, which inhibits the ingress of aggressive solution ions toward the coating.

The electrochemical data after fitting the potentiodynamic plots to Tafel regions are given in Table 3. The E_{corr} for the Al-Mg coating is -0.987 V versus Ag/AgCl and therefore provides sacrificial protection to the steel substrate. Even after 792 h of exposure, it still provides cathodic protection to the steel substrate. However, the Al-Zn coating has an E_{corr} of -0.824 V versus Ag/AgCl resulting from the blockage of the coating by corrosion products that passivate the surface to further corrosion. The corrosion current density (I_{corr}) of the Al-Zn coating is higher than that observed for the Al-Mg coating.

The corrosion rate ($\mu\text{m y}^{-1}$) for the coatings was calculated using the following equation [75]:

$$\text{Corrosion rate } (\mu\text{m/y}) = \frac{3.27 \times I_{\text{corr}} \times E.W.}{d} \quad (2)$$

The corrosion rate in Eq. (2) is expressed in $\mu\text{m/y}$, while I_{corr} has units of $\mu\text{A/cm}^2$. The value of I_{corr} was obtained by dividing the total surface area of the working electrode in the corrosion current. $E.W.$ represents the equivalent weight (g/mole), and d is the density (g/cm^3) of alloy coating. The corrosion rate of the Al-Mg coating is $5.61 \mu\text{m/y}$, whereas for the Al-Zn coating it is $86.36 \mu\text{m/y}$. The Al-Mg coating exhibits a corrosion rate that is nearly 15 times slower than the Al-Zn coating. The low corrosion rate observed for the Al-Mg coating may be due to the Mg in the Al coating healing the defects and pores and enhancing the corrosion resistance properties by depositing protective, adherent, and insoluble corrosion products.

After completion of the potentiodynamic analyses of the coatings, the morphology of the corrosion products was determined by SEM. The SEM images of the corrosion products are shown in Fig. 10. The SEM image of the corrosion products formed on the Al-Zn coating shows

Table 3 Potentiodynamic parameters for the coatings after 792 h of exposure in SAE J2334 solution

Coating ID	E_{corr} (V vs. Ag/AgCl)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate ($\mu\text{m}/\text{y}$)
Al–Zn	– 0.824	6.45	86.36
Al–Mg	– 0.987	0.497	5.61

Fig. 10 SEM images of corrosion products formed on **a** Al–Zn, **b** Al–Mg coatings after potentiodynamic analyses in SAE J2334 solution

micro-pores with a coagulated and thick morphology (Fig. 10a). This can influence the ingress of aggressive species and contribute to corrosion in later stages. However, the corrosion products formed on the Al–Mg coating surface are homogenous, regular, and form a thin film (Fig. 10b) that inhibits the penetration of corrosive species and enhances corrosion resistance at longer exposure durations.

3.5 Plausible Corrosion Mechanism

The electrochemical studies such as the EIS (Figs. 4, 5, 6, 7) and potentiodynamic (Fig. 9) analyses reveal that the Al–Mg coating has a superior performance compared to the Al–Zn coating, as a result of the more passivating nature of the corrosion products formed in the SAE J2334 solution that fill the defects and form a very thin layer of oxides under prolonged exposure.

In both coatings, there is the possibility of galvanic coupling, which affects the dissolution of coatings and formation of corrosion products from the early stages to prolonged exposures. The SEM images of the coatings show that they possess defects (Fig. 1), which also play an important role in faster dissolution and subsequent deposition of corrosion products on the coating surface. The corrosion mechanism for the coatings in the SAE J2334 solution can be derived from the reactions below.

In these coatings, Zn and Mg preferentially dissolve owing to their anodic nature at the anodic site to form Zn^{2+} and Mg^{2+} , respectively:

The cathodic reaction is an oxygen reduction reaction:

This hydroxyl ion (OH^{-}) increases the pH of the solution and affects the dissolution of Zn and Mg through following reactions [76]:

The CO_3^{2-} in Eq. (7) is a result of the solution composition.

However, Al is the main constituent of the coating which reacts with alkaline solution and form following complex:

Therefore, there is the possibility for the transformation of metal hydroxides into layered double hydroxides (LDH), as explained in the following equations. The formation of LDH is more favorable in alkaline solutions than other metal oxides [77]:

The XRD spectra of the corrosion products corroborate these reaction mechanisms as shown in Fig. 11. However, the corrosion products formed on the Al–Mg coating must contain Al, because it is main coating constituent as well as $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$, according to Eq. (10), but in the XRD results, only Al peaks are observed.

The $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ was not detected because it was leached from the surface owing to its low concentration and presence of a very thin layer [76]. Therefore, this phase is not detected by the XRD technique. This result is corroborated by the SEM image (Fig. 10b) of the corrosion products, which shows that they are very thin and have a regular plate-like morphology. Zeng et al. [78] previously noted that $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ has interlocking characteristics with a morphology of plate-like nanostructures, with an ion-exchange ability that can improve the corrosion resistance properties of coatings, and this can be clearly seen in the SEM image of the Al–Mg corrosion products in Fig. 10b.

The XRD spectra for the corrosion products formed on the Al–Zn coating consist of Al, Zn, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, and $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$, as shown in Fig. 11. The Al and Zn are detected from the coating materials, while $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ are corrosion products formed as described by the corrosion mechanisms in Eqs. (7) and (9), respectively. The formation of $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and

$\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ in corrosion products results in a reduced corrosion rate at prolonged exposure durations [79], but the presence of Zn in the corrosion products causes corrosion to occur until 792 h of exposure.

4 Conclusions

1. Mg plays a major role in the adhesion and microstructure of the Al–Mg coating. The addition of Mg in the coating affects mechanical as well as corrosion resistance properties.
2. The SEM images of the Al–Zn coating show elongated cracks with larger particle sizes, while the Al–Mg coating exhibits plate-like morphology with regular deposition.
3. The Al–Mg coating provides sacrificial protection to the steel substrate until 792 h of exposure in the SAE J2334 solution, as confirmed by the OCP plots that show -0.911 V versus Ag/AgCl, while the Al–Zn coating provides protection for up to 120 h.
4. Ennobling in the OCP of the coatings is observed after 120 h of exposure due to the deposition of corrosion products.
5. The corrosion products of the Al–Zn coating act as a barrier against the penetration of aggressive solution species, while the Al–Mg coating acts as sacrificial as well as barrier protection even after 792 h of exposure.
6. The EIS results for the Al–Mg coating at varying exposure periods reveal that R_{pore} and R_{ct} increase significantly as a result of the deposition of thin, uniform, and protective corrosion products.
7. Potentiodynamic plots show that the Al–Zn coating contributed to pit formation and mass transfer phenomena as a result of the deposition of thick, porous, and coagulated corrosion products, as corroborated by the SEM image of the corrosion products.
8. The corrosion rate of the Al–Mg coating is 15 times slower than that of the Al–Zn coating in SAE J2334 solution after 792 h of exposure.
9. The XRD analysis of the corrosion products of the coatings reveals deposition of Al in the Al–Mg coating, whereas the Al–Zn coating exhibited Al, Zn, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, and $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$. The formation of $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ on the Al–Mg coating enhances the corrosion resistance, resulting in an increase in R_{ct} and R_{pore} with the exposure periods and a reduction in the active surface area of the coating.
10. The Al–Mg coating possess self-healing properties through the formation of $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ as a

Fig. 11 XRD spectra of the corrosion products formed on Al–Zn and Al–Mg coatings after potentiodynamic analyses in SAE J2334 solution

corrosion product. The presence of Zn in the Al–Zn coating may cause dissolution of the coating due to its high activity, while at the same time, formation of $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ improves corrosion resistance. Therefore, for longer exposure durations, improved corrosion resistance is observed for these coatings.

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