

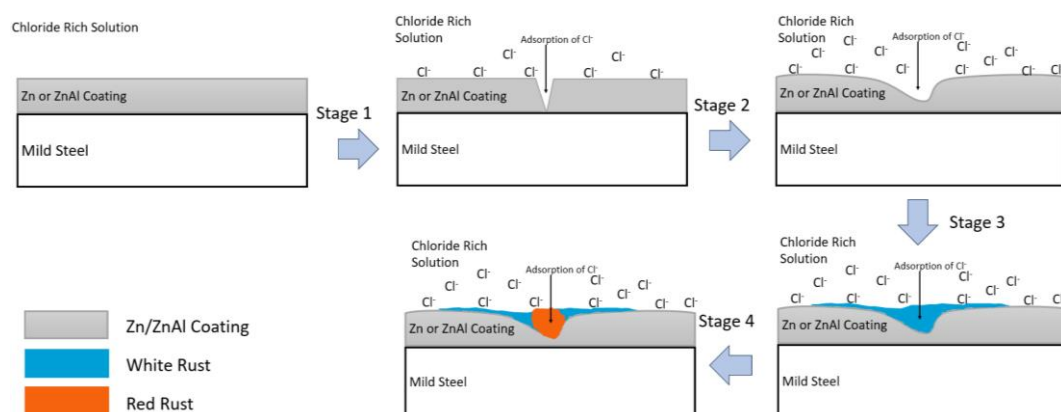
Investigating the corrosion behavior of hot-dip galvanized Zn and Zn-10Al coatings on carbon steel without top coating in chloride-rich immersion environments

Agus Solehudin^{1*}, Haipan Salam¹, Risti Ragadhita¹, Muhammad Irfansyah Maulana²

¹ Department of Chemical Engineering, Universitas Pendidikan Indonesia, Bandung 40154, **Indonesia**

² Department of Energy Science and Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, **Republic of Korea**

✉ asolehudin@upi.edu



Highlights:

- Hot-dip Zn and ZnAl coatings were applied on carbon steel for chloride tests.
- ZnAl coating exhibited smoother morphology and higher surface hardness.
- Corrosion rate was 7.89 $\mu\text{m}/\text{year}$ for Zn and $\pm 0.1 \mu\text{m}/\text{year}$ for ZnAl coatings.
- ZnAl achieved longer lifetime (~ 6.2 years) and superior structural stability.

Abstract

This study investigates the corrosion resistance, surface hardness, morphological structure, and predicted lifetime of carbon steel coated with pure zinc (Zn) and zinc aluminum alloy (ZnAl) in chloride rich environments. Coatings were applied by hot dip galvanizing, and characterized using Field Emission Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy (FESEM-EDS), Vickers hardness testing, and salt spray testing. Before exposure, both coatings confirmed homogeneity with smooth, topographically uniform surfaces, and no macroscopic defects. ZnAl coatings also delivered superior hardness compared to pure Zn and uncoated steel. After exposure, ZnAl maintained smoother, more stable surfaces with smaller and fewer pitting defects, whereas pure Zn suffered medium to severe damage. Pure Zn coatings showed fluctuating corrosion behavior with an average rate of 7.8944 $\mu\text{m}/\text{year}$, while ZnAl coatings exhibited minimal fluctuations within $\pm 0.1 \mu\text{m}/\text{year}$, indicating high resistance to chloride concentration. Predicted lifetime ranged from 3.7 to 5.5 years for pure Zn (average 4.7 years) and 5.9 to 6.5 years for ZnAl (average 6.2 years). Despite being thinner, ZnAl provided superior corrosion protection and structural stability. These findings indicate that ZnAl alloy coatings provide superior corrosion protection, structural stability, and mechanical performance for carbon steel in chloride rich environments.

Keywords: Corrosion resistance; Zinc alloy; Hot-dip galvanizing; Hardness; Carbon steel; Salt spray

Article info

Submitted:
2025-06-04

Revised:
2025-09-11

Accepted:
2025-10-18



This work is licensed under
 a Creative Commons
 Attribution-NonCommercial 4.0
 International License

Publisher

Universitas
 Muhammadiyah
 Magelang

1. Introduction

Various applications, ranging from building construction to industrial infrastructure, have utilized steel material due to its excellent mechanical properties and low production costs [1], [2],

[3]. However, steel undergoes rapid degradation when exposed to corrosive environments, especially environments with rich chloride ions, such as coastal areas or saltwater systems that threaten its structural integrity due to chloride ions (Cl^-) that penetrate the passive protective layer of the metal and initiate corrosion processes [4], [5], [6], [7], [8], [9].

In the context of marine environments or areas with high chloride content, corrosion occurs more rapidly due to the high aggressiveness of Cl^- ions, which accelerates redox reactions that damage metal structures [5], [8], [10], [11], [12]. Therefore, protection against corrosion in steel is an important aspect that continues to be developed to extend its lifespan and increase its reliability in various structural applications. Corrosion control and prevention are not only technical requirements, but also strategic for asset sustainability and industrial operational efficiency [13]. Most structural steel materials have undergone various of surface treatments, including organic and metallic coatings, to maintain corrosion-resistant performance over time. Aside from that, several methods for corrosion protection have also been developed, including thermal spray coating (such as plasma spraying, arc spraying, and laser cladding) and hot-dip immersion (such as hot-dip galvanizing) [14], [15], [16], [17]. Among many coating processes, hot-dip galvanizing is a fairly easy and cost-effective way for covering steel substrates [18], [19], while providing strong corrosion resistance and coating longevity.

Zinc (Zn) is an excellent anti-corrosion coating for steel because its corrosion potential standard is lower than that of steel. Although conventional Zn coatings are excellent in providing cathodic protection, their drawback is the instability of the passive layer they create, which can quickly erode in chloride-rich conditions [20], [21]. One of the methods devised to improve corrosion resistance involves alloying other metal components into a single metal layer, such as utilizing a zinc-aluminium (ZnAl) alloy. The aluminium content in this alloy facilitates the formation of a more stable and denser aluminium oxide-based passive layer that is better at resisting chloride penetration [22], [23]. These characteristics make it a strong candidate for coating applications that require long-term protection in harsh conditions [17], [24]. However, combining Al and Zn to form a ZnAl alloy can lead to a reduction in mechanical properties, particularly in crack resistance [25]. Consequently, while the addition of aluminium improves corrosion and wear resistance due to the formation of aluminium oxide on the substrate's surface, but it also significantly alters the microstructural characteristics of the coating. Studies show that the presence of new intermetallic phases, finer grain distribution, and changes in coating morphology can impact its structural and mechanical integrity [26].

Previous studies on anti-corrosion strategies for steel have broadly focused on the development of both metallic/inorganic coatings and polymer-based protective systems, each offering different mechanisms of corrosion mitigation. Metallic and inorganic coatings have been widely investigated due to their ability to provide sacrificial protection and to improve the electrochemical stability of steel substrates. For example, zinc phosphate coatings modified with calcium oxide have been reported to produce denser and more uniform layers, thereby enhancing the inhibition efficiency by limiting electrolyte penetration and stabilizing the passive film on the substrate surface [27]. Similarly, the application of electroplated Ni/Co/Fe alloys reinforced with zinc has shown promising improvements in corrosion resistance, which can be attributed to synergistic alloying effects that reduce anodic dissolution and strengthen the cathodic protection capability of the coating [28], [29], [30]. Oxide-based hybrid systems have also gained attention such as $\text{TiO}_2\text{--Al}_2\text{O}_3$ layers reinforced with zinc fillers demonstrated enhanced mechanical integrity and corrosion resistance, while Zn- TiO_2 composites further highlighted the benefits of combining metallic zinc with ceramic oxides to improve coating density and reduce porosity [31], [32], [33]. Beyond binary systems, more advanced alloying approaches, such as Zn-Al [34], Zn with 10, 15, 20, and 30% of aluminium [35], pure Zn and Zn alloy (i.e., Zn, Al6061, and Zn/23Al) [36], Zn-Al-Mg alloys [37], Co- CeO_2 composites [38], and Al-LDH coatings [38], have provided evidence that controlled phase distribution and the incorporation of corrosion-inhibiting elements or layered double hydroxide structures can significantly extend service life by slowing the progression of localized corrosion.

In parallel with metallic and inorganic approaches, considerable research attention has been devoted to the application of polymer-based coatings as top layers deposited over metallic systems such as Zn and ZnAl coatings. These polymeric layers, often enriched with active fillers, are designed to enhance barrier properties and inhibit electrochemical processes. For instance, epoxy coatings reinforced with zinc oxide nanoparticles at a concentration of three percent by weight have demonstrated substantial reductions in corrosion rate, primarily by increasing coating density, decreasing ion permeability, and suppressing the transport of chloride ions in marine

environments [28]. Other hybrid systems, such as epoxy matrices embedded with zinc layered double hydroxide structures [32], have been tailored to provide both physical barrier protection and active release of inhibitive species, thereby creating a dual action corrosion defense mechanism. Similarly, oxygen polyurethane acrylate coatings filled with zinc oxide particles have been reported to improve resistance against aggressive electrolytes, owing to the combined effects of polymer flexibility, filler reinforcement, and enhanced adhesion to the steel substrate [39]. Taken together, these polymer-based strategies when used as top coatings over Zn or ZnAl metallic layers are particularly effective in delaying the onset of red rust formation and significantly extending the service life of coated steel under salt spray testing.

Despite these advances, a notable research gap remains, as only a limited number of studies have directly compared the corrosion protection performance of pure Zn and ZnAl alloy coatings produced by hot dip galvanizing on carbon steel substrates without an additional top coating. Much of the previous work has concentrated on complex coating systems, such as multilayer configurations or the incorporation of additives and fillers, to enhance protective performance. In contrast, simpler yet promising approaches, such as single metallic coatings of Zn or ZnAl, have not been thoroughly examined. Moreover, the corrosion resistance of metallic coatings is strongly governed by their microstructural features, particularly phase distribution and the formation of intermetallic phases, which play a decisive role in determining long-term durability [26]. However, these aspects, especially in coating systems without a top layer, have seldom been the central focus of previous investigations, despite their critical importance in defining protective performance. In addition, no prior study has systematically compared the corrosion performance and lifetime prediction of carbon steel coated with pure Zn and ZnAl alloys. Although previous investigations have reported on the corrosion resistance of ZnAl coatings with an aluminium content of 10%, these works did not explicitly quantify corrosion rates or provide lifetime predictions. Furthermore, to date, no study has evaluated the corrosion behaviour of Zn and ZnAl coatings under varying NaCl concentrations. Therefore, the present research seeks to address these gaps by examining not only the phase distribution and intermetallic phase formation in Zn and ZnAl coatings, but also their corrosion rates and lifetime predictions across different chloride environments, thereby providing a more comprehensive understanding of their protective efficiency and durability.

The purpose of this study is to analyze and compare the effectiveness of corrosion protection provided by pure Zn coatings and ZnAl alloys applied to carbon steel substrates using the hot-dip galvanizing process. The single coating approach used in this study enables direct evaluation of the corrosion performance of each type of coating, which is innovative. This study also illustrates the potential of the ZnAl layer, which, despite its lower thickness, can provide higher corrosion resistance when compared to thicker Zn layers. In addition, factors of predicting the lifetime of each coating are investigated, a topic that has rarely been the primary focus of earlier studies. The findings from this study are expected to provide a simpler, more efficient, and economical metal coating solution for corrosion protection on various metal-based infrastructure.

2. Methods

2.1. Materials and Specimen Preparation

The material specimen used in this study was carbon steel, which is frequently used in industrial applications and prone to corrosion in harsh environments. Table 1 shows the chemical compositions of the examined substrates based on Energy Dispersive X-ray Spectroscopy (EDS, Xplore Oxford Instruments) analysis. Specimens were cut into squares of 20 × 15 × 3 mm in length, width, and thickness. Before the coating process, specimen surface preparation is an important step in ensuring the success of the coating and the stability of the bond between the protective layer and the substrate. The surface preparation procedure followed the ASTM G1-03(2017)e1 standard (Standard Practice for Corrosion Test Specimens), which regulates the cleaning of metal surfaces to remove contaminants, oxides, and other materials that can affect the quality of the coating.

The preparation process was carried out in four main stages, namely: (i) the surface of the substrate was rubbed using silicon carbide (SiC) sandpaper with various graded grit sizes (i.e., 320, 600, and 1000 grit) to produce a homogeneous surface; (ii) the substrate surface was cleaned with acetone to remove oil, dust, and other material residues that can reduce the adhesion of the coating to the steel substrate; (iii) the substrate surface was cleaned with distilled water to ensure

Table 1.
Chemical composition
of carbon steel as
specimen

Element	Content (%)
Iron (Fe)	90.43
Carbon (C)	3.65
Manganese (Mn)	3.97
Silicon (Si)	0.25
Oxygen (O)	1.69
Phosphorous (P)	0.02
Sulphur (S)	0.00

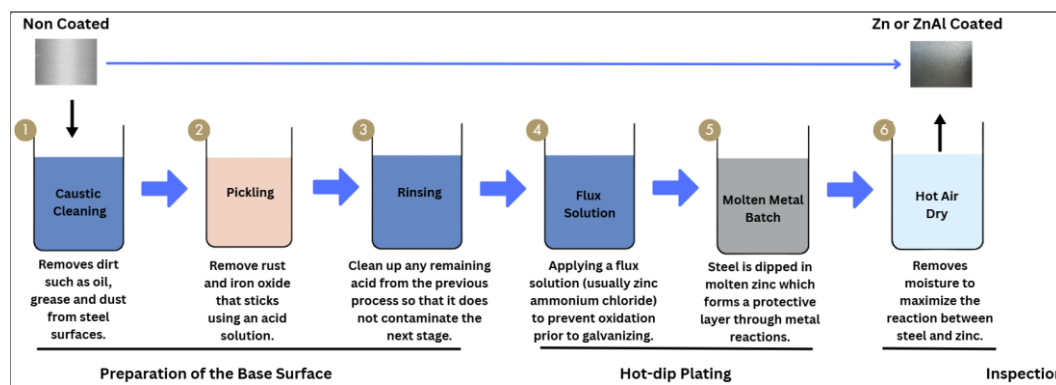
that there were no chemical residues that could potentially interfere with the coating process; and (iv) the specimen was dried naturally at room temperature to remove moisture that could affect the quality of the applied protective layer. The coating material used consists of an alloy of pure Zn and ZnAl, where ZnAl contains approximately 10% aluminium by weight.

2.2. Coating Preparation

The coating preparation process was conducted in the production workshop of PT Kabatama Raya, located in Serang, Banten, Indonesia. Both types of coatings, namely pure Zn and ZnAl alloy, were applied to carbon steel substrates via the hot-dip galvanizing method. This method involved the process of dipping steel into melted pure zinc or zinc alloy, resulting in a reaction between the coating metal and steel surface which produces a protective layer. Figure 1 illustrate the hot-dip galvanizing method. In general, hot dip galvanizing for steel coating with either Zn or ZnAl is carried out through several standard stages [20]. The process begins with heating the coating metal or alloy to its molten phase, around 450 to 500 °C for Zn and 660 to 700 °C for ZnAl, allowing the liquid metal to uniformly cover the steel surface. However, in this study the passivation treatment after coating was not performed. This means that once the steel was withdrawn from the galvanizing bath, no post treatment such as chromate or silicate passivation, which is typically applied to improve the initial resistance against white rust, was carried out. Consequently, the resulting samples only contained metallic Zn or ZnAl layers without any supplementary protective film, and thus their corrosion performance was solely determined by the microstructural characteristics of the metallic coating, including intermetallic phase formation, the distribution of Zn and Al, coating thickness, and overall homogeneity.

The substrate was dipped vertically into the molten Zn for 5 seconds. For the Zn-Al alloy, the dipping process was longer, lasting a total of 10 seconds, as it involved a two-stage process: first dipping in Zn, then in Al. Despite this difference in immersion time, the resulting coating thicknesses were comparable. This indicates that the final coating thickness, which in this study is consistent with the SNI 9039:2021 Class 2 standard, is a more critical parameter than the immersion time itself. After immersion, the samples were slowly withdrawn at a constant speed to prevent tensile cracking from rapid cooling and to allow excess molten metal to drain, forming a uniform surface. The coated specimens were then cooled in open air at ambient temperature until they reached thermal stability before being sectioned with a precision cutting machine for characterization.

Figure 1.
Main process flow
for hot-dip
galvanizing
technique



2.3. Corrosion Performance Test

Corrosion testing on carbon steel coated with pure Zn and ZnAl alloys was carried out using the neutral salt spray method following the ASTM B117-19 standard, with modifications that involved varying the concentration of the NaCl solution to assess the response of the coating to different levels of severity of corrosive environments. The corrosion test aims to assess the durability of the coating in the face of a corrosive environment simulated by continuously spraying a salt solution in a closed space. The coated carbon steel samples were first cleansed of debris and oil with isopropyl alcohol before being placed in the test chamber at a 15-30° inclination from vertical to ensure that the salt mist spreads evenly throughout the surface. The test solution was

a sodium chloride (NaCl) solution with different concentrations, specifically 1.0, 2.0, 3.0, 4.0, and 5.0% (weight/volume), with a pH ranging from 6.5 to 7.2. During testing, the temperature in the chamber was maintained at 35 ± 2 °C with a falling mist volume of 1.0 to 2.0 mL/80 cm² per hour. Samples were tested for 100 hours to simulate medium-term exposure in an aggressive environment. During the testing process, the pH and volume of the mist deposits were controlled periodically to maintain stable test conditions. After reaching the targeted testing time, the sample was taken from the chamber, cleaned with deionized water, and dried before being analyzed. Evaluation was carried out by observing the presence of corrosion in the form of white rust (an indication of degradation of the Zn or ZnAl layer) and red rust (an indication that the steel substrate is starting to corrode). To evaluate the corrosion rate based on mass loss, a method following the ASTM G31 standard was used. The corrosion rate is calculated using Eq. (1).

$$Cr = k \frac{W}{DAT} \quad (1)$$

where Cr = corrosion rate (µm/y = micrometer of penetration per year); k = constant (8.76×10^7); W = weight loss (g); A = outer exposed surface (cm²); T = time (hour); and D is density of Zn and ZnAl.

2.4. Coating Characterization

Characterization of the coating attached to the substrate was carried out before and after the corrosion exposure process. Analysis of the surface morphology and cross-section of the coating was carried out using Field Emission Scanning Electron Microscopy (FE-SEM; Sigma 360 Carl Zeiss). FE-SEM was used to observe the surface structure, cross-sectional morphology, and coating layer thickness precisely. Observation of the cross section allows measurement of the total thickness of the coating and the possibility of the formation of an intermetallic layer between the coating and the carbon steel substrate. FE-SEM was also used to identify microstructural homogeneity, the presence of microscopic defects such as cracks, pores, or delamination, as well as to analyze the interaction between the coating metal and the substrate at the microscopic level. To support morphological observations, the FE-SEM was equipped with an Energy Dispersive X-ray Spectroscopy (EDS) detector which was used to determine elemental composition at various points and coating zones, including element mapping. This analysis helps strengthen the understanding of the bond zone (interphase) between the coating and the substrate, which plays a crucial role in the corrosion resistance and long-term stability of the coating.

To assess the mechanical strength of the coating, a microhardness test was carried out using the Vickers method (Zwick Ns 61029) with a load of 100 gf and a holding time of 10 seconds. Tests were conducted from the layer surface to the core zone of the substrate to obtain a hardness distribution profile and identify changes in mechanical properties resulting from diffusion between metals. The Vickers method was used to measure hardness by pressing a diamond pyramid-shaped indenter with a peak angle of 136° onto the surface of the test material, and then measuring the diagonal of the resulting indentation trace. The working principle of this method provides an overview of the material's resistance to local deformation, especially in layered materials or those that have undergone surface treatment.

3. Results and Discussion

3.1. Corrosion Performance

The results presented in Table 2 demonstrate that the effect of NaCl concentration on the corrosion rate of Zn and ZnAl coatings is non-linear and strongly dependent on the coating composition. For Zn coatings, the corrosion rate remained relatively high at low concentrations, recorded at 7.495 µm/y in 1% NaCl and slightly decreasing to 7.293 µm/y at 2%. As the chloride

content increased to 3%, the corrosion rate rose again to 7.640 µm/y, and reached its maximum at 10.193 µm/y in 4% NaCl. Overall, Zn coatings showed fluctuating corrosion behavior with an average rate of 7.8944 µm/y. In contrast, ZnAl coatings demonstrated much more stable and reliable performance across all NaCl concentrations. At 1% NaCl, the corrosion rate was 1.078 µm/y,

Table 2.
Corrosion rate and life
time of the specimen

Concentration of NaCl (%)	Content (%)	
	Zn	Zn-Al
1	7.495	1.078
2	7.293	1.046
3	7.640	0.982
4	10.193	1.003
5	6.851	1.046
Average	7.894	1.031

which slightly decreased to 1.046 $\mu\text{m}/\text{y}$ at 2% and reached its lowest value of 0.982 $\mu\text{m}/\text{y}$ at 3%. When the concentration increased further to 4% and 5%, the corrosion rate rose only marginally to 1.003 $\mu\text{m}/\text{y}$ and 1.046 $\mu\text{m}/\text{y}$, respectively. These very small fluctuations (within ± 0.1 $\mu\text{m}/\text{y}$) indicate that ZnAl coatings are far less sensitive to chloride concentration compared to pure Zn. This demonstrates the superior protective capability of ZnAl coatings, providing more consistent long-term corrosion resistance for carbon steel in chloride-containing environments.

In the present study, the corrosion behavior of Zn coatings was found to be highly fluctuating, with rates that increased and decreased irregularly as NaCl concentration rose. In the case of Zn coatings, protection against corrosive environments is primarily achieved through the sacrificial anode action of Zn, which corrodes preferentially to carbon steel and produces corrosion products such as ZnO and Zn(OH)₂ [34]. While these products can temporarily slow down corrosion by forming surface films, they are relatively unstable in chloride-rich environments, making Zn coatings prone to breakdown and reformation cycles [20]. This explains why, in the present study, Zn coatings exhibited a fluctuating corrosion rate as NaCl concentration increased, reflecting the inability of Zn corrosion films to provide long-term stability. The repeated dissolution and reformation of Zn-based films not only reduce their protective efficiency but also increase susceptibility to localized attack such as pitting [31]. This is in line with previous studies showing that, particularly in environments with high salt content, unstable corrosion products such as zinc chloride hydroxide monohydrate (simonkolleite) are formed on the surface, providing a temporary barrier effect and demonstrating even better corrosion resistance [40]. In addition, Zhang *et al.* [41] examined the progression of corrosion products on carbon steel exposed to marine conditions by combining field studies, compositional characterization, and electrochemical analyses. They reported that the evolution of corrosion films follows three successive phases: an early stage of formation and release, a middle stage involving adhesion and transformation, and a final stage characterized by breakdown and dissolution. This highlights the transient and unstable nature of protective films, which is consistent with the fluctuating corrosion behavior observed for Zn coatings in the present work.

By contrast, ZnAl coatings protect the substrate through a dual mechanism. In addition to Zn sacrificial behavior, the presence of aluminum promotes the formation of a stable and adherent Al₂O₃ passive layer alongside Zn corrosion products. This alumina layer is more compact and resistant to chloride penetration, preventing rapid film breakdown and significantly reducing the likelihood of localized corrosion [34]. Consistent with this mechanism, ZnAl coatings in our study showed a more stable performance with a gradual decrease in corrosion rate as NaCl concentration increased. The interdendritic microstructure of ZnAl coatings further enhances this protective effect by localizing Zn dissolution while maintaining overall surface passivity [42], [43]. These results are consistent with earlier reports emphasizing the importance of oxide film formation in improving the corrosion resistance of Zn- and Al-based coatings exposed to saline environments [44]. Other studies have further demonstrated that alloying or modifying Al coatings can enhance their durability and improve resistance against cavitation erosion [45]. For ZnAl systems specifically, earlier study observed that the reduced corrosion rate in 3.5 wt.% NaCl was linked to the accumulation of corrosion products within the coating pores, which effectively blocked aggressive ions from reaching the substrate [46]. Similarly, previous study confirmed that Al-based coatings could provide robust protection in saline and salt-spray conditions, making them particularly suitable for coastal applications [47].

Across all chloride concentrations, ZnAl coatings consistently outperform pure Zn coatings. This clear difference shows that ZnAl coatings provide stronger and more stable corrosion protection, even in highly aggressive environments. These findings are well aligned with earlier reports that highlighted the shortcomings of pure Zn coatings for long-term corrosion protection. Pure Zn tends to generate corrosion products that are porous and unstable in marine conditions, causing rapid coating degradation [44], [48], [49]. Wu *et al.* [44] demonstrated that among Zn, Al, and ZnAl coatings deposited by arc spraying, ZnAl exhibited the best electrochemical stability. Lee *et al.* [50] reported similar results with plasma arc-sprayed Zn and ZnAl15 coatings in seawater, where ZnAl significantly outperformed Zn. Milz *et al.* [51] further revealed that ZnAl coatings benefited from a self-sealing effect of their corrosion products, which filled surface defects and blocked ion penetration. Table 3 shows the comparison between the average corrosion rates of Zn and ZnAl coatings obtained in this study and the corrosion rates of Zn reported in previous studies. Although Zn exhibits lower protection compared to ZnAl, the results clearly demonstrate that both Zn and ZnAl coatings developed in this study show superior corrosion resistance relative to those reported previously.

Table 3.

The comparison between the average corrosion rate of Zn and ZnAl coatings obtained in the present study with the corrosion rates of Zn (in various saline solution) reported in previous studies

Sources	Specimen	Testing Solution	Method	Corrosion Rate ($\mu\text{m/y}$) of coating	Ref.
Other works	Zn	5wt% NaCl	Arc Thermal Spray	3237.55	[34]
		3.5wt% NaCl		1441.75	
		5wt% Sea Salt		1200.85	
		3.5wt% Sea Salt		919.80	
		Seawater		580.35	
Our study	Zn	NaCl (from average corrosion rate in various NaCl concentration)	Hot-Dip Galvanized	7.8944	-
	ZnAl	NaCl (from average corrosion rate in various NaCl concentration)		1.031	

The superior behavior of ZnAl arises from its dual protection mechanism: sacrificial galvanic protection from Zn and passive barrier protection from Al. Zinc, with its more negative reduction potential ($E^\circ = -0.76 \text{ V vs. SHE}$) compared to steel (-0.44 V vs. SHE), preferentially oxidizes when exposed to electrolytes such as NaCl solution, as shown in Eq. (2). The electrons released by Zn migrate to the steel substrate, enabling the cathodic oxygen reduction reaction (Eq. (3)) and thereby preventing the oxidation of iron to Fe^{2+} , which initiates corrosion [52], [53], [54].



While this sacrificial protection is effective, pure Zn coatings show limitations in highly concentrated chloride environments due to the formation of porous $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, which provides insufficient long-term stability. In ZnAl coatings, however, the presence of Al fundamentally changes the corrosion pathway. Aluminum spontaneously forms a stable and adherent oxide film, Al_2O_3 (Eq. (4)), which is highly resistant to chloride-induced attack [53], [55]. This passive layer not only shields the alloy surface but also promotes the formation of compact and adherent corrosion products such as $\text{Zn}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$, which reinforce the protective barrier. The combination of Al_2O_3 passivation and dense hydroxycarbonate films minimizes oxygen and moisture ingress, providing a synergistic improvement in corrosion resistance well beyond that of pure Zn [56], [57], [58], [59].

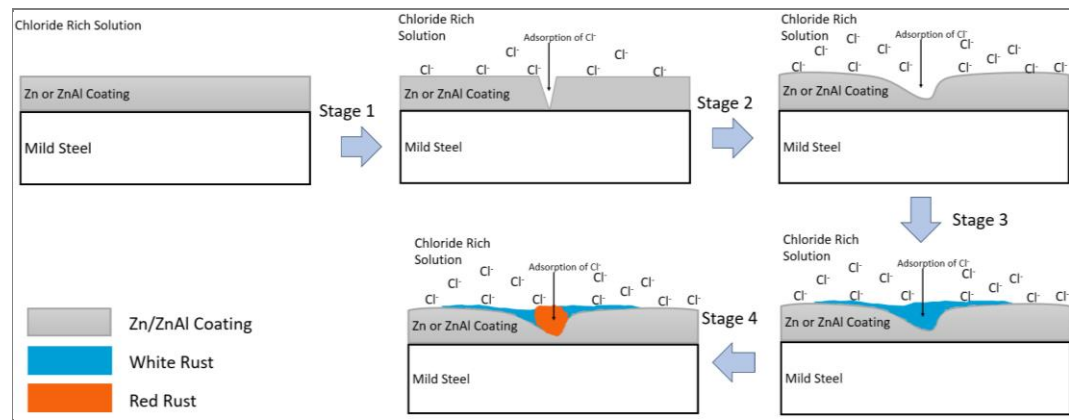


Moreover, the present results indicate that the effect of NaCl concentration on corrosion rate does not exhibit a simple linear correlation. Although higher chloride content is generally expected to accelerate corrosion, our findings show that this relationship is more complex and context-dependent. Similar inconsistencies have been reported in previous studies. For instance, reducing the NaCl concentration from 3% to 1.5% was found to decrease the corrosion rate of carbon steel by approximately 20% under cyclic SAE J2334 conditions, whereas further increasing the salt concentration to 6% produced no significant change [60]. Calero *et al.* [61] also reported that immersion duration plays a decisive role: in short-term exposure, corrosion accelerated with increasing salt concentration, but in long-term immersion the trend reversed. Comparable non-linear behavior was observed in the corrosion of 20# steel in sulfuric acid, where the corrosion rate increased as concentration rose from 80% to 98% at 40°C , but sharply declined once the concentration reached 98% [62]. Collectively, these findings highlight that electrolyte concentration alone cannot fully predict corrosion severity, as the outcome is strongly influenced by solution chemistry, exposure time, and surface film stability.

In our case, the instability of passive films at elevated chloride concentrations provides a likely explanation. At moderate NaCl levels, the formation of corrosion products or passive films can partially inhibit further attack. However, as the chloride concentration rises to 5%, the passive film becomes unstable and eventually breaks down, leading to accelerated localized corrosion processes such as pitting [63], [64]. On the other hand, the presence of aluminum helps retain higher corrosion potentials due to the stability of the Al_2O_3 passive layer [65]. Other studies stated that film stability is also influenced by pH. At low pH, the passive layer cannot remain intact, resulting in uniform corrosion, while at high pH, passive films form more easily but can still be disrupted by chloride ions that penetrate the film and trigger pitting [66]. Pitting corrosion initiates the breakdown of passive films by allowing chloride ions, due to their small size and strong affinity for metals, to penetrate and destabilize the protective layer [66]. Chloride ions, due to their small size and strong affinity with metals, can penetrate the passive layer and destabilize it [63], [64].

Once penetration occurs, the corrosion process develops in stages: chloride ions first break through the outer precipitated layer (stage 1–2 in [Figure 2](#)), then reach the inner barrier oxide (stage 3, in [Figure 2](#)), where instability begins. At this point, oxygen depletion favors pit initiation (stage 4 in [Figure 2](#)). Because Cl^- is uniquely aggressive compared to other halides, localized corrosion develops rapidly, leading to severe damage even though it affects only limited areas of the surface [35].

Figure 2.
Illustration of passive
film breakdown of
galvanized steel in
chloride rich
environment



3.2. Microhardness Analysis

Table 4 presents the results of microhardness testing on carbon steel specimens before and after coating. Testing was conducted at three test sites for each condition, and the results were averaged to provide an overall representation of the hardness change caused by the coating treatment. **Table 4** demonstrates that the coating causes a significant increase in surface hardness. The average hardness value of carbon steel without coating is 47.5 HV (Vickers Hardness) at a load of 0.3 kgf, indicating that carbon steel's original mechanical qualities are comparatively soft and easy to form. After being coated with Zn, the hardness value increased to 65.6 HV, demonstrating that the Zn coating can provide further mechanical protection to the steel surface. However, this increase, while notable, is still relatively minor [67]. Although Zn has a higher hardness than steel, its relative softness compared to other coating metals limits the overall improvement in hardness [68]. The variation of hardness for uncoated substrate and Zn coatings was relatively small, which may be attributed to their susceptibility to deformation.

Table 4.
Microhardness testing data
of carbon steel before and
after coating with Zn and
ZnAl

Specimen	Test Point	Hardness (HV.0.3kgf)		
		Uncoated	Coated	
Carbon Steel	1	46.5	Zn	65.7
	2	48.4	Zn	65.5
	3	47.6	ZnAl	115.8
	Average	47.5	Zn	116.7

A significantly higher increase was observed in steel coated with ZnAl alloy, where the average hardness value reached 116.7 HV. This indicates that the addition of Al to the Zn coating makes a significant contribution to enhancing the mechanical strength of the protective layer [54]. Aluminum in this alloy not only improves corrosion resistance by forming a passive oxide layer (Al_2O_3), but also modifies the microstructure of the coating layer, making it harder and denser [54], [69], [70]. ZnAl alloys tend to form stronger intermetallic phases, thus providing higher mechanical protection against scratches, deformation, and surface wear [71]. Thus, ZnAl coating is not only effective in protecting steel from corrosion attacks (especially in environments containing chloride ions), but also greatly improves the mechanical resistance of the steel surface [72]. Beyond corrosion resistance, these systems have demonstrated additional functionalities such as enhanced hardness properties. Taken together, these findings reinforce the position of ZnAl as an ideal multifunctional coating material for demanding environments, offering both chemical protection and superior surface performance.

These results align with previous studies that emphasize the critical role of even small amounts of aluminum in enhancing coating performance. The incorporation of aluminum increases coating reactivity, improves adhesion to the substrate, and provides superior corrosion resistance [67], [73]. Furthermore, aluminum suppresses the formation of brittle Fe/Zn phases, resulting in a

more ductile coating that resists cracking and brittleness [67]. Comparative findings from earlier research further highlight the advantages of ZnAl coatings. While Zn coatings exhibited relatively low hardness values (29.5 HV0.5), Zn/23Al coatings demonstrated intermediate hardness (47.1 HV0.5), and Al alloy coatings achieved values as high as 141.5 HV0.5 [36]. Another study reported average hardness values of 44.7 HV for Zn coatings and 56.4 HV for Al coatings [34], both notably lower than those obtained in this study. These discrepancies can likely be attributed to variations in the microstructural features of the coatings. Nevertheless, the consistent trend across multiple studies confirms that ZnAl coatings deliver superior hardness compared to pure Zn and uncoated steel. This makes them highly promising candidates for applications requiring both enhanced wear resistance and maximum corrosion protection, such as automotive components and industrial equipment exposed to harsh environments.

3.3. Morphological Structure of Coated Layers Pre- and Post-Corrosion Exposure and Its Correlation to Lifetime Prediction

To gain a more comprehensive understanding of the coating performance, it is essential to examine not only the electrochemical behavior and mechanical properties but also the morphological evolution of the coated layers. The surface and cross-sectional morphologies before and after corrosion exposure provide critical insights into coating integrity, defect formation, and degradation mechanisms. Such microstructural observations enable the establishment of a clear correlation between morphological changes and the lifetime prediction of the coatings, thereby complementing the corrosion and hardness analyses presented in the previous sections.

Figure 3 illustrates the cross-sectional morphology of carbon steel substrates after the coating process but prior to corrosion exposure. Figure 3a and Figure 3b shows specimens coated with pure Zn and ZnAl alloy, respectively. At a magnification of 1000 $\times$, the distinction between the steel substrate and the coating layer is clearly observed, where the deposited coatings exhibit a well-defined two-layer structure comprising a diffusion layer adjacent to the substrate and an outer layer as reported in previous study [68]. In the Zn-coated specimen, regions with dark-grey contrasts are predominant, while in the ZnAl-coated specimen, a combination of bright-white and dark-grey contrasts is observed, corresponding to Zn-rich and Al-rich phases, respectively, as consistently reported in previous studies [54]. Moreover, the Zn coating predominantly displays laminar features, whereas the ZnAl alloy coating is characterized by aluminium-rich dendrites in which zinc-rich particles are embedded within an aluminium-rich matrix, forming a typical layered structure as reported in earlier literature [69], [74].

The inset figures in the upper right corner of Figure 3a and Figure 3b further confirm the homogeneity of the coatings, as evidenced by smooth, topographically uniform surfaces without noticeable variations in thickness [70], [71]. No macroscopic defects, such as microcracks, porosity, pinholes, or delamination, were detected [72], which reflects excellent adhesion between the Zn/ZnAl coatings and the steel substrate. Such adhesion is crucial to prevent coating detachment and subsequent substrate degradation in aggressive environments. The uniformity of the layers also reduces the likelihood of galvanic corrosion, which typically arises in areas of non-uniform thickness [75]. Furthermore, the indistinguishable boundary between coated and uncoated regions indicates complete surface coverage by the Zn-based coatings. This comprehensive coverage is particularly important, as any exposed substrate area can serve as an initiation site for corrosion [76]. Therefore, the observations presented in Figure 3 provide not only morphological evidence but also empirical confirmation that Zn and ZnAl coatings ensure full surface protection and act as effective physical barriers against the ingress of corrosive ions such as Cl^- and H^+ .

Figure 3c and Figure 3d present the elemental mapping obtained by the EDS technique from the substrate coated with Zn and ZnAl, respectively. In Figure 3c, the distribution of elements clearly distinguishes Fe (green) concentrated in the substrate and Zn (red) concentrated in the coating layer. The sharp and well-defined transition zone between Zn and Fe indicates minimal elemental diffusion, suggesting that the integrity of the interface is preserved during the coating process. This distinct boundary reflects not only strong adhesion between the protective layer and the base metal but also effective integration that minimizes the risk of coating delamination when exposed to aggressive environments. In comparison, Figure 3d illustrates the elemental distribution of the ZnAl coating, where Fe (green) originates from the substrate, while Zn (red) and Al (blue) are distributed within the coating layer. The overlapping distribution of Zn and Al confirms that these elements are homogeneously intermixed across the coating, leading to the formation of both Zn-rich and Al-rich phases. Such an intermixed microstructure provides a more complex protective

system, as the combination of phases not only strengthens the coating but also enhances its barrier properties. The presence of a sharp yet continuous transition zone between the Fe substrate and the ZnAl layer further demonstrates the formation of a robust interfacial bond, with the potential development of intermetallic compounds that are well known to improve corrosion resistance.

Overall, the Zn and ZnAl coating exhibits uniformity across the surface, with no evidence of porosity, cracks, or discontinuities, thereby confirming a consistent and high-quality deposition process that ensures structural stability throughout the entire layer [77]. These findings are in good agreement with previous studies [76], [78], which similarly reported that Zn coatings form a uniform protective barrier with minimal defects, while ZnAl coatings provide superior corrosion resistance due to their dual-phase distribution and the possible formation of intermetallic compounds. Collectively, the EDS elemental mapping results in Figure 3c and Figure 3d provide empirical evidence that ZnAl coatings offer superior protection compared to pure Zn coatings, owing to their enhanced interfacial bonding, improved homogeneity, and more complex microstructural characteristics, which altogether contribute to a more efficient and durable barrier against corrosive attack. Because of these microstructural advantages, it is further proven that carbon steel coated with ZnAl exhibits a lower corrosion rate and a better lifetime prediction than carbon steel coated with Zn alone.

The film thickness of the Zn and ZnAl layers grown on the carbon steel substrate can also be clearly observed as shown in Figure 3a and Figure 3b. According to these figures, the Zn layer has a considerable thickness of 37.35 μm , while the ZnAl layer is much thinner, measuring only about 6.377 μm . Even though the ZnAl layer is thinner, the combination of Zn and Al components provides superior rust protection as indicated by the data of corrosion rate of the specimen (see Table 2). This enhanced protection is attributed to the presence of aluminium, which can form a strong, thin protective layer on the surface, known as aluminium oxide layer (Al_2O_3). This layer acts as a shield that protects the surface from water, oxygen, and other corrosive substances such as salt. Unlike the pure Zn layer which only protects the steel by “sacrificing itself” (meaning zinc rusts first), the ZnAl layer does not only rely on that method. The aluminium helps resist corrosion by forming a stable and durable chemical barrier that provides dual protection (Zn that prevents corrosion electrochemically, and Al that forms a hard-to-penetrates protective layer). This makes the ZnAl coating effective even though it is significantly thinner than a conventional Zn coating [52], [53], [54], [79]. In order to enhance the corrosion protection of zinc coatings without increasing coating thickness, the addition of aluminum to the coating systems is a promising approach as align with previous study [77].

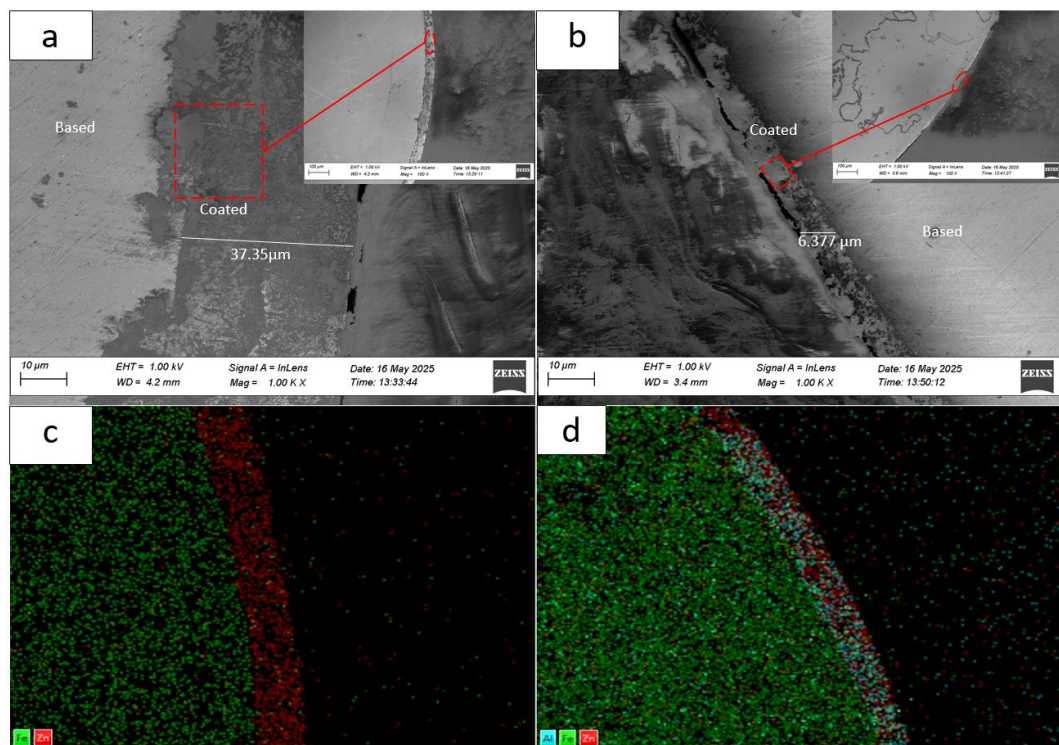


Figure 3. Cross-sectional images of carbon steel coated with Zn (a) and ZnAl (b) and EDS elemental mapping of carbon steel substrate coated with Zn (c) and ZnAl (d)

Finally, degradation due to corrosion is a critical factor in determining the durability of protective coatings, and lifetime prediction (see [Table 5](#)) is generally calculated by dividing the effective coating thickness by the experimentally measured corrosion rate [80]. A lower corrosion rate directly indicates an extended service life, emphasizing the practical importance of improving corrosion resistance. Based on the present findings, the predicted lifetime of the pure Zn coating ranges from 3.7 to 5.5 years with an average of 4.7 years, whereas the ZnAl coating shows a longer projected lifetime, ranging from 5.9 to 6.5 years with an average of 6.2 years. Notably, although the ZnAl layer has a much smaller thickness (6.377 μm) compared to the Zn coating (37.35 μm), its significantly lower corrosion rate enables it to deliver a longer service life. These finding highlights that the effectiveness of a coating is not solely governed by its thickness, but more critically by the inherent protective mechanism of the material. In the case of pure Zn, corrosion protection is primarily based on sacrificial anodic action, where zinc preferentially corrodes to protect the underlying steel [34]. While this mechanism is effective, it results in continuous consumption of the coating material, meaning that a thicker layer is required to ensure long-term protection. In contrast, ZnAl coatings benefit from a dual mechanism: Zn still acts sacrificially, but the presence of Al leads to the formation of a dense and adherent passive oxide layer (Al_2O_3) that serves as a chemical barrier against aggressive ions such as chloride and oxygen [42], [43]. This barrier reduces the overall corrosion rate of the coating and slows down the depletion of the Zn layer.

Table 5.
Lifetime prediction of Zn
and ZnAl in obtained study

Concentration of NaCl (%)	Thickness		Lifetime Prediction ($\mu\text{m}/\text{y}$)	
	Initial Zn Thickness (μm)	Initial ZnAl Thickness (μm)	Zn	ZnAl
1.0	37.35	6.377	4.5	5.9
2.0			5.1	6.1
3.0			4.9	6.5
4.0			3.7	6.4
5.0			5.5	6.1
Average			4.7	6.2

As a result, even though the ZnAl coating is nearly six times thinner than the Zn coating, it achieves a higher efficiency in terms of lifetime extension per unit thickness. In practical terms, this means that ZnAl coatings consume less raw material while still outperforming thicker Zn layers in durability, making them both cost-effective and environmentally sustainable. This superior performance is particularly valuable in marine or chloride-rich environments, where thinner yet more corrosion-resistant coatings translate into longer intervals between maintenance cycles, lower lifecycle costs, and reduced resource consumption. Therefore, ZnAl not only demonstrates enhanced protective capabilities but also provides a more efficient and sustainable solution compared to conventional Zn coatings.

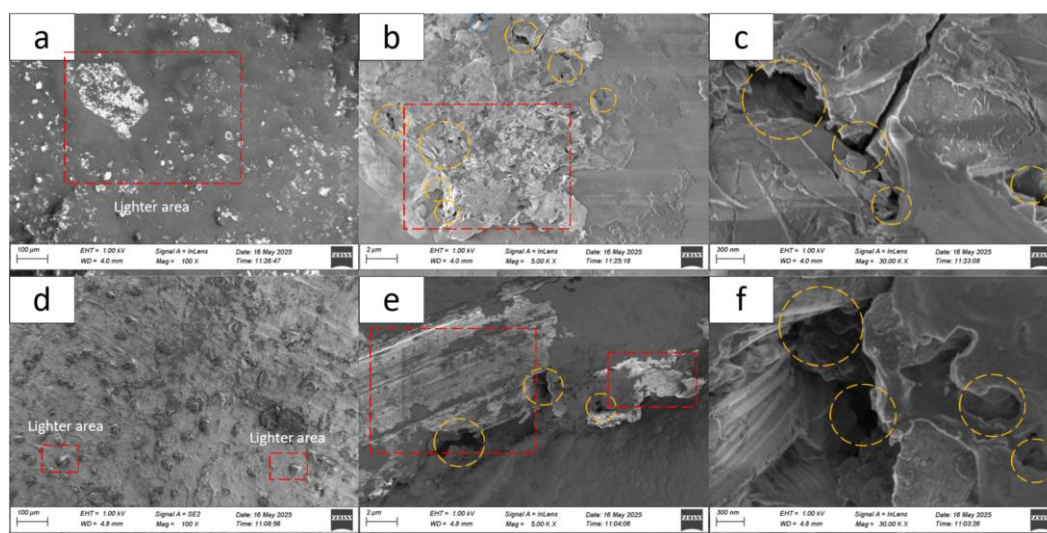
The differences in lifetime prediction between Zn and ZnAl coatings are further supported by morphological observations after corrosion exposure. Surface and cross-sectional analyses clearly reveal that the Zn-coated specimens experienced more severe degradation compared to those coated with ZnAl. [Figure 4](#) shows the results of the morphology analysis of carbon steel surfaces coated with Zn and ZnAl after corrosion exposure. The morphological structure analysis after corrosion exposure is consistent with previous studies [34], [36]. Based on [Figure 4](#), the surface area that appears lighter in color indicates the presence of white corrosion products known as white rust. White rust is a typical form of corrosion that occurs on zinc (Zn) or its alloys when exposed to a humid or water-containing environment for a certain period of time, especially if it is not protected by additional coatings (such as paint or passivation). In [Figure 4a](#) (Zn coating), the lighter area (see the box with the dashed line) spread across the surface and indicates the initial corrosion attack that forms white rust [34], [36]. However, in the ZnAl coating ([Figure 4d](#)), the intensity and number of these bright areas appear fewer and more spread out, indicating that white corrosion occurs on a smaller and more controlled scale. The inclusion of aluminium in the ZnAl coating creates a passive and stable layer of aluminium oxide (Al_2O_3), which effectively prevents white rust formation. The bright areas in the SEM images are visual indicators of white rust, indicated that corrosion does occur, but still remains within tolerable limits. In addition, no red rust was found, indicating that damage only occurs in the coating layer, without penetrating the steel substrate, thereby maintaining the integrity of the steel structure.

Furthermore, based on [Figure 4](#), the corrosion resistance of Zn and ZnAl coatings on carbon steel substrates can be better understood. Corrosion tests reveal that the predominant type of damage is pitting corrosion occurring on a very small scale, which demonstrates the resilience of this coatings [34], [36]. On Zn-coated steel, the surface appears to have experienced minor damage

in the form of pitting or small holes resulting from corrosion attacks (as indicated by circles with dotted lines in Figure 4a to Figure 4c). From the images in Figure 4a to Figure 4c, it is evident that the surface looks no longer flat; some areas appear lifted or peeled off, and the structure of the coating beginning to break down. The size of the pitting holes ranges from 300 nm to less than 2 μm , with some of them appearing quite deep. This suggests that the Zn layer is starting to erode, and its protection is starting to weaken at some points. Nevertheless, this damage is relatively minor and does not spread extensively, allowing the Zn coating to continue providing effective protection, which can last up to approximately 4.7 years.

Meanwhile, on ZnAl-coated steel (Figure 4d to Figure 4f), the surface after corrosion appears smoother and more stable. The damage that occurs is also in the form of pitting, but the size is smaller, ranging from less than 300 nanometers to less than 2 μm , and the amount is also less. The surface of the ZnAl layer appears denser, with few cracks or peeling are visible, indicating that the ZnAl layer is more resistant to the penetration of corrosive ions (such as Cl^-) due to its more compact structure and the presence of aluminium, which forms a protective passive layer. With a more stable surface condition after corrosion, the ZnAl layer provides longer protection for the steel, even though its thickness is thinner than that of the Zn layer. Therefore, the ZnAl surface that remains intact and minimally damaged after exposure to corrosion is one of the main reasons why its protection life can reach 6.2 years.

Figure 4. Carbon steel surface after corrosion test: (a–c) Zn layer shows a rough surface with indication of white rust (bright area) and pitting measuring 300 nm–2 μm ; (d–f) ZnAl layer shows a smoother, denser surface, with fewer white rust and smaller pitting (<300 nm– $\leq$ 2 μm)



4. Conclusion

Based on the present study, carbon steel coated with ZnAl exhibits superior corrosion protection performance compared to pure Zn coatings. Under varying NaCl concentrations, the corrosion rate of Zn was 6–7 times higher than that of ZnAl, while ZnAl showed only very small fluctuations ($\pm 0.1 \mu\text{m}/\text{y}$), indicating that ZnAl coatings are much less sensitive to chloride concentration. Additionally, ZnAl possesses higher hardness than Zn, making it less prone to deformation. Although the ZnAl coating is much thinner (6.377 μm) than the Zn coating (37.35 μm), it demonstrates a lower corrosion rate and longer predicted lifetime, with an average of 6.2 years (range 5.9–6.5 years) compared to Zn's average of 4.7 years (range 3.7–5.5 years). Morphological analysis after corrosion exposure also showed that Zn-coated steel experienced moderate-to-severe damage, with pitting sizes ranging from 300 nm to less than 2 μm , some of which were quite deep. In contrast, ZnAl-coated steel exhibited a smoother and more stable surface, with smaller pitting sizes (less than 300 nm to <2 μm) and fewer pits overall. Therefore, the combination of lower corrosion rate, higher hardness, and more stable morphology makes ZnAl coatings more effective in protecting carbon steel than pure Zn coatings.

Acknowledgements

The author would like to thank the Director of Research and Community Service of the Ministry of Higher Education, Science, and Technology for Fiscal Year 2025, who financed this research, as well as Riki Yuli from PT. Kabatama Raya, for their assistance with the hot-dip galvanising process.

Authors' Declaration

Authors' contributions and responsibilities - The authors made substantial contributions to the conception and design of the study. The authors took responsibility for data analysis, interpretation and discussion of results. The authors read and approved the final manuscript.

Funding – Director of Research and Community Service of the Ministry of Higher Education, Science, and Technology for Fiscal Year 2025.

Availability of data and materials - All data is available from the authors.

Competing interests - The authors declare no competing interests.

Additional information – No additional information from the authors.

References

- [1] N. Hossain, M. A. Chowdhury, M. Rana, M. Hassan, and S. Islam, "Terminalia arjuna leaves extract as green corrosion inhibitor for mild steel in HCl solution," *Results in Engineering*, vol. 14, p. 100438, Jun. 2022, doi: 10.1016/j.rineng.2022.100438.
- [2] A. Pal and C. Das, "A novel use of solid waste extract from tea factory as corrosion inhibitor in acidic media on boiler quality steel," *Industrial Crops and Products*, vol. 151, p. 112468, Sep. 2020, doi: 10.1016/j.indcrop.2020.112468.
- [3] R. O. Medupin, K. O. Ukoba, K. O. Yoro, and T.-C. Jen, "Sustainable approach for corrosion control in mild steel using plant-based inhibitors: a review," *Materials Today Sustainability*, vol. 22, p. 100373, Jun. 2023, doi: 10.1016/j.mtsust.2023.100373.
- [4] M. Mobin, K. Cial, R. Aslam, S. Zamindar, and P. Banerjee, "Mitigation effect of a biodegradable surfactant N,N,N-trimethyl-2-(((hexadecyloxy)carbonyl)oxy)ethan-1-aminiumiodide for mild steel corrosion in 5% HCl: Experimental and theoretical insights," *Materials Today Communications*, vol. 41, p. 110696, Dec. 2024, doi: 10.1016/j.mtcomm.2024.110696.
- [5] H. Chen, H. Cui, Z. He, L. Lu, and Y. Huang, "Influence of chloride deposition rate on rust layer protectiveness and corrosion severity of mild steel in tropical coastal atmosphere," *Materials Chemistry and Physics*, vol. 259, p. 123971, Feb. 2021, doi: 10.1016/j.matchemphys.2020.123971.
- [6] N. Deng, Y. Wu, S. Wang, R. Hao, Z. Xiong, and D. Huang, "Fractal theory-based analysis of strength degradation in steel slag powder-stabilized soil under chloride ion environment," *Scientific Reports*, vol. 15, no. 1, p. 22875, Jul. 2025, doi: 10.1038/s41598-025-04177-z.
- [7] J. Yuan, P. Li, H. Zhang, S. Yin, M. Xu, and A. Zhou, "The Effects of Alloying Elements on the Corrosion of Rebar Steel in a Chloride Environment," *Metals*, vol. 15, no. 4, p. 383, Mar. 2025, doi: 10.3390/met15040383.
- [8] C. Li et al., "Insight to atmosphere corrosion behavior of Q345NH steel in Wenchang tropical marine environment," *Journal of Materials Research and Technology*, vol. 24, pp. 5755–5768, May 2023, doi: 10.1016/j.jmrt.2023.04.128.
- [9] H. Parangusan, J. Bhadra, and N. Al-Thani, "A review of passivity breakdown on metal surfaces: influence of chloride- and sulfide-ion concentrations, temperature, and pH," *Emergent Materials*, vol. 4, no. 5, pp. 1187–1203, Oct. 2021, doi: 10.1007/s42247-021-00194-6.
- [10] K. Sun et al., "Research Progress on the Corrosion Mechanism and Protection Monitoring of Metal in Power Equipment," *Coatings*, vol. 15, no. 2, p. 119, Jan. 2025, doi: 10.3390/coatings15020119.
- [11] G. Zhang et al., "Dynamic self-balanced electrochemical model for non-uniform corrosion of steel reinforcement in concrete under combined effects of heat-moisture-chlorine-oxygen," *Journal of Building Engineering*, vol. 80, p. 108117, Dec. 2023, doi: 10.1016/j.jobbe.2023.108117.
- [12] E. Gomez, B. Leporace-Guimil, A. Conforti, G. Plizzari, G. Duffó, and R. Zerbino, "A practical approach for monitoring reinforcement corrosion in steel fiber reinforced concrete elements exposed to chloride rich environments," *Structural Concrete*, vol. 24, no. 1, pp. 318–331, Feb.

2023, doi: 10.1002/suco.202200302.

- [13] C. V. Amaechi et al., "Guidelines on Asset Management of Offshore Facilities for Monitoring, Sustainable Maintenance, and Safety Practices," *Sensors*, vol. 22, no. 19, p. 7270, Sep. 2022, doi: 10.3390/s22197270.
- [14] Q. Li et al., "Plastic metallic-barrier layer for crack propagation within plasma-sprayed Cu/ceramic coatings," *Surface and Coatings Technology*, vol. 360, pp. 259–268, Feb. 2019, doi: 10.1016/j.surfcoat.2018.12.124.
- [15] Y. Li, P. Zhang, P. Bai, L. Wu, B. Liu, and Z. Zhao, "Microstructure and properties of Ti/TiBCN coating on 7075 aluminum alloy by laser cladding," *Surface and Coatings Technology*, vol. 334, pp. 142–149, Jan. 2018, doi: 10.1016/j.surfcoat.2017.11.034.
- [16] S. Lu, X. Sun, B. Zhang, and J. Wu, "Review of Cathode Plasma Electrolysis Treatment: Progress, Applications, and Advancements in Metal Coating Preparation," *Materials*, vol. 17, no. 16, p. 3929, Aug. 2024, doi: 10.3390/ma17163929.
- [17] K. R. A. A. K. Parashar, N. Ginni, R. Banoth, G. Balan, and A. A. Hameed, "Microwave-Assisted Cladding of Ni-BaTiO₃ Mixture onto SS-304 for Enhancing the Wear Resistance and Surface Hardness," *E3S Web of Conferences*, vol. 507, p. 01014, Mar. 2024, doi: 10.1051/e3sconf/202450701014.
- [18] A. Dan, P. K. Bijalwan, A. S. Pathak, and A. N. Bhagat, "A review on physical vapor deposition-based metallic coatings on steel as an alternative to conventional galvanized coatings," *Journal of Coatings Technology and Research*, vol. 19, no. 2, pp. 403–438, Mar. 2022, doi: 10.1007/s11998-021-00564-z.
- [19] Y. Feng et al., "Effect of ZnO as corrosion product on corrosion behavior of zinc-iron corrosion protection systems," *Corrosion Science*, vol. 227, p. 111802, Feb. 2024, doi: 10.1016/j.corsci.2023.111802.
- [20] Q. Liu et al., "Hot-Dip Galvanizing Process and the Influence of Metallic Elements on Composite Coatings," *Journal of Composites Science*, vol. 8, no. 5, p. 160, Apr. 2024, doi: 10.3390/jcs8050160.
- [21] A. Ayatilhaq, P. H. Setyarini, Margono, and D. Setiadhi, "The Effect of Mangan on Hardness and Corrosion Rate of Biodegradable Implants of Zn-Mn Alloy," *Mechanics Exploration and Material Innovation*, vol. 1, no. 1, pp. 1–6, 2024, doi: 10.21776/ub.memi.2024.001.01.1.
- [22] D. B. Wang, S. D. Zhang, Q. Wang, L. M. Zhang, and J. Q. Wang, "Underlying mechanism for the effects of composition and microstructure on the corrosion resistance of Al-based amorphous alloys: a review," *Critical Reviews in Solid State and Materials Sciences*, vol. 49, no. 6, pp. 1120–1152, Nov. 2024, doi: 10.1080/10408436.2024.2311414.
- [23] J. P. Calderón et al., "Corrosion Behavior of Al Modified with Zn in Chloride Solution," *Materials*, vol. 15, no. 12, p. 4229, Jun. 2022, doi: 10.3390/ma15124229.
- [24] S. Hidayatullah, A. M. Sulaiman, and E. N. Iftitah, "Durio Zibethinus Extract Performance as Corrosion Inhibitor in Simulated Seawater," *Mechanics Exploration and Material Innovation*, vol. 1, no. 1, pp. 27–34, Jan. 2024, doi: 10.21776/ub.memi.2024.001.01.4.
- [25] E. De Bruycker, Z. Zermout, and B. C. De Cooman, "Zn-Al-Mg Coatings: Thermodynamic Analysis and Microstructure Related Properties," *Materials Science Forum*, vol. 539–543, pp. 1276–1281, Mar. 2007, doi: 10.4028/www.scientific.net/MSF.539-543.1276.
- [26] A. S. Gnedenkov, S. L. Sinebryukhov, D. V. Mashtalyar, I. M. Imshinetskiy, I. E. Vyaliy, and S. V. Gnedenkov, "Effect of Microstructure on the Corrosion Resistance of TIG Welded 1579 Alloy," *Materials*, vol. 12, no. 16, p. 2615, Aug. 2019, doi: 10.3390/ma12162615.
- [27] A. A. Ayoola, B. M. Durodola, R. Babalola, O. D. Adeniyi, and C. E. Ilobinso, "Corrosion inhibitive effects of calcium-modified zinc phosphate coating on A36 mild steel," *Results in Engineering*, vol. 17, p. 100880, Mar. 2023, doi: 10.1016/j.rineng.2023.100880.
- [28] N. F. Ibrahim, W. R. Wan Abdullah, M. S. Rooshde, M. S. Mohd Ghazali, and W. N. W. Mohd Norsani, "Corrosion Inhibition Properties of Epoxy-Zinc Oxide Nanocomposite Coating on Stainless Steel 316L," *Solid State Phenomena*, vol. 307, pp. 285–290, Jul. 2020, doi: 10.4028/www.scientific.net/SSP.307.285.
- [29] G. Sundaramali et al., "Experimental investigations of electrodeposited Zn–Ni, Zn–Co, and Ni–Cr–Co–based novel coatings on AA7075 substrate to ameliorate the mechanical, abrasion, morphological, and corrosion properties for automotive applications," *Reviews on advanced*

- materials science*, vol. 62, no. 1, Jul. 2023, doi: 10.1515/rams-2022-0324.
- [30] R. S. Bhat, M. K. Balakrishna, P. Parthasarathy, and A. C. Hegde, "Structural Properties of Zn-Fe Alloy Coatings and Their Corrosion Resistance," *Coatings*, vol. 13, no. 4, p. 772, Apr. 2023, doi: 10.3390/coatings13040772.
 - [31] K. K. Maniam and S. Paul, "Corrosion Performance of Electrodeposited Zinc and Zinc-Alloy Coatings in Marine Environment," *Corrosion and Materials Degradation*, vol. 2, no. 2, pp. 163–189, Apr. 2021, doi: 10.3390/cmd2020010.
 - [32] M. Sajjadnejad, S. Karkon, and S. M. S. Haghshenas, "Corrosion Characteristics of Zn-TiO₂ Nanocomposite Coatings Fabricated by Electro-Codeposition Process," *Advanced Journal of Chemistry, Section A*, vol. 7, no. 2, pp. 209–226, 2024, doi: 10.48309/ajca.2024.418391.1425.
 - [33] M. Margono et al., "Optimized deposition parameters for titanium nitride coatings: Enhancing mechanical properties of Al 6011 substrates via DC sputtering," *Mechanical Engineering for Society and Industry*, vol. 4, no. 2, pp. 252–262, Dec. 2024, doi: 10.31603/mesi.12266.
 - [34] T.-C. Chen, T.-Y. Yung, C.-C. Chou, and Y.-M. Wang, "Investigating the corrosion resistance of Zn and Al coating deposited by arc thermal spraying process," *Surface and Coatings Technology*, vol. 484, p. 130684, May 2024, doi: 10.1016/j.surfcoat.2024.130684.
 - [35] A. Al-Negheimish, R. R. Hussain, A. Alhozaimy, and D. D. N. Singh, "Corrosion performance of hot-dip galvanized zinc-aluminum coated steel rebars in comparison to the conventional pure zinc coated rebars in concrete environment," *Construction and Building Materials*, vol. 274, p. 121921, Mar. 2021, doi: 10.1016/j.conbuildmat.2020.121921.
 - [36] J. Zheng et al., "Surface characteristic and corrosion resistance of different plasma-sprayed coatings (Zn, Al6061 and Zn/23Al) on S960 high strength steel with subsequent micro-shot peening," *Surface and Coatings Technology*, vol. 451, p. 129046, Dec. 2022, doi: 10.1016/j.surfcoat.2022.129046.
 - [37] D. Kim, N. Takata, H. Yokoi, A. Suzuki, and M. Kobashi, "Microstructural factors controlling crack resistance of Zn–Al–Mg alloy coatings prepared via hot-dip galvanizing process: Combined approach of in-situ SEM observation with digital image correlation analysis," *Journal of Materials Research and Technology*, vol. 29, pp. 1535–1541, Mar. 2024, doi: 10.1016/j.jmrt.2024.01.235.
 - [38] M. Riđošić, N. D. Nikolić, A. Salicio-Paz, E. García-Lecina, L. S. Živković, and J. B. Bajat, "Zn-Co-CeO₂ vs. Zn-Co Coatings: Effect of CeO₂ Sol in the Enhancement of the Corrosion Performance of Electrodeposited Composite Coatings," *Metals*, vol. 11, no. 5, p. 704, Apr. 2021, doi: 10.3390/met11050704.
 - [39] M. M. Ariffin, M. M. Aung, L. C. Abdullah, and M. Z. Salleh, "Assessment of corrosion protection and performance of bio-based polyurethane acrylate incorporated with nano zinc oxide coating," *Polymer Testing*, vol. 87, p. 106526, Jul. 2020, doi: 10.1016/j.polymertesting.2020.106526.
 - [40] S.-H. Kim, S.-Y. Jin, J.-H. Yang, J.-H. Yang, M.-H. Lee, and Y.-S. Yun, "Self-Healing Phenomenon at the Cut Edge of Zn-Al-Mg Alloy Coated Steel in Chloride Environments," *Coatings*, vol. 14, no. 4, p. 485, Apr. 2024, doi: 10.3390/coatings14040485.
 - [41] W. Zhang et al., "Research on the evolution of corrosion products of 17-4 PH martensitic stainless steel in the tropical marine environment," *Journal of Materials Research and Technology*, vol. 29, pp. 3849–3865, Mar. 2024, doi: 10.1016/j.jmrt.2024.02.117.
 - [42] A. D. Malla et al., "Influence of Mg and Al alloying additions on the corrosion mechanisms of Hot-dipped Zn-Mg-Al coatings: role of microstructure and phase distribution," *npj Materials Degradation*, vol. 9, no. 1, p. 96, Jul. 2025, doi: 10.1038/s41529-025-00647-x.
 - [43] A. Martin et al., "Influence of the Al Content on the Electrochemical Behavior of Zn-Al Cold-Sprayed Coatings in the Context of the Deep Geological Disposal of Radioactive Waste," *Coatings*, vol. 14, no. 3, p. 261, Feb. 2024, doi: 10.3390/coatings14030261.
 - [44] W. Wu, G. Sun, Q. Wang, and S. Lin, "Preparation, Wear Resistance, and Corrosion Performance of Arc-Sprayed Zn, Al, and Zn-Al Coatings on Carbon Steel Substrates," *Journal of Materials Engineering and Performance*, vol. 32, no. 23, pp. 10542–10555, Dec. 2023, doi: 10.1007/s11665-023-07889-3.
 - [45] L. Wang, K. Liu, J. Li, and S. Geng, "A Review on Corrosion Behavior and Surface Modification

- Technology of Nickel Aluminum Bronze Alloys: Current Research and Prospects," *Advanced Engineering Materials*, vol. 27, no. 1, Jan. 2025, doi: 10.1002/adem.202401779.
- [46] Y. Wang et al., "Investigation of Corrosion Resistance of 60Si2MnA Spring Steel Coated with Zn-Al in Atmospheric Environments," *Materials*, vol. 18, no. 14, p. 3215, Jul. 2025, doi: 10.3390/ma18143215.
- [47] R. T. Loto et al., "Comprehensive investigation of corrosion resistance of magnesium–titanium, aluminum, and aluminum–vanadium alloys in dilute electrolytes under zero-applied potential conditions," *Open Engineering*, vol. 15, no. 1, Apr. 2025, doi: 10.1515/eng-2025-0110.
- [48] M. K. Yadav et al., "Microstructural, mechanical, corrosion, and biological behavior of spark plasma sintered commercially pure zinc for biomedical applications," *Materials Advances*, vol. 6, no. 11, pp. 3546–3560, 2025, doi: 10.1039/D5MA00092K.
- [49] S. R. Siasi Rad and K. Dehghani, "The role of MgO nanoparticles on the corrosion resistance of hot-dip Al–Zn coating," *Heliyon*, vol. 11, no. 1, p. e41391, Jan. 2025, doi: 10.1016/j.heliyon.2024.e41391.
- [50] H.-S. Lee and J. K. Singh, "Deposition and corrosion studies of plasma arc thermal sprayed Zn and 85Zn–15Al films on steel surface," *Journal of Materials Science*, vol. 57, no. 41, pp. 19650–19665, Nov. 2022, doi: 10.1007/s10853-022-07815-3.
- [51] M. P. Milz et al., "Corrosion Fatigue Behavior of Twin Wire Arc Sprayed and Machine Hammer Peened ZnAl4 Coatings on S355 J2C + C Substrate," *Corrosion and Materials Degradation*, vol. 3, no. 1, pp. 127–141, Mar. 2022, doi: 10.3390/cmd3010007.
- [52] F. Feldmann, L. L. E. Mears, M. Roth, and M. Valtiner, "Characterisation of the galvanic protection of zinc flake coating by spectroelectrochemistry and industrial testing," *Materials and Corrosion*, vol. 74, no. 8, pp. 1148–1158, Aug. 2023, doi: 10.1002/maco.202213719.
- [53] K. Xiao et al., "Effect of Concentrations of Fe²⁺ and Fe³⁺ on the Corrosion Behavior of Carbon Steel in Cl[–] and SO₄^{2–} Aqueous Environments," *Metals and Materials International*, vol. 27, no. 8, pp. 2623–2633, Aug. 2021, doi: 10.1007/s12540-019-00590-y.
- [54] Y. Ding et al., "Effect of Al Content on the Long-Term Corrosion Behavior of Arc-Sprayed ZnAl Alloy Coatings," *Coatings*, vol. 13, no. 10, p. 1720, Oct. 2023, doi: 10.3390/coatings13101720.
- [55] T. Wirtanen, T. Prenzel, J.-P. Tessonier, and S. R. Waldvogel, "Cathodic Corrosion of Metal Electrodes—How to Prevent It in Electroorganic Synthesis," *Chemical Reviews*, vol. 121, no. 17, pp. 10241–10270, Sep. 2021, doi: 10.1021/acs.chemrev.1c00148.
- [56] S. Tokuda, Y. Nishida, M. Nishimoto, I. Muto, and H. Shoji, "Initial dissolution of Mg-containing phase and corrosion product formation in cut-edge corrosion of Zn-11%Al-3%Mg-0.2%Si coated steel," *Corrosion Science*, vol. 225, p. 111605, Dec. 2023, doi: 10.1016/j.corsci.2023.111605.
- [57] S. Wang et al., "Study on the structure and corrosion behavior of hot-dipped Zn–6Al–3Mg alloy coating in chlorine-containing environment," *Corrosion Science*, vol. 231, p. 112001, May 2024, doi: 10.1016/j.corsci.2024.112001.
- [58] M. Ahmadi, B. Salgin, B. J. Kooi, and Y. Pei, "The effect of grain refinement on the deformation and cracking resistance in Zn–Al–Mg coatings," *Materials Science and Engineering: A*, vol. 840, p. 142995, Apr. 2022, doi: 10.1016/j.msea.2022.142995.
- [59] X. He et al., "Influence mechanism of different elements and alloy phases on the corrosion resistance of Zn-Al-Mg coated steel in the atmospheric environment: A review," *Corrosion Communications*, vol. 13, pp. 49–59, Mar. 2024, doi: 10.1016/j.corcom.2023.11.001.
- [60] K. Popova and T. Prošek, "Mechanism of Carbon Steel Corrosion in Accelerated Corrosion Tests," *Materials and Corrosion*, vol. 76, no. 4, pp. 486–509, Apr. 2025, doi: 10.1002/maco.202414606.
- [61] J. Calero et al., "Wet/dry accelerated laboratory test to simulate the formation of multilayered rust on carbon steel in marine atmospheres," *Corrosion Engineering, Science and Technology*, vol. 52, no. 3, pp. 178–187, Apr. 2017, doi: 10.1080/1478422X.2016.1244619.
- [62] G. Ou, X. Cao, Y. M. Mohammed, and W. Wu, "Failure Analysis and Corrosion Resistance of Carbon Steel Pipelines in Concentrated Sulfuric Acid," *Metals*, vol. 15, no. 5, p. 506, Apr. 2025, doi: 10.3390/met15050506.
- [63] P. Shen, B. Zhang, Z. Li, X. Pang, and W. Deng, "Forming mechanism, mechanical properties,

- and corrosion properties of aluminum alloy sheet with gradient structure processed by plastic flow machining," *Journal of Alloys and Compounds*, vol. 933, p. 167800, Feb. 2023, doi: 10.1016/j.jallcom.2022.167800.
- [64] M. Ciemiorek, A. Ambroziak, K. Majchrowicz, M. Lewandowska, and J. Goliński, "Ductility and formability of ultrafine-grained 5754 aluminium alloy under various strain rates and temperatures," *Materials Science and Engineering: A*, vol. 848, p. 143375, Jul. 2022, doi: 10.1016/j.msea.2022.143375.
- [65] L. Benea, N. Simionescu – Bogatu, and R. Chiriac, "Electrochemically obtained Al₂O₃ nanoporous layers with increased anticorrosive properties of aluminum alloy," *Journal of Materials Research and Technology*, vol. 17, pp. 2636–2647, Mar. 2022, doi: 10.1016/j.jmrt.2022.02.038.
- [66] P. Chilimoniuk, M. Michalska-Domańska, and T. Czujko, "Formation of Nanoporous Mixed Aluminum-Iron Oxides by Self-Organized Anodizing of FeAl₃ Intermetallic Alloy," *Materials*, vol. 12, no. 14, p. 2299, Jul. 2019, doi: 10.3390/ma12142299.
- [67] A. Chaouki et al., "Optimizing corrosion protection: Performance comparison of Zn and Zn-Al-Mg alloys Hot-Dip galvanized coatings," *Journal of Alloys and Compounds*, vol. 1007, p. 176371, Dec. 2024, doi: 10.1016/j.jallcom.2024.176371.
- [68] A. Marek, V. Steinerová, P. Pokorný, H. Kania, and F. Berger, "High-Temperature Zn-5Al Hot Dip Galvanizing of Reinforcement Steel," *Coatings*, vol. 14, no. 8, p. 959, Aug. 2024, doi: 10.3390/coatings14080959.
- [69] H. Kania, "Structure and Corrosion Resistance of Coatings Obtained by the Batch Double Hot Dip Method in Eutectoid ZnAl Bath with the Addition of Mg and Si," *Coatings*, vol. 12, no. 8, p. 1207, Aug. 2022, doi: 10.3390/coatings12081207.
- [70] T. N. Myasoedova, R. Kalusulingam, and T. S. Mikhailova, "Sol-Gel Materials for Electrochemical Applications: Recent Advances," *Coatings*, vol. 12, no. 11, p. 1625, Oct. 2022, doi: 10.3390/coatings12111625.
- [71] P. Panjan, A. Drnovšek, N. Mahne, M. Čekada, and M. Panjan, "Surface Topography of PVD Hard Coatings," *Coatings*, vol. 11, no. 11, p. 1387, Nov. 2021, doi: 10.3390/coatings11111387.
- [72] G. H. Mohamed, K. Karuppasamy, M. Alrwashdeh, I. Barsoum, S. Alameri, and A. Alfantazi, "Unveiling the latest progresses in chromium-coated Zircaloy cladding ATF materials: Fabrication techniques, performance metrics, and beyond," *Alexandria Engineering Journal*, vol. 108, pp. 13–39, Dec. 2024, doi: 10.1016/j.aej.2024.07.041.
- [73] A. Trentin, R. Samiee, A. H. Pakseresht, A. Duran, Y. Castro, and D. Galusek, "Influence of pre-treatments on adhesion, barrier and mechanical properties of epoxy coatings: A comparison between steel, AA7075 and AA2024," *Applied Surface Science Advances*, vol. 18, p. 100479, Dec. 2023, doi: 10.1016/j.apsadv.2023.100479.
- [74] I. Al-Nafai, K. Rzeszutek, S. Lyon, C. Jones, and D. Beaumont, "How aluminium additions improve the performance of zinc-rich organic coatings," *Materials and Corrosion*, vol. 76, no. 1, pp. 53–70, Jan. 2025, doi: 10.1002/maco.202414529.
- [75] M. F. Bolsanello et al., "Contributions to a More Realistic Characterization of Corrosion Processes on Cut Edges of Coated Metals Using Scanning Microelectrochemical Techniques, Illustrated by the Case of ZnAlMg-Galvanized Steel with Different Coating Densities," *Materials*, vol. 17, no. 7, p. 1679, Apr. 2024, doi: 10.3390/ma17071679.
- [76] M. Dursunlar, Z. Taş, M. Çelebi, B. Akgül, and H. Çuğ, "Enhanced corrosion resistance of high-speed railway fastening systems: ZnAl coating on 38Si7 steel," *Kovove Materialy-Metallic Materials*, vol. 63, no. 2, May 2025, doi: 10.31577/km.2025.2.119.
- [77] T. T. Pham et al., "Study of the formation and anti-corrosion properties of Zn Al hydrotalcite conversion films grown 'in situ' on different zinc alloys coated steel," *Progress in Organic Coatings*, vol. 173, p. 107221, Dec. 2022, doi: 10.1016/j.porgcoat.2022.107221.
- [78] V. Sivalingam and R. Thirumalaisamy, "Microstructure and Corrosion Study on Friction Surfaced Aluminum Alloy Coatings over Mild Steel," *Periodica Polytechnica Chemical Engineering*, vol. 68, no. 3, pp. 382–397, Aug. 2024, doi: 10.3311/PPch.37018.
- [79] M. Zubielewicz et al., "Concepts of steel protection by coatings with a reduced content of zinc pigments," *Progress in Organic Coatings*, vol. 161, p. 106471, Dec. 2021, doi: 10.1016/j.porgcoat.2021.106471.

- [80] W. Ni, P. Li, Y. Zhu, Z. Di, L. Guo, and Y. Liu, "Comparative Study of Anti-Corrosion Properties and Lifespan Prediction Model for Inorganic Zinc-Rich Coating and Thermal-Spray Zinc Coating," *Coatings*, vol. 12, no. 4, p. 505, Apr. 2022, doi: 10.3390/coatings12040505.