

Article

Effects of Ni and Al Addition on the Microstructure and Properties of Hot-Dip Galvanized Coatings on Q235 Steel

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Abstract

This study systematically investigates the effects of Ni and Al addition to a zinc bath on the microstructure, corrosion resistance and Vickers hardness of hot-dip galvanized coatings on Q235 steel. The Zn, Zn–0.04 wt.% Ni and Zn–0.04 wt.% Ni–1 wt.% Al coatings are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), neutral salt spray (NSS) testing, electrochemical measurements and Vickers hardness testing. The addition of Ni refines and thins the ζ phase, increases the thickness of the δ phase, reduces the total coating thickness to $56.33 \pm 0.89 \mu\text{m}$ and improves the corrosion resistance. With further Al addition, a continuous and dense inhibition layer forms at the interface, and the coating consists solely of this inhibition layer and the η phase; the total thickness is drastically reduced to $17.66 \pm 1.78 \mu\text{m}$, accompanied by a substantial improvement in both corrosion resistance and hardness. Electrochemical analysis reveals that the Zn–0.04 wt.% Ni–1 wt.% Al coating exhibits the most negative corrosion potential (0.61 V) and the smallest corrosion current density ($2.07 \mu\text{A}\cdot\text{cm}^{-2}$). Characterization of the corrosion products reveals that Al helps to stabilize $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$ and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, thereby enhancing the corrosion resistance of the coating.

Keywords: hot-dip galvanizing; Zn–Ni–Al alloy; microstructure; corrosion resistance; electrochemical analysis



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1. Introduction

Steel, as the most widely used material in industrial production, is subject to varying degrees of corrosion when exposed to soil, atmospheric, or marine environments. The annual loss of steel materials caused by corrosion represents approximately 10% of the total annual steel output [1]. Steel corrosion is a pervasive problem across industrial production, daily life, and socio-economic activities. Hot-dip galvanizing, recognized as one of the most effective methods for protecting steel materials against corrosion [2], has been widely applied in petrochemical, construction, agricultural, machinery manufacturing, marine engineering, power transmission, and other fields [3–7] due to its mature technology, low cost, and excellent corrosion resistance [8].

With the continuous advancement of steel smelting technology, the Si content in steel has generally increased. During conventional hot-dip galvanizing at 450–480 °C,

excessive silicon in the steel substrate induces an overly vigorous Fe–Zn reaction, leading to abnormal growth of the brittle ζ phase in the coating. This results in a dull, excessively thick coating with poor adhesion—a phenomenon known as the “Sandelin effect” [9]. This issue substantially impairs both the aesthetic quality and mechanical properties of the coating, and has become one of the key factors limiting the advancement of traditional hot-dip galvanizing technology.

To effectively suppress the Sandelin effect, numerous studies have investigated the composition of the zinc bath. By adding elements such as Al, Ni, Bi, Mg, and Re to the zinc bath, the microstructure and properties of coatings on Si-containing reactive steel can be effectively controlled. Among these, Ni and Al have become research highlights in this field owing to their remarkable inhibition effect and high process feasibility. Kania et al. [10] pointed out that the optimal Ni concentration in a Zn bath is in the range of 0.04 wt.% to 0.06 wt.%, within which the Sandelin effect can be effectively suppressed and the coating structure approaches that of low-silicon steel. Excessive Ni not only increases cost but also leads to dross formation, contaminating the zinc bath. Zhang et al. [11] showed that a Zn–Ni alloy bath containing 0.045 wt.% Ni substantially inhibits the ζ phase of the coating, resulting in a denser and considerably thinner coating compared to a pure zinc coating, while also improving corrosion resistance. Wang et al. [12] investigated the effects of Al and Mg contents in the zinc bath on the microstructure and corrosion performance of the coating. They found that adding Al and Mg to the bath produces a Zn–Al–Mg coating with clearly identifiable Zn/MgZn₂ binary eutectic phases and Zn/Al/MgZn₂ ternary eutectic phases. Increasing the Al and Mg content further improves the corrosion resistance of the coating. Kania et al. [10] also noted that researchers have attempted to control steel reactivity by increasing the Al content in the zinc bath. The results indicate that an Al content of 0.1 wt.% to 1.0 wt.% effectively reduces the reactivity of the steel.

In addition, Guo et al. [13] gradually optimized the composition of the galvanizing bath to improve the corrosion resistance of the galvanized coating by introducing elements such as Al, Ni, and Re. Bondareva et al. [14] found that adding Ni to the zinc bath inhibits the Fe–Zn reaction, thereby reducing the coating thickness. This provides a theoretical reference for the alloy design in the present study. Existing research has mostly focused on single-element addition or the development of multi-element systems, with limited systematic studies on the microstructural evolution, corrosion resistance, and hardness of coatings under the combined addition of Al and Ni. Furthermore, current investigations into Zn–Ni–Al coatings are predominantly restricted to baths with low Al concentrations, typically ranging from 0 wt.% to 0.15 wt.% [15], which essentially fall within the regime of trace-Al-modified hot-dip galvanized layers. In contrast, the exploration of Zn–Ni–Al coatings with a substantially elevated Al level, specifically up to 1 wt.%, constitutes a previously uncharted domain in the literature.

Therefore, this study uses Q235 steel as the substrate and selects three bath compositions, namely Zn, Zn–0.04 wt.% Ni, and Zn–0.04 wt.% Ni–1 wt.% Al, as the research objects to systematically explore the effects of Ni and Al on the microstructure, corrosion resistance, and hardness of the coatings. This provides a theoretical basis for the composition design and process optimization of high-performance hot-dip coatings.

2. Materials and Methods

2.1. Materials

In this study, Q235 steel plates (purchased from Qing County Jifeng Steel and Iron Co., Ltd., Qingxian, China) with dimensions of 50 mm × 50 mm × 2 mm were used as the substrate material. The chemical composition of the substrate material is presented in Table 1.

Table 1. Composition of Q235 steel (wt.%).

C	Mn	P	Si	S
0.15	0.42	0.021	0.18	0.021

The raw materials for the hot-dip galvanizing alloy zinc bath in this study consisted of industrial pure zinc ingots (purchased from Shaanxi Dongling Smelting Co., Ltd., Baoji, China), industrial commercial zinc ingots (supplied by Shandong Qixing Iron Tower Co., Ltd., Zouping, China) and self-made Zn–50Al alloy ingots, which were fabricated by melting pure aluminum and pure zinc ingots at 660 °C, holding at this temperature for 5 h with thorough stirring, and subsequent casting. The chemical composition of self-made Zn–50Al alloy ingots was determined by inductively coupled plasma optical emission spectrometry (ICAP-PRO). The compositions of raw materials for the zinc bath are presented in Table 2.

Table 2. Chemical compositions of raw materials for the zinc bath (wt.%).

Ingot Type	Zn	Al	Fe	Ni	Pb	Sn	Cu	Other Impurities
Industrial pure zinc	Bal.	0.001	0.001	—	0.003	0.001	0.001	—
Industrial commercial zinc	Bal.	0.0093	0.0219	0.0364	0.0024	—	—	—
Zn–50Al alloy	48.92	50.86	—	—	—	—	—	Bal.

2.2. Sample Preparation

The specimens were pickled, rinsed with water, fluxed, dried, and subsequently prepared for galvanizing. During the experiment, the specimens were vertically immersed in a bath at 445 °C, vertically withdrawn after 75 s, air-cooled to room temperature, and subsequently passivated. The hot-dip galvanizing process parameters are listed in Table 3.

Table 3. Hot-dip galvanizing process parameters.

Zinc Alloy Bath	Temperature (°C)	Time (s)	Cooling Method
Zn	445	75	Air cooling
Zn–0.04 wt.% Ni	445	75	Air cooling
Zn–0.04 wt.% Ni–1 wt.% Al	445	75	Air cooling

2.3. Experimental Tests

The passivated specimens were cut into small pieces of 10 mm × 10 mm, mounted, and subsequently ground, polished, and etched until the surfaces were scratch-free. A field emission scanning electron microscope (FESEM, JEOL, Tokyo, Japan, model JSM–7610F) was used to observe the phase distribution and microstructure of the coating cross-section. An energy dispersive spectrometer (EDS, JEOL, Tokyo, Japan, model JSM–7610F) was used for micro-area compositional analysis of different phase regions in the coating, determining the content and distribution of Fe, Zn, Ni, and Al in each phase region. The surface hardness of the three coatings was evaluated using a Vickers hardness tester (HV, Laizhou Huayu Zhongxin, Laizhou, China, model HVS–1000AT) under a 200 g load and a 15 s dwell time, producing diamond-shaped indentations. For each coating type, five independently prepared specimens were tested. On each specimen, five indentations were made at designated locations (the four corners and the center), and the readings were averaged to obtain a representative hardness value for that specimen. The final hardness for each coating was then expressed as the mean and standard deviation of the values obtained from the five specimens. The surface hardness of the three coatings was compared to investigate the effects of Ni and Al on the hardness of hot-dip galvanized coatings.

In this study, a neutral salt spray (NSS) test was conducted according to GB/T 10125–2021 [16], “Corrosion tests in artificial atmospheres—Salt spray tests”, to evaluate the corrosion resistance of the coatings. The specific experimental parameters are presented in Table 4. For each coating type, three parallel specimens were prepared and tested. Specimens were removed every 24 h to observe the surface corrosion morphology and to capture photographic records. The time at which corrosion products initially appear on the specimen surface is used as the criterion for evaluating the corrosion resistance of the coatings. An X-ray diffractometer (XRD, Rigaku, Tokyo, Japan, model MinFlex 600) was used to analyze the XRD patterns of the corrosion products on the coating surface. The patterns were compared with standard PDF (Powder Diffraction File) cards to identify the phase composition of the corrosion products. Furthermore, electrochemical measurements were performed using a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China) to obtain Tafel curves for the different coating specimens. The corrosion current density was determined by Tafel extrapolation to evaluate the corrosion resistance of the coated specimens. A conventional three-electrode cell configuration was employed: the working electrode was the coated specimen sealed with silicone rubber, leaving an exposed area of 1 cm²; the reference electrode was a saturated calomel electrode (SCE); and the counter electrode was a platinum plate. The electrolyte was a 3.5 wt.% NaCl solution at room temperature. Prior to measurement, each working electrode was immersed in the electrolyte for 30 min to stabilize the open-circuit potential (OCP). Potentiodynamic polarization was then performed over a potential range from −0.4 V to +0.9 V versus OCP at a scan rate of 1 mV·s^{−1}. Owing to the destructive nature of the electrochemical test, each coated specimen was measured only once.

Table 4. Parameters of the neutral salt spray test.

NaCl Solution	pH	Temperature (°C)	Spray Pressure
50 g/L ± 5 g/L	6.5–7.2	35 °C ± 2 °C	98 kPa ± 10 kPa

3. Results

3.1. Microstructural Evolution Analysis

As shown in Figure 1, both the Zn coating and the Zn–0.04 wt.% Ni coating consist of the δ phase (FeZn₇) adjacent to the substrate, the ζ phase (FeZn₁₃) in the middle, and the outermost η phase, which is a solidified layer of free zinc. The δ phase is located immediately adjacent to the steel substrate. Owing to its hexagonal crystal structure, the δ phase exhibits high hardness and good ductility. Its continuous and dense morphology benefits both the adhesion between the coating and the substrate and the corrosion resistance of the coating. The ζ phase in the middle grows as columnar crystals perpendicular to the substrate surface. The ζ phase has a monoclinic structure with poor symmetry and high brittleness, which is detrimental to the adhesion of the coating. Moreover, the loose ζ phase poorly resists water and atmospheric penetration, thereby accelerating corrosion of the substrate. The η phase is located in the outermost layer of the coating. It has a hexagonal close-packed structure, high stability, strong interatomic bonding, and a certain degree of strength and hardness. A continuous and intact η phase layer enables the coating surface to retain a metallic luster for an extended period. As can be seen by comparing Figure 1a,b, after the addition of 0.04 wt.% Ni, the thickness of the brittle ζ phase in the alloy coating is reduced and its porosity is alleviated compared with the pure zinc coating, while the thickness of the ductile δ phase increases. This change benefits the adhesion between the coating and the substrate and enhances the corrosion protection performance.

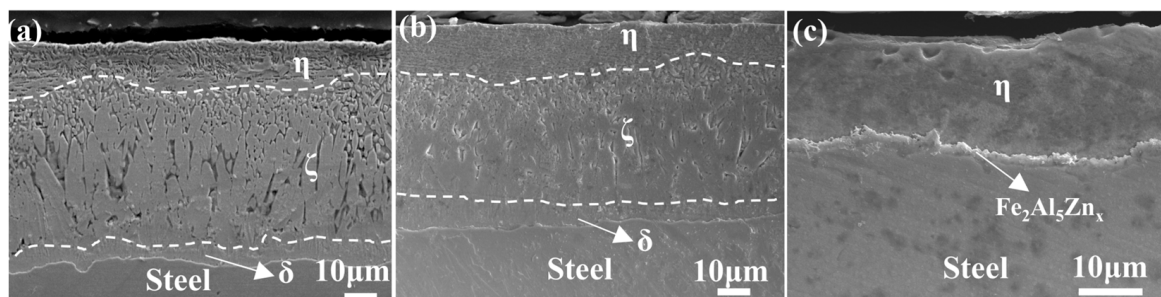


Figure 1. Cross-sectional SEM images of the three coatings (a) Zn; (b) Zn–0.04 wt.% Ni; (c) Zn–0.04 wt.% Ni–1 wt.% Al.

Compared with the Zn coating and the Zn–0.04 wt.% Ni coating, the addition of Al brings about a fundamental change in the coating microstructure. Figure 2a shows the cross-sectional SEM image of the Zn–0.04 wt.% Ni–1 wt.% Al coating, Figure 2b presents the EDS line-scan results along the thick arrow path in Figure 2a, and Table 5 lists the point-scan results for the points marked in Figure 2a. After analysis, the hot-dip Zn–0.04 wt.% Ni–1 wt.% Al coating consists only of an Fe–Al–Zn inhibition layer and a single η -phase outer layer. Previous studies [17,18] have shown that this inhibition layer is most likely the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ intermetallic phase. From the line scan data in Figure 2b along the arrow path, the Zn content gradually decreases while the Fe and Al contents gradually increase. Furthermore, Al and Ni are enriched at the interface, which is consistent with the EDS data at point 1 (see Table 5), indicating the formation of the phase that is most likely $\text{Fe}_2\text{Al}_5\text{Zn}_x$ at that location.

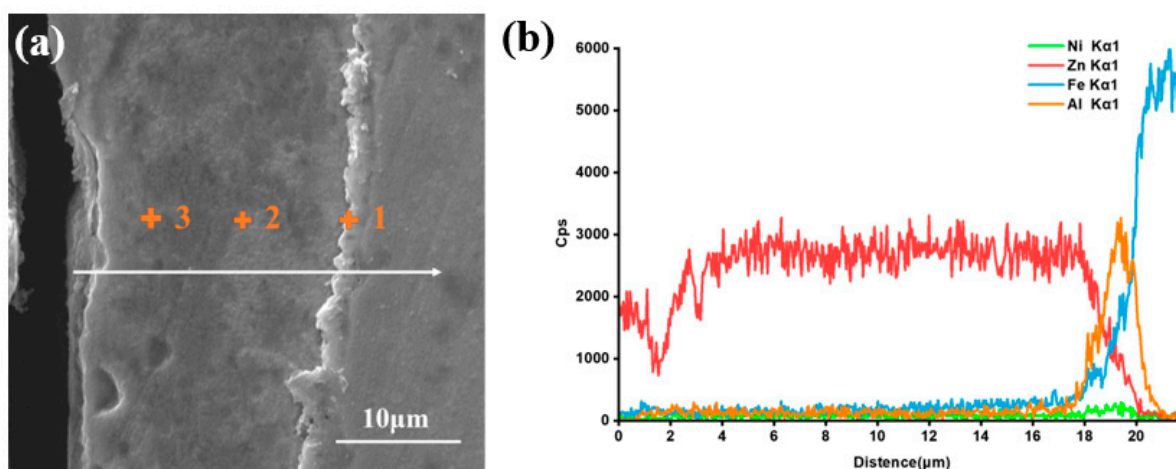


Figure 2. Cross-sectional SEM image (a) and EDS line-scan (b) of the Zn–0.04 wt.% Ni–1 wt.% Al coating.

Table 5. Results of EDS analysis of point 1~3 in Figure 2 (at.%).

Point	Zn	Al	Fe	Ni	Possible Phase
1	21.4	53.8	22.3	2.5	$\text{Fe}_2\text{Al}_5\text{Zn}_x$
2	96.25	1.68	1.97	0.11	η
3	97.52	1.20	1.28	0.00	η

For each coating type, three replicate specimens were analyzed. Using Image Pro Plus 6.0 software, the thicknesses of the individual phase layers and the total coating were measured independently from cross-sectional SEM images. Mean values and standard deviations were calculated and are presented in Table 6. As can be seen from Table 6,

after the addition of 0.04 wt.% Ni, the coating thickness decreases from $65.34 \pm 2.64 \mu\text{m}$ to $56.33 \pm 0.89 \mu\text{m}$. When the bath contains 1 wt.% Al, the overall coating thickness is substantially reduced compared with Al-free coatings, reaching only $17.66 \pm 1.78 \mu\text{m}$, which is approximately one-third or even less than the thickness of the Al-free coating. The Zn–0.04 wt.% Ni–1 wt.% Al coating consists solely of the Fe–Al–Zn inhibition layer and the η phase, resulting in a substantially reduced coating thickness and further lowering zinc consumption.

Table 6. Thickness of three coatings.

Zinc Alloy Bath	δ (μm)	ζ (μm)	η (μm)	Total Thickness (μm)
Zn	6.33 ± 0.4	44.29 ± 2.47	13.71 ± 3.2	65.34 ± 2.64
Zn–0.04 wt.% Ni	8.55 ± 0.71	34.52 ± 2.66	13.18 ± 3.42	56.33 ± 0.89
Zn–0.04 wt.% Ni–1 wt.% Al	—	—	—	17.66 ± 1.78

3.2. Corrosion Resistance Analysis

3.2.1. Neutral Salt Spray Test Results

To investigate the long-term corrosion resistance of the three coatings in a simulated marine atmospheric environment, neutral salt spray (NSS) tests were conducted on the Zn, Zn–0.04 wt.% Ni, and Zn–0.04 wt.% Ni–1 wt.% Al coated samples. Figure 3 shows photographs of the hot-dip galvanized samples prepared with the three bath compositions. Figure 4 presents the macroscopic morphologies of each coating after 800 h, 1000 h, and 1600 h of salt spray testing. After 800 h of NSS testing, white rust appeared on the surface of all three coatings, whereas yellow rust appeared only on the Zn coating surface. This confirms that Ni, by adjusting the thickness ratio of the phase layers, thins the ζ phase while thickening the δ phase, thereby improving the corrosion resistance of the coating. After 1000 h of NSS testing, yellow rust appeared on the surface of the Zn–0.04 wt.% Ni coating, whereas the Zn–0.04 wt.% Ni–1 wt.% Al coating showed no yellow rust. When the salt spray test was extended to 1600 h, the Zn–0.04 wt.% Ni–1 wt.% Al coating still exhibited only white rust on its surface, indicating that Al preferentially reacts with Fe to form a continuous and dense Fe–Al–Zn inhibition layer, which drastically reduces the coating thickness while simultaneously improving the corrosion resistance.

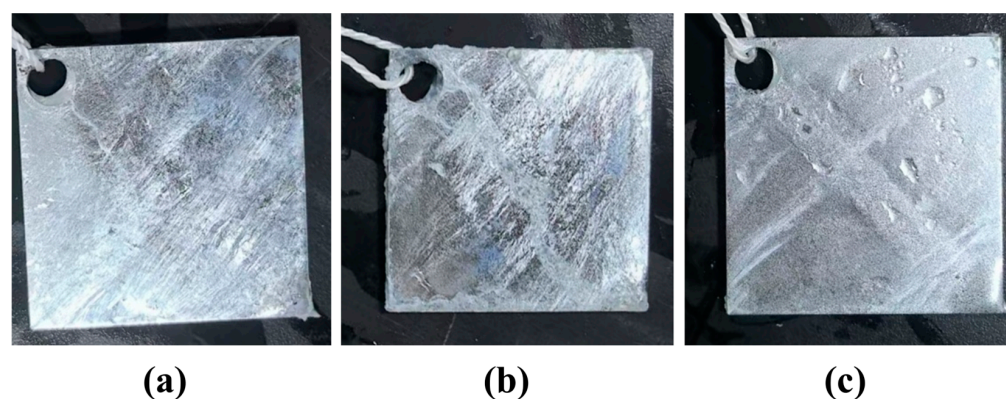


Figure 3. Photograph of the samples. (a) Zn; (b) Zn–0.04 wt.% Ni; (c) Zn–0.04 wt.% Ni–1 wt.% Al.

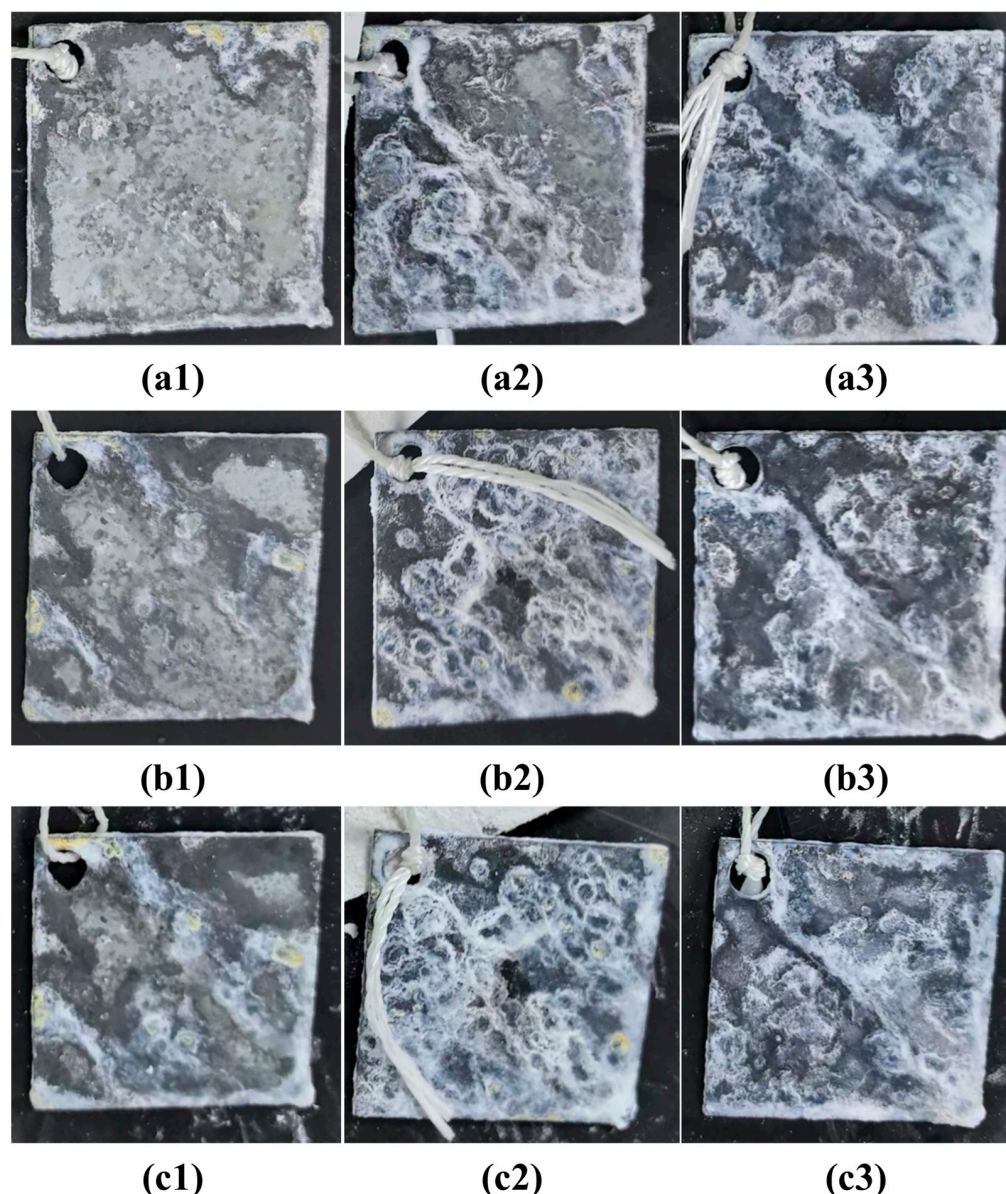


Figure 4. Macroscopic morphologies of coatings after different salt spray exposure times under three bath compositions. 800 h: (a1) Zn; (a2) Zn–0.04 wt.% Ni; (a3) Zn–0.04 wt.% Ni–1 wt.% Al; 1000 h: (b1) Zn; (b2) Zn–0.04 wt.% Ni; (b3) Zn–0.04 wt.% Ni–1 wt.% Al; 1600 h: (c1) Zn; (c2) Zn–0.04 wt.% Ni; (c3) Zn–0.04 wt.% Ni–1 wt.% Al.

3.2.2. Electrochemical Testing Analysis

Electrochemical tests were carried out on the three coatings, and the results are presented in Figure 5. The fitting results of the polarization curves are given in Table 7. Under the corrosion conditions of the present experiment, the corrosion current density is proportional to the corrosion rate. The Zn coating exhibits a corrosion current density of $2.82 \mu\text{A}\cdot\text{cm}^{-2}$. After the addition of 0.04 wt.% Ni, the corrosion current density decreases to $2.71 \mu\text{A}\cdot\text{cm}^{-2}$, confirming that the addition of Ni improves the phase distribution of the coating and enhances its corrosion resistance. This result is consistent with the NSS test findings. However, because the electrochemical measurements were performed only once per coating type, this observed improvement requires further verification through replicated measurements in future studies. After the addition of 1 wt.% Al, the Zn–0.04 wt.% Ni–1 wt.% Al coating exhibits the lowest corrosion current density of only $2.07 \mu\text{A}\cdot\text{cm}^{-2}$.

and, consequently, the best corrosion resistance. This finding is also consistent with the NSS test results.

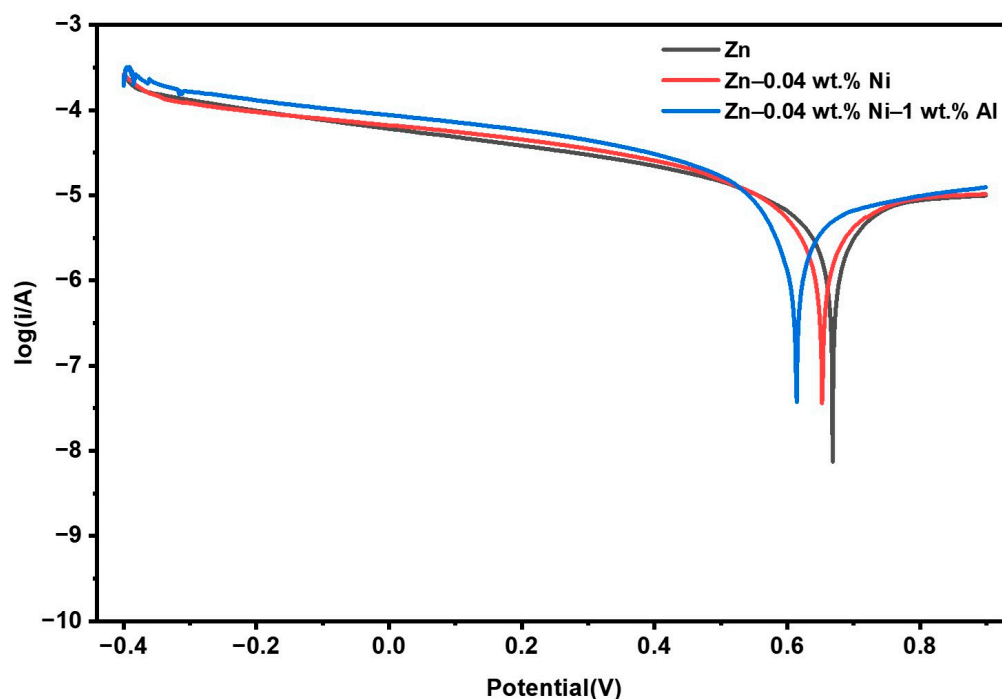


Figure 5. Tafel polarization curve of three alloy coatings in 3.5% NaCl solution.

Table 7. Fitting results of polarization curves.

Samples	E _{corr} (V)	I _{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)
Zn	0.67	2.82
Zn-0.04 wt.% Ni	0.65	2.71
Zn-0.04 wt.% Ni-1 wt.% Al	0.61	2.07

3.2.3. Composition Analysis of Corrosion Products After Salt Spray Testing

The corrosion products on the surfaces of the Zn, Zn-0.04 wt.% Ni, and Zn-0.04 wt.% Ni-1 wt.% Al specimens after 1600 h of NSS testing were analyzed by XRD, and the results are presented in Figure 6. The XRD phase analysis indicates that the corrosion products consist of $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, and ZnO. Among these, ZnO has high electrical conductivity, a loose and porous structure [19], and poor adhesion to the substrate; therefore, the formation of ZnO should be avoided as much as possible. Compared with the pure zinc coating and the Zn-0.04 wt.% Ni coating, the XRD pattern of the corrosion products on the Zn-0.04 wt.% Ni-1 wt.% Al coating exhibits relatively weaker diffraction peaks corresponding to ZnO, while the peaks corresponding to $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$ and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ become relatively more prominent.

3.3. Study on Coating Hardness

Coating hardness may potentially contribute to the improvement of scratch resistance and wear resistance. The hardness of the mean and standard deviation was calculated for each coating. The results are presented in Figure 7. Compared with the Zn coating, the Zn-0.04 wt.% Ni coating exhibits a slightly lower overall hardness. The hardness of the Zn-0.04 wt.% Ni-1 wt.% Al coating is substantially higher than that of the Zn and Zn-0.04 wt.% Ni coatings.

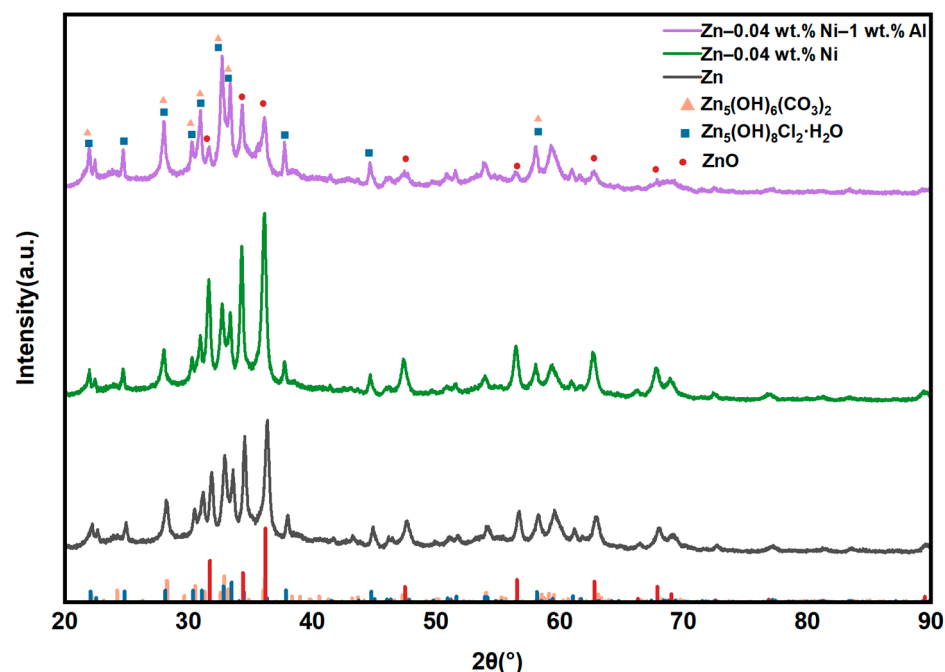


Figure 6. XRD patterns of corrosion products of the three coatings.

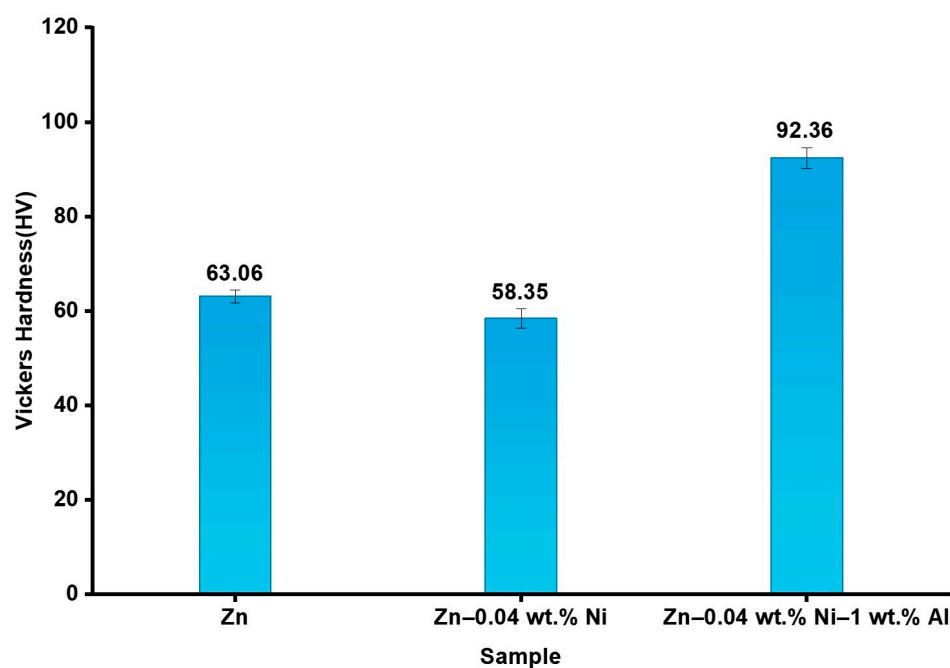


Figure 7. Vickers hardness analysis of the three coatings.

4. Discussion

4.1. Mechanism of the Combined Addition of Ni and Al on the Microstructure of the Coating

After adding 0.04 wt.% Ni, the coating thickness decreases from $65.34 \pm 2.64 \mu\text{m}$ to $56.33 \pm 0.89 \mu\text{m}$. Specifically, the thickness of the ζ phase decreased from $44.29 \pm 2.47 \mu\text{m}$ to $34.52 \pm 2.66 \mu\text{m}$, while the δ phase increased from $6.33 \pm 0.4 \mu\text{m}$ to $8.55 \pm 0.71 \mu\text{m}$ (Table 6). During the galvanizing process, it was visually observed that, compared with the pure Zn bath, the Zn-0.04 wt.% Ni bath exhibited superior fluidity during stirring and specimen withdrawal, with the molten bath draining more readily from the specimen surface. This observation suggests enhanced wettability between the bath and the steel substrate, which is consistent with the mechanism reported in the literature [10] that Ni

reduces bath viscosity. This allows Fe and Zn atoms to contact more easily and rapidly form a refined ζ phase. Subsequently, the pinning effect of Ni hinders the interdiffusion of Fe and Zn atoms, resulting in a thinner and less porous ζ phase. At the same time, the high wettability also promotes the growth of the δ phase, which benefits the adhesion between the coating and the substrate, as well as the corrosion resistance of the coating. Furthermore, owing to the improved fluidity of the bath, the zinc liquid on the specimen surface drains away quickly during vertical withdrawal, thereby reducing the overall coating thickness and zinc consumption.

The addition of Ni effectively suppresses the Sandelin effect. Compared with the Zn coating, the Zn–Ni coating exhibits a reduced thickness and a denser structure, which is consistent with the findings of Kania et al. [10] and Zhang et al. [11] regarding the role of Ni.

The addition of 1 wt.% Al completely transforms the coating structure. When Q235 steel is immersed in a zinc bath containing 1 wt.% Al, the Fe on the steel substrate surface preferentially reacts with Al in the bath, forming a continuous Fe–Al–Zn inhibition layer at the interface. Once this inhibition layer is formed, it acts as a physical diffusion barrier between Fe and Zn atoms. This layer is dense and continuous, effectively hindering the further dissolution of Fe atoms into the zinc bath. The atomic interdiffusion required for the Fe–Zn reaction is blocked, and the growth of Fe–Zn intermetallic compounds is effectively hindered under the present experimental conditions and within the resolution of the applied characterization methods. As a result, Fe–Zn intermetallic compounds such as the ζ and δ phases cannot nucleate or grow. The coating consists solely of an extremely thin inhibition layer (approximately 1–2 μm) and the η phase.

4.2. Mechanism of the Combined Addition of Ni and Al on the Corrosion Resistance of the Coating

After 800 h of salt spray testing, white rust appeared on the surface of all three coatings, while yellow rust began to appear on the pure zinc coating. When the test was extended to 1000 h, yellow rust started to appear on the Zn–0.04 wt.% Ni coating, confirming that the addition of Ni improves the corrosion resistance. The mechanism can be described as follows: by adjusting the thickness ratio of the phase layers, Ni thins the ζ phase while thickening the δ phase, resulting in a denser coating and thus improved corrosion resistance.

After 1600 h of salt spray testing, no yellow rust was observed on the Zn–0.04 wt.% Ni–1 wt.% Al coating. Among the three coatings tested, the Zn–0.04 wt.% Ni–1 wt.% Al coating exhibits the best corrosion resistance. XRD analysis revealed that, compared with the other two coatings, the diffraction pattern of the Zn–0.04 wt.% Ni–1 wt.% Al coating exhibits relatively weaker diffraction peaks for ZnO and stronger peaks corresponding to $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$. The dense and compact $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ can effectively block the penetration of corrosive species such as Cl^- and CO_2 , thereby providing excellent barrier protection [20,21], whereas porous ZnO cannot offer such protective effects. The preferential formation of these dense corrosion products on the Zn–0.04 wt.% Ni–1 wt.% Al coating is attributed to the Al-modified coating structure, which differs fundamentally from the coatings reported in previous low-Al systems [15]. In those systems, the Al content was limited to 0.08–0.15 wt.%, and the coatings consisted primarily of δ and ζ phases with no continuous inhibition layer. By contrast, the present study employed a higher Al content of 1 wt.%, which enabled the formation of a continuous Fe–Al–Zn inhibition layer. This structural distinction, rather than compositional variation alone, is considered the primary factor underlying the superior long-term corrosion resistance of the Zn–0.04 wt.% Ni–1 wt.% Al coating. Therefore, the Zn–0.04 wt.% Ni–1 wt.% Al coating exhibits the best corrosion resistance.

4.3. Mechanism of the Combined Addition of Ni and Al on the Coating Hardness

Compared with the Zn coating, the Zn–0.04 wt.% Ni coating exhibits a slightly lower overall hardness owing to the thinning of the hard and brittle ζ phase.

The hardness of the Zn–0.04 wt.% Ni–1 wt.% Al coating is substantially higher than that of the Zn and Zn–0.04 wt.% Ni coatings. This increase in hardness originates from the continuous and dense Fe–Al–Zn inhibition layer formed at the interface. According to the literature findings, the microhardness of the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ phase can reach approximately 1100 HV [22–24], which is substantially higher than that of Zn–Fe intermetallic compounds (typically ranging from 300 to 500 HV) [25]. This provides further evidence that the Fe–Al–Zn inhibition layer most likely corresponds to the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ phase. Therefore, it can be inferred that despite the inhibition layer being only 1–2 μm in thickness, it still makes a substantial contribution to the overall hardness enhancement of the Zn–0.04 wt.% Ni–1 wt.% Al coating. Furthermore, Ni dissolves in this inhibition layer, forming fine and relatively hard Ni–Al solid solutions [26], which substantially increase the coating hardness and may consequently improve wear resistance.

5. Conclusions

In this study, three coatings with different compositions were prepared on the surface of Q235 steel by hot-dip galvanizing. The effects of Ni and Al on the microstructure, corrosion resistance, and hardness of the coatings were investigated using various characterization techniques, including SEM, EDS, XRD, neutral salt spray (NSS) testing, electrochemical measurements, and Vickers hardness testing.

- (1) The Zn coating consists of δ , ζ , and η phases. Si in the steel matrix induces an excessively vigorous Fe–Zn reaction, leading to abnormal growth of the brittle ζ phase. This results in a dull, excessively thick coating with poor adhesion and corrosion resistance.
- (2) In the Zn–0.04 wt.% Ni coating, Ni improves the wettability between the bath and the steel substrate, refines the columnar grains of the ζ phase, inhibits the thickening of the ζ phase, and promotes the growth of the δ phase. Compared with the pure zinc coating, the overall thickness is reduced, the Sandelin effect is effectively suppressed, the corrosion resistance is improved, and zinc consumption is lowered.
- (3) In the Zn–0.04 wt.% Ni–1 wt.% Al coating, a continuous and dense inhibition layer forms at the interface. The coating consists solely of this inhibition layer and the η phase from solidified free zinc, resulting in a substantially reduced thickness and greatly increased hardness. In the corrosion products of the Zn–0.04 wt.% Ni–1 wt.% Al coating, dense $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ fill the corrosion crevices, and the coating shows the best corrosion resistance among the three coatings tested.

Based on the current findings, future research may be pursued in the following directions:

- (1) The present study fixes the Ni content at 0.04 wt.% and the Al content at 1 wt.%, confirming that the combined addition of Ni and Al improves the coating performance. However, the individual contribution of Al to the coating microstructure and properties, as well as the synergistic effect between Ni and Al, warrant further investigation. Future work could establish a more extensive composition by systematically examining the microstructural and property evolution of coatings with varying Al contents, both in the presence and absence of Ni addition. Furthermore, response surface methodology could be employed to reveal the synergistic mechanisms of Ni and Al on the overall coating performance.
- (2) Based on the comparative investigation of three fixed-composition alloy coatings in this study, future attempts may be directed toward the further incorporation of alloying elements such as Mg and RE. Through compositional design of multi-

component alloy coatings, the synergistic regulatory mechanisms among multiple elements could be elucidated, potentially leading to substantial enhancements in coating performance.

- (3) The neutral salt spray test in the present study was conducted for a duration of 1600 h. Subsequent research could extend the neutral salt spray testing period or conduct outdoor exposure tests to systematically investigate the long-term evolution of corrosion products such as $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, as well as their regulatory effects on the coating protective performance, thereby enabling a more in-depth evaluation of coating corrosion resistance. Meanwhile, a multi-dimensional quantitative evaluation framework for neutral salt spray test results should be established in future studies. This may include: quantitative analysis of the percentage of corroded surface area and the temporal evolution of rust coverage using image processing techniques; precise determination of corrosion rate per unit area through mass loss measurements; and direct quantification of coating corrosion degree via thickness loss measurements.

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