

Article

Effect of Cr–Ni Co-Alloying on Corrosion Behavior and Rust-Layer Evolution of HRB500 Rebar in Chloride-Containing Environments

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Abstract

This study investigated how increased Cr and Ni contents affect the corrosion behavior and rust layer evolution of HRB500 rebar in chloride-containing environments. Corrosion of the Cr- and Ni-alloyed rebars was characterized by distinct stages: in the initial stage, before a stable rust layer formed, the corrosion rate increased; with continued immersion, corrosion products progressively covered the surface and became more compact, and the overall corrosion rate decreased. Higher Cr and Ni contents were found to mitigate overall corrosion damage, markedly suppress localized corrosion, and shift the corrosion morphology toward a more uniform attack. Electrochemical measurements showed a noble shift in corrosion potential, a reduction in corrosion current density, and significant increases in low-frequency impedance and charge transfer resistance, indicating enhanced barrier properties against charge transfer and ionic migration. With corrosion progression, rust layer phases evolved from an Fe₃O₄-dominated assemblage to enrichment in stable iron oxyhydroxides; the fraction of α -FeOOH increased, raising the α/γ^* index and suggesting improved rust layer stability and protectiveness. Mechanistically, Cr and Ni enrichment was found to facilitate the conversion of metastable products to α -FeOOH and to promote the formation of compact spinel oxides FeCr₂O₄ and NiFe₂O₄, thereby hindering chloride ion ingress and interfacial corrosion reactions and markedly improving corrosion resistance. Overall, this work elucidated the Cr–Ni co-alloying mechanism for rust layer stabilization and pitting suppression. At 504 h, the high Cr–Ni rebar reduced the maximum pit depth by approximately 61.8% and lowered i_{corr} to approximately 43% of that of the low Cr–Ni rebar, thereby providing quantitative guidance for marine-grade rebar design.



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1. Introduction

The durability of reinforced concrete structures in marine environments has been recognized as a major concern in civil engineering. Penetration of chloride ions (Cl[−]) through the concrete cover to the steel surface can trigger localized breakdown of the passive film, resulting in pitting corrosion, cracking, and spalling of the concrete cover, thereby markedly shortening the service life of reinforced concrete structures. To address this issue, studies

aimed at enhancing rebar corrosion resistance in chloride-bearing environments have primarily focused on two approaches: (i) investigating rebar corrosion behavior in simulated concrete pore solutions and (ii) tailoring alloy composition to regulate the microstructure and rust-layer characteristics, thereby improving corrosion resistance at the source [1–5]. Accordingly, the development of low-cost, high-performance, low-alloy, corrosion-resistant rebar steels, together with clarification of their rust-layer evolution mechanisms in chloride-bearing environments, is of substantial scientific and engineering significance.

Low alloying has been widely regarded as a feasible approach for mitigating chloride-induced corrosion of reinforcing steel. Its core advantage lies in the fact that both the base steel microstructure and the compactness and stability of the rust layer can be regulated synergistically. In chloride environments, localized corrosion of reinforcing steel is often initiated at microstructural heterogeneities (such as inclusions, segregation bands, and coarse second phases). These heterogeneities readily trigger microgalvanic coupling and generate local chemical gradients, thereby promoting preferential dissolution and pit initiation. It has been demonstrated in both theoretical and experimental studies that microalloying elements can act as “microstructure modifiers”; grains are refined, precipitation behavior is altered, and inclusion morphology and distribution are tailored, thereby reducing preferential anodic sites and suppressing pit initiation and growth [6–8]. By combining first-principles calculations with experiments, Zeng et al. showed that trace Nb can affect the stability of the corrosion layer and the rust layer steel interface, suggesting that microalloying modifies not only the matrix microstructure but also influences rust layer formation and evolution under chloride attack [9]. Xu et al. further reported that adjusting the N and Si contents in V-containing HRB400e steel significantly altered the microstructure and mechanical properties [10]. This finding is relevant to corrosion resistance because composition and microstructure coupling may shift the balance between stable passivation and susceptibility to depassivation. Li et al. likewise reported that variations in Cr content can markedly influence the microstructure, κ carbide precipitation, and recrystallization behavior of lightweight steels, highlighting the critical role of Cr in microstructure property coupling [11]. Huang et al. further noted that a small Ni addition can significantly modify HSLA steel microstructural characteristics by reducing M–A constituents and promoting acicular ferrite formation, demonstrating Ni’s capability for microstructural control [12]. Taken together, prior studies indicate that compositional optimization through microalloying can reduce microscale electrochemical heterogeneity and promote more uniform interfacial reactions and a more stable rust layer in chloride environments, thereby improving corrosion resistance and service reliability.

Among alloying elements, sustained attention has been paid to Cr and Ni because passive film integrity and rust layer protectiveness can be directly modified, often in a stage-dependent manner. Cr has been commonly associated with enhanced passivation and improved resistance to early-stage anodic dissolution. In marine-related environments, Cr-alloyed rebars have been reported to exhibit surface enrichment of Cr and the formation of denser oxide and hydroxide films, which retard anodic dissolution and delay the onset of localized corrosion [13]. Consistently, in simulated concrete pore solutions, improved passivation behavior was observed for chromium-alloyed high-strength rebars, highlighting the role of Cr in stabilizing the passive film under alkaline conditions and increasing tolerance to chloride-induced perturbation [14]. In contrast, Ni has been frequently linked to the long-term stabilization of corrosion products after depassivation has occurred. Studies on Ni-containing steels exposed to chloride environments indicated that Ni promotes the formation of more compact and protective rust phases (e.g., spinel-type products), increasing rust layer potential and compactness and thereby hindering electrolyte penetration and Cl^- ingress during prolonged exposure [15,16]. This mechanistic distinction suggests a

complementary strategy. Cr primarily strengthens the initial passive barrier and delays depassivation, whereas Ni mainly improves the transport blocking capability and stability of the rust layer at later stages. Such prior findings provide a clear theoretical basis for optimizing low-alloy rebar designs that balance early-stage passivity retention with long-term rust layer protectiveness.

Although the effects of individual elements have been extensively investigated, the synergistic effect between Cr and Ni cannot be considered a simple additive superposition. Wang and co-workers examined the effects of Cr and Ni on the microstructure and corrosion resistance of high-strength low-alloy steel and reported that, in chloride-bearing environments, appropriate Cr–Ni alloying markedly improved corrosion resistance [17]. Existing work shows that Cr and/or Ni can improve corrosion resistance in chloride media, but a key gap remains in linking Cr and Ni co-alloying to rust layer evolution and pitting suppression under wet–dry exposure. Specifically, the coupled role of Cr and Ni in promoting protective α -FeOOH and compact spinel oxides, and the quantitative connection between these rust layer changes and reductions in pit depth and i_{corr} , remain insufficiently established. Accordingly, low-alloy steel specimens with varying Cr–Ni contents were designed using HRB500 as the base material. A 2 wt.% NaCl wet–dry cyclic immersion accelerated corrosion test was conducted in combination with microstructural characterization, electrochemical measurements, and phase analysis to investigate how Cr–Ni co-alloying (together with the associated microstructure refinement) influences rust-layer evolution and localized corrosion, thereby providing a theoretical basis for compositional design of corrosion-resistant rebars for marine engineering.

2. Materials and Methods

2.1. Materials and Alloy Design

Using HRB500 rebar as the base material, two experimental steels were produced by adding different amounts of Cr and Ni. The resulting corrosion-resistant rebars were designated as LCN and HCN. The main chemical compositions of the two steels, measured by inductively coupled plasma mass spectrometry (ICP–MS), are summarized in Table 1.

Table 1. The chemical compositions of the experimental steels (wt.%).

Steel	C	Si	Mn	S	P	V	Cr	Ni	Nb	Fe
LCN	0.1919	0.5084	1.4737	0.0045	0.0052	0.0343	0.3233	0.1107	0.0129	Bal.
HCN	0.1912	0.5222	1.4671	0.0045	0.0052	0.0313	3.0843	0.4952	0.0135	Bal.

2.2. Specimen Preparation and Initial Microstructure

Specimens with dimensions of 10 mm × 10 mm × 5 mm were machined from the steel plate. The specimen surfaces were sequentially ground using SiC papers up to 2000 grit and then polished stepwise with diamond suspensions (2.5 μm and 0.5 μm) to obtain a mirror-like finish. After surface preparation, the specimens were etched by immersion in 5 vol.% nital solution. Finally, the surface morphology was examined using a scanning electron microscope (SEM; FEI Quanta 250, FEI Company, Hillsboro, OR, USA).

2.3. Cyclic Immersion Corrosion Test

The accelerated corrosion test for deformed rebar was conducted in accordance with GB/T 43356-2023 [18] and was performed using a custom-built EA-08 cyclic immersion chamber. A neutral 2 wt.% NaCl solution was used as the corrosive medium. Four exposure durations were selected for sampling: 72, 168, 336, and 504 h. Prior to exposure, specimens (50 mm × 25 mm × 3 mm) were ground sequentially to 1500 grit, cleaned, and dried,

after which their dimensions were measured and the mass was recorded to 0.0001 g. The wet–dry cyclic parameters were set to a 60 min cycle, consisting of 12 min wetting at 45 °C followed by 48 min drying at 70 °C and 70% RH. During exposure, 100 mL of deionized water was replenished every 24 h to maintain a constant solution volume, and the corrosive solution was replaced every 168 h to stabilize the medium pH. At each sampling point, five replicate specimens were retrieved and allocated as follows: three specimens were used for rust scraping for phase analysis, after which chemical rust removal was performed to determine the corrosion rate and to quantify pit depth; one specimen was first used for rust-layer surface morphology observation and subsequently for cross-sectional elemental distribution analysis. The remaining specimen was used for electrochemical impedance spectroscopy (EIS) measurements.

2.4. Electrochemical Tests of Rusted Samples

All electrochemical measurements were performed using a PARSTAT 4A electrochemical workstation (Princeton Applied Research, Oak Ridge, TN, USA) with a conventional three-electrode configuration. Deformed rebar specimens retrieved after the cyclic immersion test at the four exposure durations were subjected to electrochemical testing on the as-formed rust layers. A clamp-type electrochemical cell was employed, and the exposed working area was confined to a circular region 10 mm in diameter. A platinum sheet served as the counter electrode, and a saturated calomel electrode (KCl) was used as the reference electrode. The electrolyte was identical to that used in the cyclic immersion test (2 wt.% NaCl).

Prior to each test, the open-circuit potential (OCP) was monitored for 60 min to allow stabilization of the electrode surface. A steady state was assumed when the potential drift was ≤ 10 mV over a continuous 5 min period. EIS was then conducted at OCP over a frequency range of 100 kHz to 10 mHz with a 10 mV sinusoidal perturbation. The impedance data were fitted to equivalent electrical circuits using ZsimpWin 3.20, and the results were presented as Nyquist and Bode plots ($|Z|$ and phase angle). Potentiodynamic polarization (PDP) was subsequently performed at a scan rate of 0.5 mV s^{-1} , starting from -0.25 V vs. OCP in the cathodic direction and sweeping into the anodic region. The scan was terminated when the anodic current density reached 1 mA cm^{-2} . All measurements were conducted at room temperature, and each test was repeated at least three times to ensure the reliability and reproducibility of the results.

2.5. Corrosion Rate and Morphology Characterization

After completion of the cyclic immersion test, specimens from the four exposure periods were oven dried, and macroscopic appearances before and after rust removal were recorded using a digital camera. Subsequently, one specimen from each exposure period was selected for each steel, and the corrosion morphology of the rust-covered surface was examined by scanning electron microscopy (SEM; FEI Quanta 250, FEI Company, Hillsboro, OR, USA). Finally, the rusted specimens were cold mounted in epoxy resin, and the side surfaces were sequentially ground with SiC papers and polished to expose the rust layer steel interface. After preparation, the cross-sectional morphology and elemental distribution of the rust layer were characterized by SEM equipped with energy dispersive X-ray spectroscopy (EDS) on the same instrument (FEI Quanta 250).

Rust-layer corrosion products were mechanically removed by scraping the rust layers from the specimens at each exposure duration (including both outer- and inner-rust constituents) and then ground into fine powders in an agate mortar for phase and chemical-state characterization. Phase identification of the corrosion products was performed by X-ray diffraction (XRD; D8 ADVANCE, Mannheim, Bruker, Germany) at a tube voltage

of 40 kV and a tube current of 150 mA, with 2θ scanned from 10° to 80° at 3° min^{-1} . The chemical states of Fe, Cr, and Ni in the rust layer were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA) using a non-monochromated Al K α X-ray source operated at 250 W. High-resolution spectra were acquired with a constant pass energy of 15 eV. The photoelectron take-off angle was normal (vertical) to the specimen surface, and the analyzed spot diameter was approximately 0.6 mm. All binding energies were calibrated by referencing the adventitious C 1s peak at 284.8 eV.

After rust-layer sampling, chemical rust removal was performed in accordance with GB/T 16545-2015 [19]. The derusting solution was prepared at room temperature by mixing 500 mL of concentrated HCl with 500 mL of deionized water, followed by the addition of 3.5–10 g hexamethylenetetramine as a corrosion inhibitor. After derusting, the specimens were thoroughly rinsed with deionized water and dried, and the mass was measured using an analytical balance ($\pm 0.0001 \text{ g}$). The mass loss was determined from the difference between the pre- and post-corrosion masses, and the corrosion rate was calculated accordingly. Subsequently, the derusted substrate surface was scanned using a laser confocal scanning microscope (CLSM; VK-9700, KEYENCE, Osaka, Japan) to obtain three-dimensional topography data and to quantify the maximum pit depth. The corrosion rate was calculated using the following equation.

$$v = \frac{87,600 \times \Delta m}{S \times T \times \rho} \quad (1)$$

where v is the corrosion rate of the rebar steel ($\text{mm} \cdot \text{a}^{-1}$); Δm is the mass difference before and after rust removal (g); S is the exposed surface area (cm^2); T is the exposure time (h); and ρ is the density of the rebar steel ($\text{g} \cdot \text{cm}^{-3}$); 87,600 is the unit conversion factor equal to $8760 \text{ h} \cdot \text{a}^{-1} \times 10 \text{ mm} \cdot \text{cm}^{-1}$, which converts the thickness loss rate from $\text{cm} \cdot \text{h}^{-1}$ to $\text{mm} \cdot \text{a}^{-1}$.

3. Results

3.1. Materials Characterization and Corrosion Performance

Figure 1 presents the microstructural morphologies of the two experimental steels. As shown in Figure 1a, the LCN steel was characterized by a typical ferrite–pearlite (F–P) microstructure, in which the matrix was composed of polygonal ferrite, while the dark pearlite colonies were distributed in an island-like manner along ferrite grain boundaries. In contrast, with increasing Cr and Ni contents, the microstructure of the HCN steel was markedly altered. As shown in Figure 1b, the HCN steel was primarily composed of fine lath bainite (LB) with a minor fraction of granular bainite (GB), and the overall microstructure was refined. This difference was mainly attributed to the higher Cr and Ni additions, by which the hardenability of the steel was increased and the diffusional transformation of austenite to high-temperature ferrite and pearlite was suppressed; consequently, undercooled austenite was transformed within a lower temperature range to form a dense lath-bainitic microstructure [20,21].

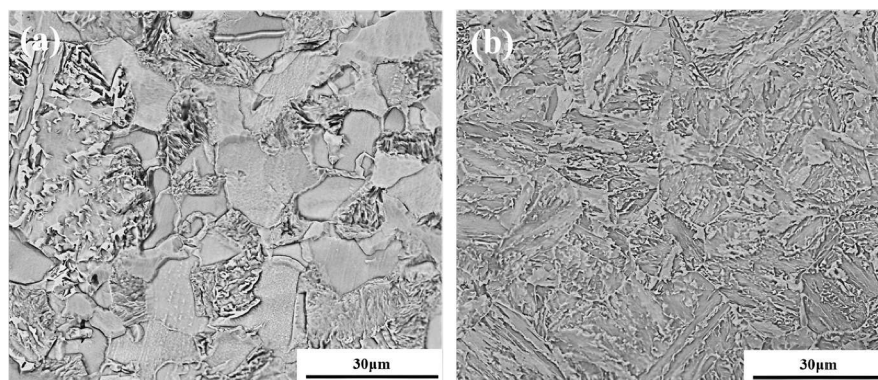


Figure 1. Microstructures of the experimental rebar steels: (a) LCN steel; (b) HCN steel.

Figure 2 summarizes the evolution of corrosion mass loss and corrosion rate for the two Cr–Ni steels after the cyclic immersion accelerated corrosion test. As shown in Figure 2a, the corrosion mass loss of both steels increased in an approximately linear manner with increasing exposure time. Throughout the entire exposure period, the corrosion mass loss of the HCN steel remained lower than that of the LCN steel. At 504 h, the mass loss of the HCN steel was approximately 13.6% lower than that of the LCN steel, suggesting that higher Cr and Ni additions effectively suppressed matrix dissolution. As shown in Figure 2b, the corrosion rate was defined as the average value over the 0– t interval (converted from cumulative mass loss) and did not vary monotonically with time. An anomalous increase in corrosion rate was observed at 168 h relative to 72 h: the LCN steel increased from 6.22 to 6.55 $\text{mm}\cdot\text{a}^{-1}$, whereas the HCN steel increased from 5.24 to 5.38 $\text{mm}\cdot\text{a}^{-1}$. With further exposure, the corrosion rate gradually decreased for both steels, reaching 4.91 $\text{mm}\cdot\text{a}^{-1}$ for the LCN steel and 4.25 $\text{mm}\cdot\text{a}^{-1}$ for the HCN steel by 504 h.

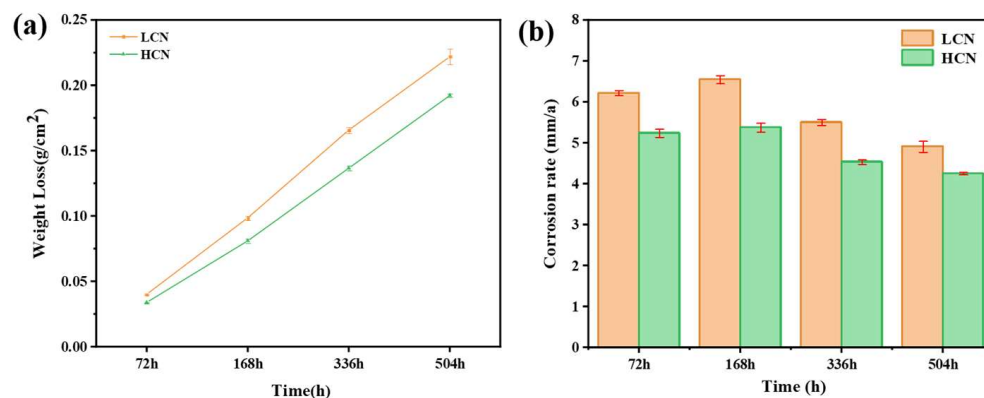


Figure 2. Corrosion data of Cr–Ni steels in a 2 wt.% NaCl solution: (a) mass loss, (b) corrosion rate.

3.2. Evaluation of Localized Corrosion

Rebar is susceptible to corrosion in marine environments, where chloride-induced pitting is a major contributor to the shortened service life of reinforced concrete structures [22,23]. Accordingly, pit depth—particularly the maximum pit depth—was used as a key metric for assessing localized corrosion severity and structural safety [24]. The derusted surface topography of the two Cr–Ni steels after different immersion durations was characterized by three-dimensional laser confocal scanning microscopy. For each condition, a randomly selected area of $2500\ \mu\text{m} \times 2500\ \mu\text{m}$ was analyzed, as shown in Figure 3. At the early stage (72 h), numerous dispersed pits were initiated on both steels. With increasing exposure to 168 h, the pits began to grow and coalesce. At 168 h, the pits on the LCN steel increased markedly in both maximum depth and diameter, indicating

pronounced localized corrosion. In contrast, the pits on the HCN steel remained relatively shallow and scattered.

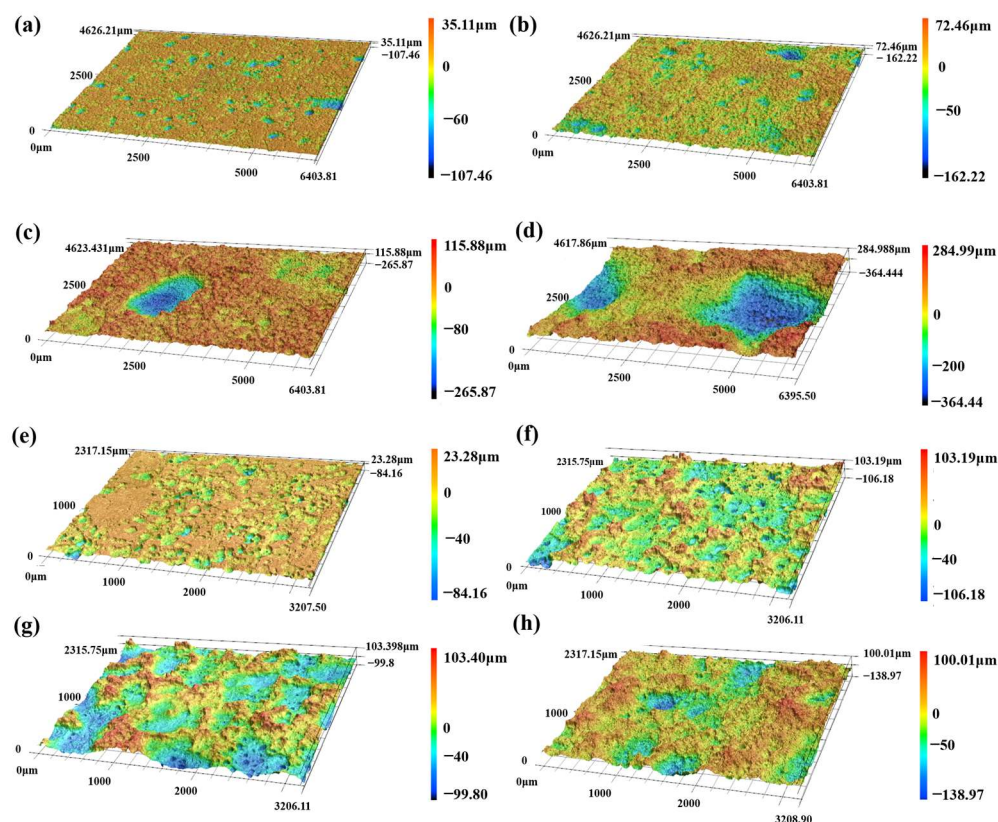


Figure 3. 3D surface morphology of LCN and HCN steel specimens after weekly immersion and subsequent rust removal. (a–d) LCN steel: 72, 168, 336, and 504 h; (e–h) HCN steel: 72, 168, 336, and 504 h.

During the mid-to-late corrosion stage (336–504 h), the two steels exhibited fundamentally different corrosion morphologies. As shown in Figure 3c,d, pits on the LCN steel began to coalesce, leading to the formation of dominant wide and deep cavities. The maximum pit depth increased from 265.87 μm to 364.44 μm . In contrast, as shown in Figure 3g,h, the HCN steel at the same stage remained dominated by dispersed, shallow pits, with the maximum pit depth increasing only slightly from 99.80 μm to 138.97 μm . At 504 h, the maximum pit depth of the HCN steel was 61.8% lower than that of the LCN steel. Moreover, the corrosion morphology of the HCN steel tended to shift from localized pitting toward a more uniform attack. Overall, higher Cr–Ni contents effectively suppressed pit initiation and growth and reduced the maximum pit depth, thereby limiting pit penetration into the substrate and substantially lowering the risk of pitting-induced perforation in rebar [25,26].

To further elucidate differences in derusted surface morphology between the LCN and HCN steels, the pit morphologies of specimens retrieved after different immersion durations were statistically analyzed. The maximum depth and the equivalent horizontal Feret diameter of individual pits were used as key parameters, and the depth-to-diameter ratio (K) was introduced as a quantitative descriptor of localized corrosion severity. A smaller K value indicates that pits tend to be shallower and wider, and the corrosion morphology approaches a more uniform attack; conversely, a larger K value corresponds to deeper and narrower pits, indicating a stronger propensity for localized corrosion [27].

As shown in Figure 4a,b, the average K value of the LCN steel decreased continuously from 0.28 to 0.20 with increasing immersion duration. This trend suggests that pits on

the LCN steel evolved from relatively deep and narrow to shallow and wide, and that localized corrosion severity decreased with exposure time; correspondingly, the late-stage morphology exhibited a tendency toward a more uniform attack. In contrast, Figure 4e–h shows that the HCN steel exhibited an overall lower average K value: K increased slightly from 0.20 to 0.21 at the early stage, then decreased modestly and stabilized at 0.16. Overall, pits on the HCN steel also shifted toward shallower and wider geometries, indicating a progressive reduction in localized corrosion tendency and a morphology closer to a uniform-corrosion regime.

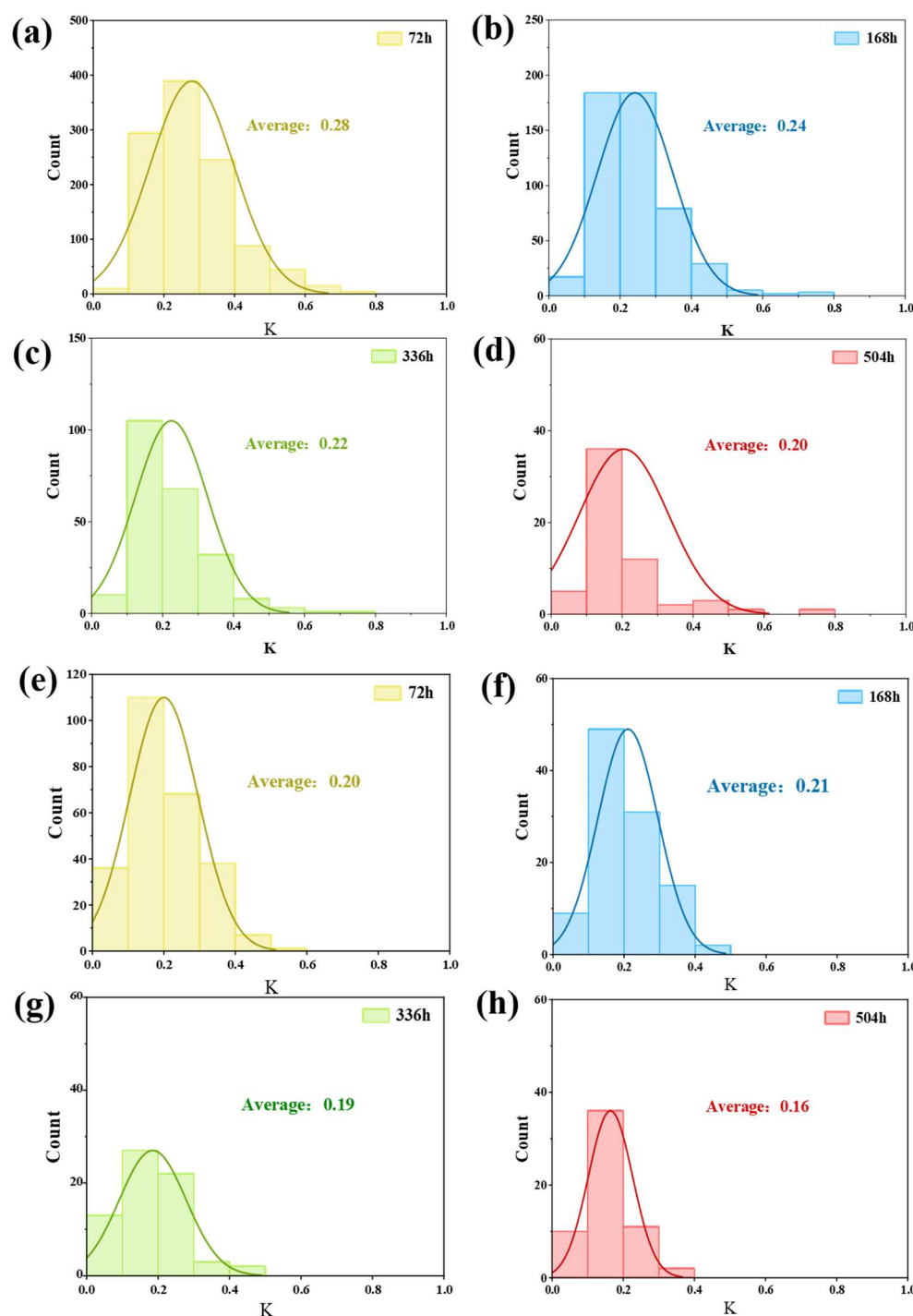


Figure 4. Statistical distributions of pit depth-to-diameter ratio (K) for derusted LCN and HCN steel specimens after cyclic immersion corrosion. (a–d) LCN steel: 72, 168, 336, and 504 h; (e–h) HCN steel: 72, 168, 336, and 504 h.

3.3. Electrochemical Analysis of the Rust Layer

3.3.1. Potentiodynamic Polarization Curves

Figure 5 presents the PDP curves of as-corroded (rust-covered) specimens for the two steels after the cyclic immersion accelerated corrosion test in a 2 wt.% NaCl solution at four exposure durations. The electrochemical parameters derived from Tafel extrapolation are summarized in Figure 5. As shown in Figure 5, the PDP curves of both steels at different exposure durations exhibited similar electrochemical features: the cathodic branch was dominated by the oxygen reduction reaction, whereas the anodic branch corresponded to active dissolution of the steel substrate. No distinct stable passive region was observed, indicating that corrosion in the chloride-containing solution was governed primarily by active dissolution for both steels. These results suggest that the addition of Cr and Ni did not alter the fundamental corrosion reaction pathway of the steels in the chloride-bearing environment.

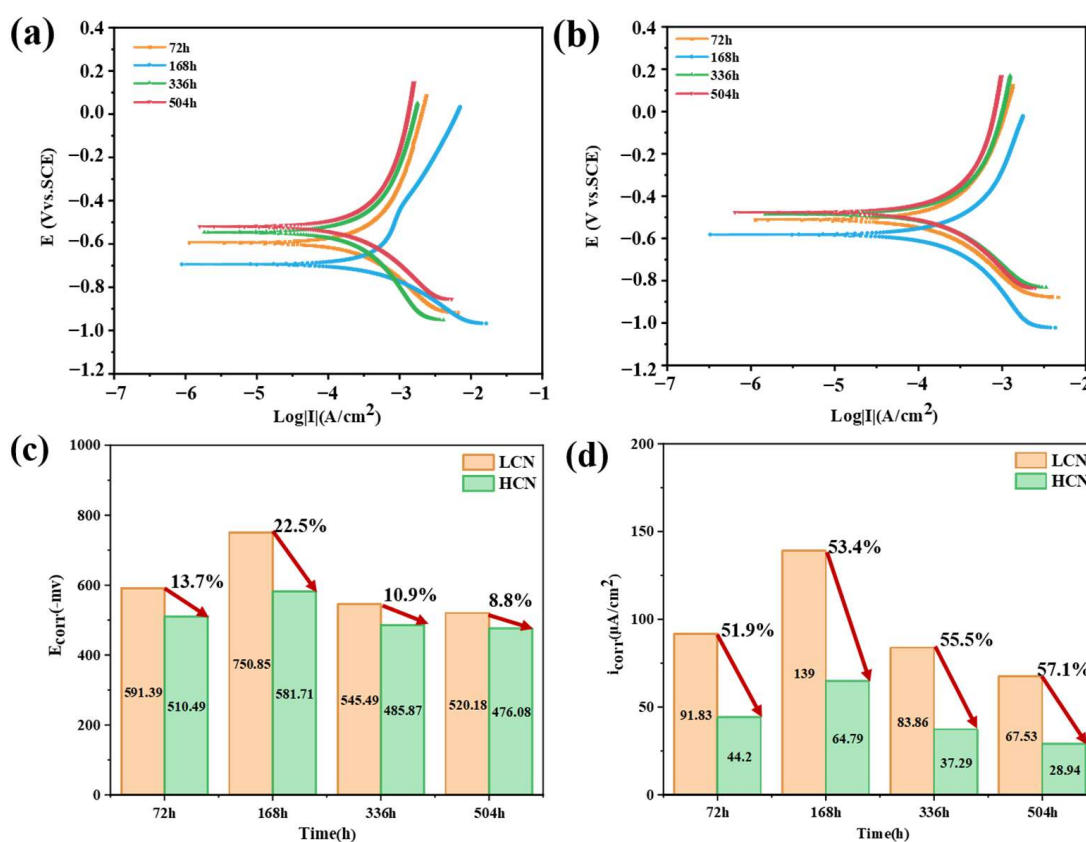


Figure 5. Potentiodynamic polarization curves and Tafel fitting results of the two tested steels in a 2 wt.% NaCl solution. (a) LCN steel; (b) HCN steel; (c) E_{corr} ; (d) i_{corr} .

At the early stage, both the LCN and HCN steels exhibited a similar trend: relative to 72 h, the PDP curves at 168 h shifted overall toward the lower-right, accompanied by a more negative E_{corr} and an increased i_{corr} . With continued exposure, the PDP curves of both steels gradually shifted leftward, i.e., E_{corr} shifted in the noble direction and i_{corr} decreased. Specifically, for the LCN steel, E_{corr} shifted from -750.85 to -520.18 mV, while i_{corr} decreased from 139.0 to 67.53 $\mu\text{A}/\text{cm}^2$; for the HCN steel, E_{corr} shifted from -581.71 to -476.08 mV, and i_{corr} decreased from 64.79 to 28.94 $\mu\text{A}/\text{cm}^2$.

Comparison of the electrochemical parameters of the two Cr–Ni steels across the four exposure durations revealed that the HCN steel consistently exhibited a more noble corrosion potential and a lower corrosion current density. In particular, at 504 h, the i_{corr} of the HCN steel was approximately 43% of that of the LCN steel, further indicating

that higher Cr and Ni contents effectively reduced the corrosion rate in chloride-bearing environments and enhanced corrosion resistance [28].

3.3.2. Electrochemical Impedance Spectroscopy

At the end of each immersion period, EIS was performed on the surface rust layers of the LCN and HCN steels, and the results are presented in Figure 6. In Figure 6a,a1 correspond to the Nyquist and Bode plots of the LCN steel, whereas Figure 6b,b1 correspond to those of the HCN steel. In the Nyquist plots (Figure 6a,b), the capacitive arc radii of both steels were relatively small at the early stage, indicating that a stable corrosion-product layer had not yet developed on the surface. With continued corrosion, the arc radii increased gradually, suggesting enhanced barrier (shielding) effects of the rust layer at later stages [29]. In the Bode plots (Figure 6a1,b1), the low-frequency impedance modulus $|Z|_{0.01\text{Hz}}$ generally increased with exposure time. At 504 h, $|Z|_{0.01\text{Hz}}$ reached $230 \Omega \cdot \text{cm}^2$ for the HCN steel, compared with $150 \Omega \cdot \text{cm}^2$ for the LCN steel.

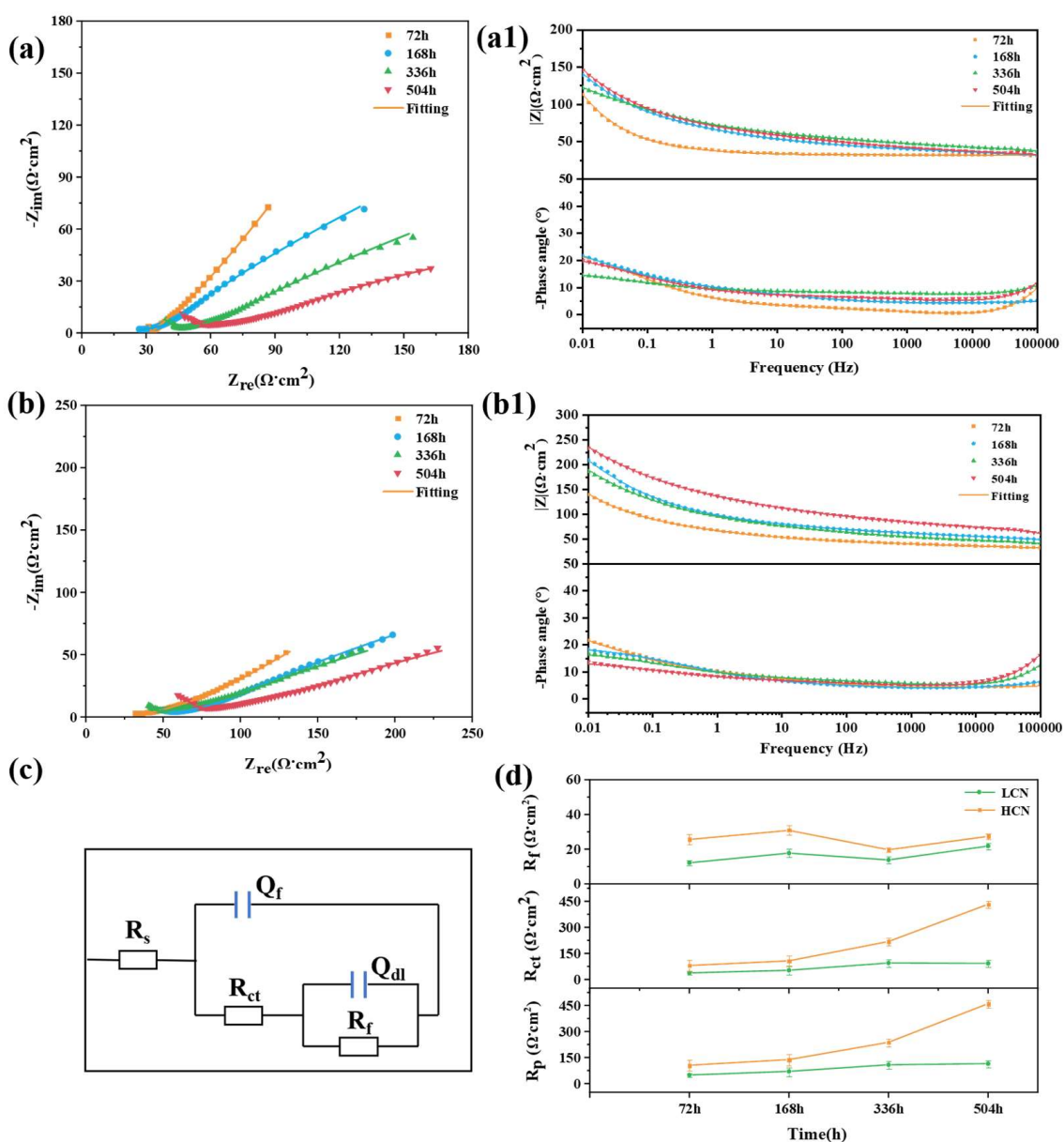


Figure 6. EIS results and fitting analysis of rusted rebar specimens of the two tested steels after cyclic immersion. (a,a1) LCN steel: Nyquist and Bode plots; (b,b1) HCN steel: Nyquist and Bode plots; (c) equivalent electrical circuit used for fitting; (d) fitted EEC parameters of the rust layer.

To comparatively assess the electrochemical processes associated with the rust layers on the Cr–Ni rebars, the impedance spectra were fitted using the equivalent circuit shown in Figure 6c. The fitting results are presented in Figure 6d and Table 2. Here, R_s denotes the solution resistance; Q_{dl} and R_{ct} represent the double-layer capacitance and charge-transfer resistance at the metal/rust-layer interface, respectively; and R_f and Q_f correspond to the rust-layer resistance and the interfacial capacitance at the rust layer/solution interface, respectively. The parameter R_{ct} is commonly employed as an indicator related to interfacial charge-transfer kinetics [30]. As shown in Figure 6d, the R_{ct} of the LCN steel increased from $37.47 \Omega \cdot \text{cm}^2$ at 72 h to $92.64 \Omega \cdot \text{cm}^2$ at 504 h. The overall magnitude remained relatively low, indicating that the rust layer provided limited protection to the substrate. With higher Cr–Ni contents, the R_{ct} of the HCN steel increased markedly: values of 80.17, 107.30, 218.30, and $432.80 \Omega \cdot \text{cm}^2$ were obtained at 72, 168, 336, and 504 h, respectively, indicating superior corrosion resistance compared with the LCN steel. In the 2 wt.% NaCl solution, R_f was relatively small; therefore, the polarization resistance R_p ($R_p = R_f + R_{ct}$) exhibited the same trend as R_{ct} . Accordingly, R_p is used as a comparative indicator of the rust-covered surface's resistance to electrochemical polarization, rather than as a direct measure of rust-layer permeability or ionic transport.

Table 2. Two Cr–Ni steels' impedance spectra fitting results.

Steel	Time h	R_s $\Omega \cdot \text{cm}^2$	R_f $\Omega \cdot \text{cm}^2$	Q_{dl}		R_{ct} $\Omega \cdot \text{cm}^2$	Q_f		R_p $\Omega \cdot \text{cm}^2$	$\chi^2 (\times 10^{-5})$
				Y0 ($\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n		Y0 ($\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n		
LCN	72	30.4	12.17	6.74	0.54	37.47	2.22	0.64	49.64	7.04
	168	27.7	17.45	4.02	0.53	52.62	1.20	0.66	70.07	2.47
	336	38.8	13.78	2.50	0.57	94.72	1.09	0.51	108.5	4.64
	504	45.7	21.79	1.11	0.61	92.64	0.92	0.55	114.43	9.51
HCN	72	32.8	25.57	1.64	0.59	80.17	1.03	0.57	105.74	4.29
	168	54.8	30.85	1.59	0.52	107.3	1.05	0.62	138.15	3.67
	336	46.6	19.66	1.57	0.47	218.3	0.90	0.60	237.96	5.39
	504	74.3	27.41	1.06	0.46	432.8	0.74	0.49	460.21	4.84

3.4. Surface and Cross-Sectional Characterization of Rust Layers

Figure 7 presents the macroscopic corrosion morphologies of the LCN and HCN steels after cyclic immersion in neutral 2 wt.% NaCl for 72, 168, 336, and 504 h. As shown in Figure 7a–h, relatively limited corrosion products were observed at 72 h for both steels, and the surfaces were mainly covered by a nearly uniform, light brown rust layer. After 168 h, corrosion products increased markedly, and the surface color gradually shifted from light brown to yellowish brown, indicating increased rust coverage and thickness. In general, α -FeOOH is brown and relatively stable, γ -FeOOH is often yellow and less stable, whereas Fe_3O_4 typically appears as a black corrosion product [31]. Accordingly, when the immersion time was extended to 336 and 504 h, darker regions gradually developed on the specimen surfaces, reflecting further evolution of the rust layer toward a denser, more compact structure. Notably, distinct differences were observed at later times. From 336 h onward, the LCN steel exhibited more localized corrosion spots and discontinuities in the rust layer, and by 504 h, more pronounced local spallation and delamination were observed, suggesting weaker rust adhesion and integrity. In contrast, although localized corrosion features also developed on the HCN steel, its rust layer remained more continuous with less spallation, and the overall macroscopic damage remained relatively limited. The comparison after rust removal further corroborates these observations. The LCN substrate retained more numerous corrosion spots and pit traces, whereas the HCN surface appeared more uniform, indicating a lower degree of substrate damage. This trend is consistent

with the detailed characterization of rust-removed macroscopic morphology discussed in Section 3.2.

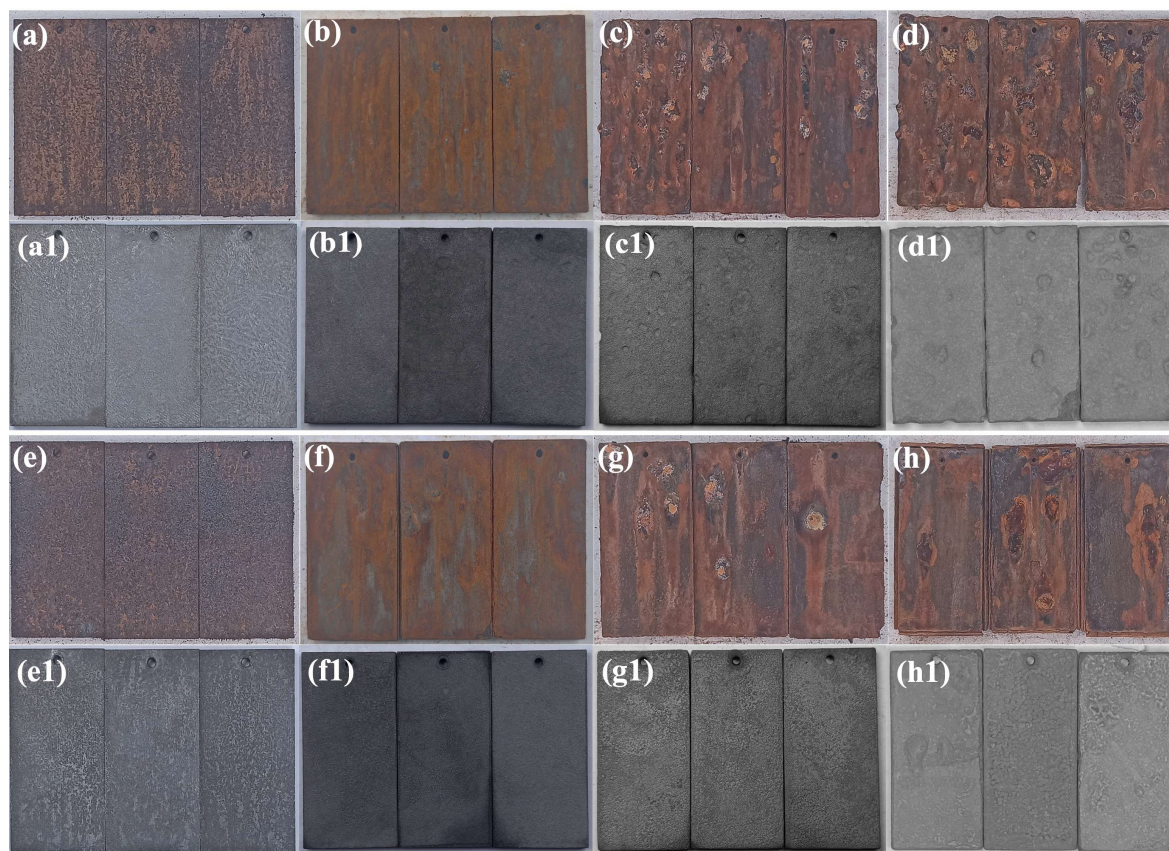


Figure 7. Macroscopic appearance of LCN and HCN steels before and after rust removal following wet-dry cyclic immersion in neutral 2 wt.% NaCl for up to 504 h. (a–d) LCN before rust removal at 72, 168, 336, and 504 h; (a1–d1) corresponding LCN after rust removal. (e–h) HCN before rust removal at 72, 168, 336, and 504 h; (e1–h1) corresponding HCN after rust removal.

Figure 8a–f show the microstructural features of the corrosion products formed on the LCN and HCN steels after the four immersion durations, respectively. Three major iron-containing corrosion products were identified: Fe_3O_4 , $\alpha\text{-FeOOH}$, and $\gamma\text{-FeOOH}$. Fe_3O_4 typically appeared as dense, dark regions or annular (“donut”-like) structures. $\alpha\text{-FeOOH}$ was characterized by needle-like (acicular) bundles and hair-/filament-like crystals, which were often aggregated in a radial or flocculent manner. $\gamma\text{-FeOOH}$ typically manifested as fine powder- or sand-like particles and stacked thin flakes/lamellae, resembling scale-like, petal-like, or layered plate-like structures [31].

As shown in Figure 8a–d, during the early stage (72–168 h), the corrosion products on the LCN steel surface were dominated by annular Fe_3O_4 and granular $\gamma\text{-FeOOH}$, and the rust layer contained abundant pores. At 336 h, needle-bundle $\alpha\text{-FeOOH}$ was first observed in localized regions. With further exposure to 504 h, although the fraction of the stable $\alpha\text{-FeOOH}$ phase increased, the overall rust layer remained rich in cracks and pores, indicating insufficient compactness.

As shown in Figure 8e,f, at 72 h the HCN steel surface already exhibited large areas of relatively compact Fe_3O_4 together with granular $\gamma\text{-FeOOH}$; however, the rust layer still showed relatively high porosity. At 168 h, pronounced radially arranged needle-bundle/feather-like clusters were observed, indicating that the stable $\alpha\text{-FeOOH}$ phase had formed abundantly at an earlier stage. With further exposure, the stable $\alpha\text{-FeOOH}$ phase increased markedly and accumulated on the surface, thereby enhancing rust-layer

compactness. At 504 h, compared with the LCN steel, fine needle-like α -FeOOH on the HCN steel formed an interwoven network that filled pores, leading to a substantial reduction in surface voids.

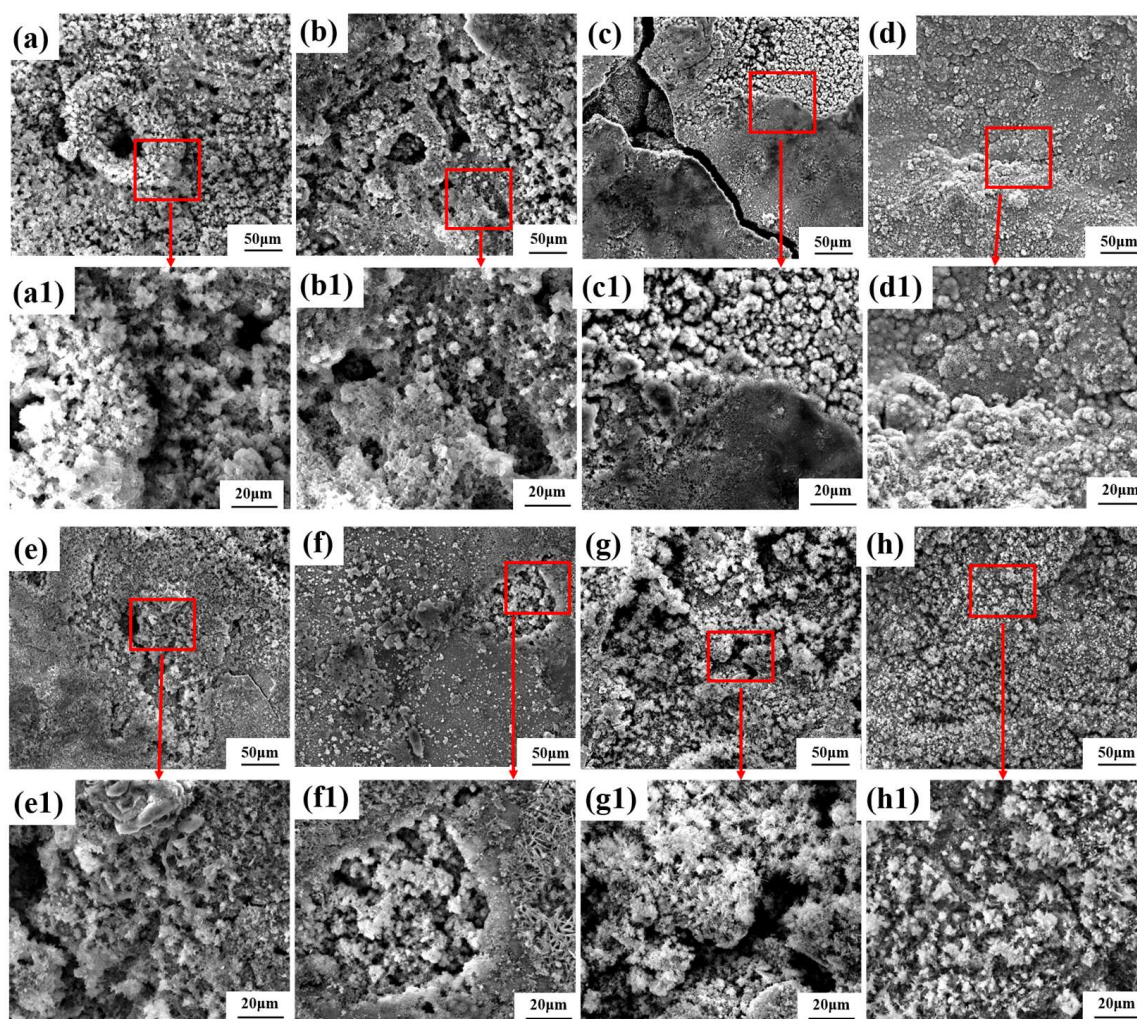


Figure 8. Micro-morphology of corrosion on LCN and HCN steels after multiple cycles. (a–d) LCN steel: 72, 168, 336, and 504 h; (e–h) HCN steel: 72, 168, 336, and 504 h. (a1–h1) Higher-magnification images of the areas marked by the red boxes in (a–h), respectively.

After four wet–dry cycles, the cross-sectional morphology and elemental distributions of the rust layers on the LCN and HCN steels were examined by SEM coupled with EDS, as shown in Figures 9 and 10. As shown in Figure 9, the rust layer on the LCN steel was mainly composed of Fe and O. During the early stage (72–168 h), repeated volumetric expansion and contraction of the rust layer during wet–dry cycling generated internal stresses, which led to interfacial gaps between the substrate and the rust layer. With further exposure, the interfacial gap disappeared and the corrosion-product layer continued to thicken, reaching $158.0 \pm 3.8 \mu\text{m}$ at 504 h; however, numerous cracks and pores remained within the rust layer. EDS mapping showed that Cl^- was widely distributed within the rust layer and tended to concentrate near cracks and pores, indicating that the porous rust layer was ineffective in blocking electrolyte ingress. Consequently, Cl^- could migrate inward along defect pathways to the steel surface and promote substrate corrosion [32].

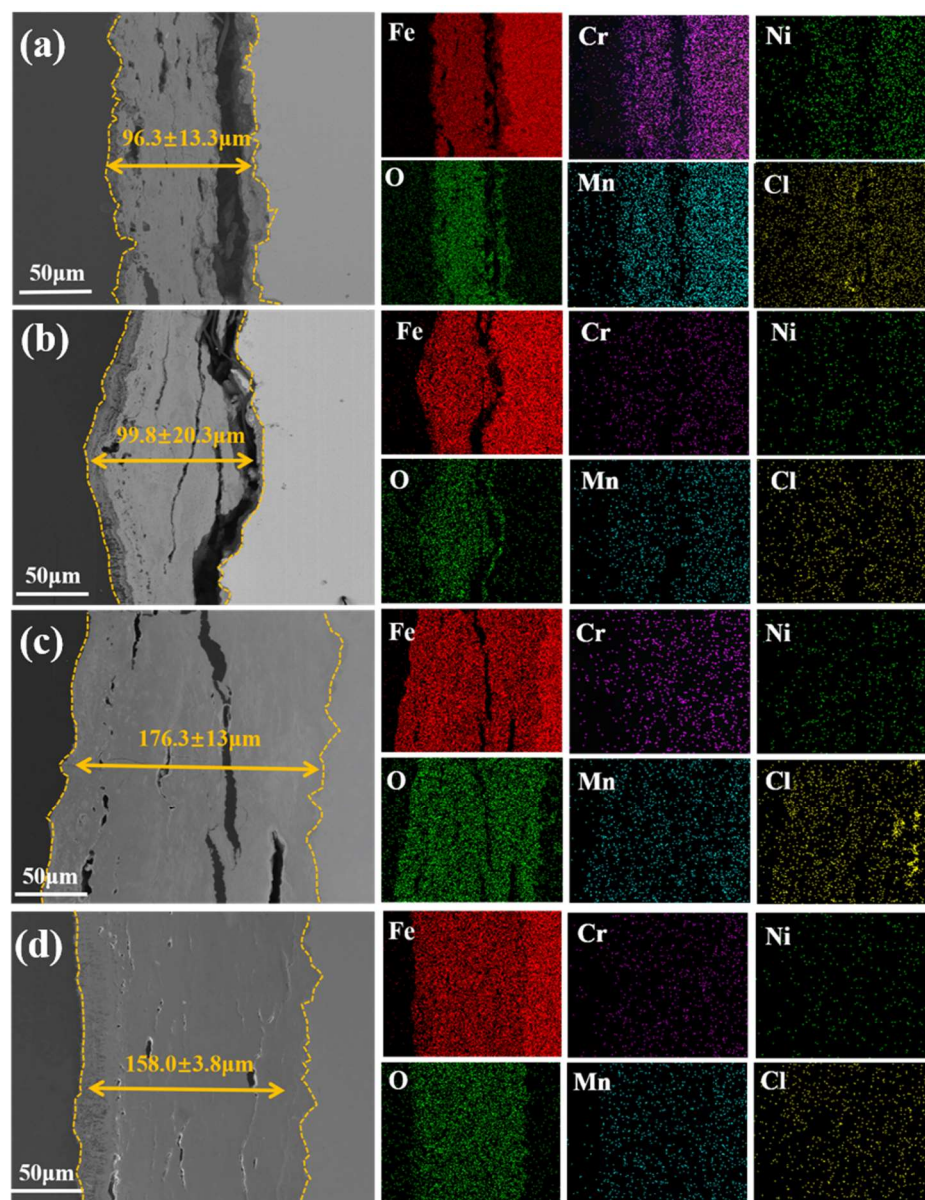


Figure 9. Cross-sectional SEM–EDS images of the rust layer on LCN steel in a chloride-containing environment: (a) 72 h, (b) 168 h, (c) 336 h, and (d) 504 h.

As shown in Figure 10, the HCN steel exhibited a superior rust-layer structure. Although the rust layer was also dominated by Fe and O, pronounced enrichment of Cr and Ni was observed in the inner rust-layer region adjacent to the substrate. This enrichment suggests that the alloying elements were actively involved in the modification and stabilization of the inner rust layer. With increasing exposure time, the corrosion-product layer on the HCN steel thickened progressively, increasing from $55.3 \pm 5.8 \mu\text{m}$ to $146.0 \pm 15.8 \mu\text{m}$. Meanwhile, the rust layer became more continuous and compact, with fewer cracks and pores than that on the LCN steel. More importantly, the presence of a dense, Cr/Ni-enriched inner rust layer effectively impeded Cl^- ingress. EDS mapping further showed that most Cl^- was confined to the outer rust layer and rarely penetrated into the Cr/Ni-enriched inner region.

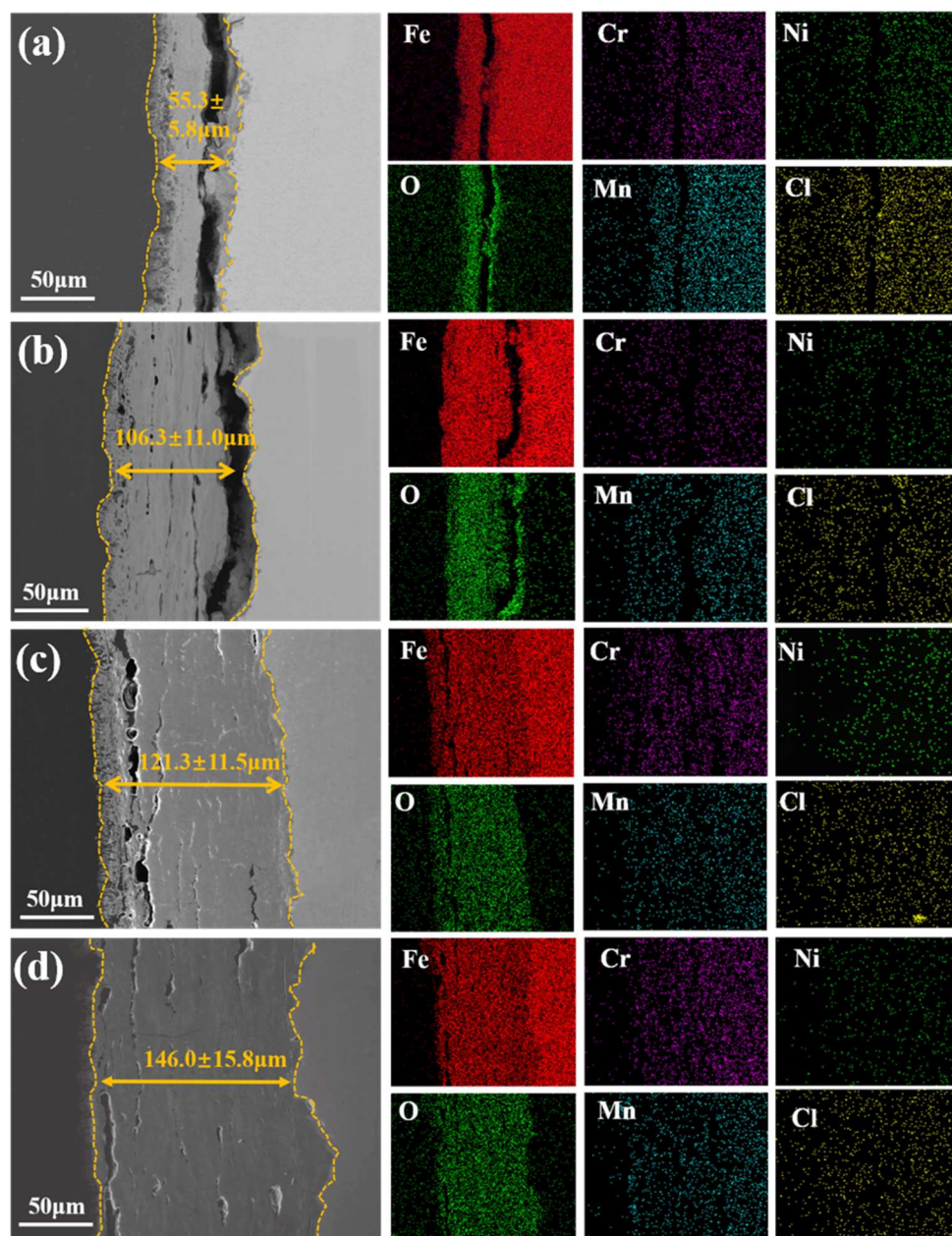


Figure 10. Cross-sectional SEM–EDS images of the rust layer on HCN steel in a chloride-containing environment: (a) 72 h, (b) 168 h, (c) 336 h, and (d) 504 h.

3.5. Phase and Chemical-State Analysis of Rust Products

XRD was employed to analyze the phase constituents of the rust layers formed on the LCN and HCN steels after different immersion durations. Figure 10a,b present the XRD patterns of the rust layers on the LCN and HCN steels at different immersion durations. For semi-quantitative comparison of rust-layer phases across the exposure durations, the relative intensities ratio (RIR) method was applied to estimate the relative fraction of each phase [33], and the results are summarized in Figure 11a1,b1. It should be noted that RIR-based phase fractions are semi-quantitative and may be affected by crystallinity, preferred orientation (texture), and particle size/microstrain effects, which can be particularly pronounced for heterogeneous and partially amorphous corrosion products. Therefore, the estimated phase fractions are used here primarily to indicate relative trends with exposure time and between steels, rather than to provide absolute quantitative phase contents.

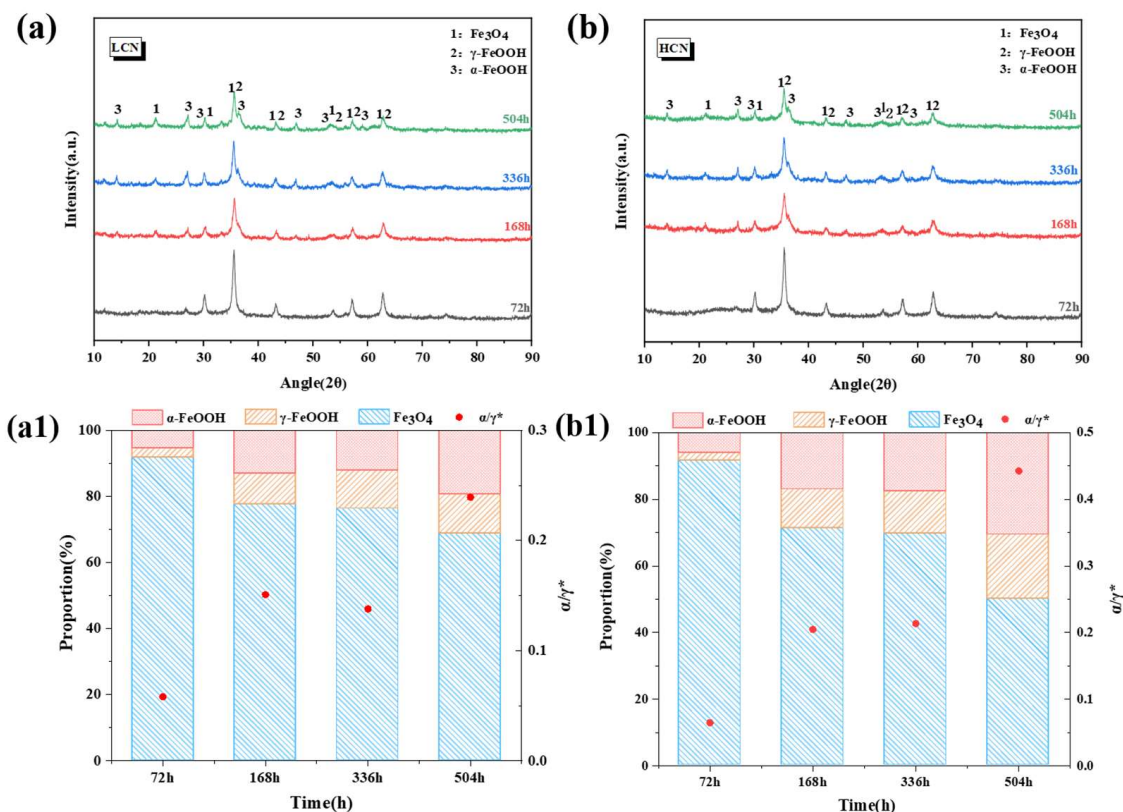


Figure 11. Phase composition of rust layers formed on Cr–Ni steels after the cyclic immersion corrosion test: (a) LCN steel, (b) HCN steel; quantitative phase fractions and α/γ^* ratios of the rust layers: (a1) LCN steel, (b1) HCN steel.

As shown in Figure 11a,b, the rust layers formed on both steels at all exposure durations contained the same phases, namely Fe₃O₄, γ-FeOOH, and α-FeOOH. This observation indicates that Cr–Ni alloying did not fundamentally alter the phase assemblage of the corrosion products; however, as corrosion progressed, the characteristic peaks exhibited marked differences in intensity and breadth, suggesting that the relative fractions of the individual phases were modified. The physicochemical properties of these phases govern the eventual protectiveness of the rust layer. According to thermodynamic considerations of corrosion products, γ-FeOOH, which is often an early-formed rust constituent, is thermodynamically metastable and highly reactive, with a relatively loose and porous structure; therefore, it is unfavorable for the development of a stable, protective rust layer [34]. Although Fe₃O₄ is structurally denser than γ-FeOOH, it exhibits relatively high electrical conductivity and can be readily reduced [35]. In contrast, α-FeOOH is thermodynamically stable and features a compact structure with good insulating properties, thereby enhancing rust-layer stability [36].

As shown in Figure 11a1,b1, the relative phase fractions changed markedly with exposure time. At 72 h, the rust layers on both steels were dominated by Fe₃O₄, whereas γ-FeOOH and α-FeOOH were present at lower levels. With prolonged exposure, the fraction of Fe₃O₄ decreased, while γ-FeOOH and α-FeOOH increased progressively. At 504 h, Fe₃O₄ in the LCN steel decreased to ~70%, whereas α-FeOOH increased to approximately 20%. In the HCN steel, a larger decrease in Fe₃O₄ (to approximately 50%) and a more pronounced increase in α-FeOOH (to approximately 30%) were observed, indicating that higher Cr and Ni contents favored the formation and enrichment of the stable α-FeOOH phase.

The α/γ^* index was further introduced to assess rust-layer stability, where α denotes the fraction of α-FeOOH and γ^* is defined as the sum of the fractions of Fe₃O₄ and γ-

FeOOH [37]. With increasing immersion duration, α/γ^* increased overall for both steels, and the HCN steel maintained higher values than the LCN steel during the mid-to-late stage, with a particularly pronounced increase at 504 h. These results suggest that rust-layer protectiveness increased with corrosion progression for both steels; moreover, the higher Cr and Ni contents in the HCN steel were associated with a rust maturation trend, reflected by a reduced Fe_3O_4 contribution and an increased α -FeOOH fraction, which—together with the observed rust-layer morphology and electrochemical responses—indicates a more stable and potentially less permeable rust layer.

Because XRD is primarily used to identify Fe-containing crystalline phases and their relative fractions in the rust layer, it cannot unambiguously determine the chemical states and bonding environments of other alloying elements. To further elucidate the chemical states of Cr and Ni in the rust layer, XPS was performed for in-depth analysis. Figure 12a–c present the Fe $2p_{3/2}$, Cr $2p_{3/2}$, and Ni $2p_{3/2}$ XPS spectra of the rust layers formed on the two Cr–Ni steels after 504 h of immersion, together with the corresponding peak deconvolution results. Figure 12d summarizes the relative fractions of the fitted chemical components based on peak-area integration.

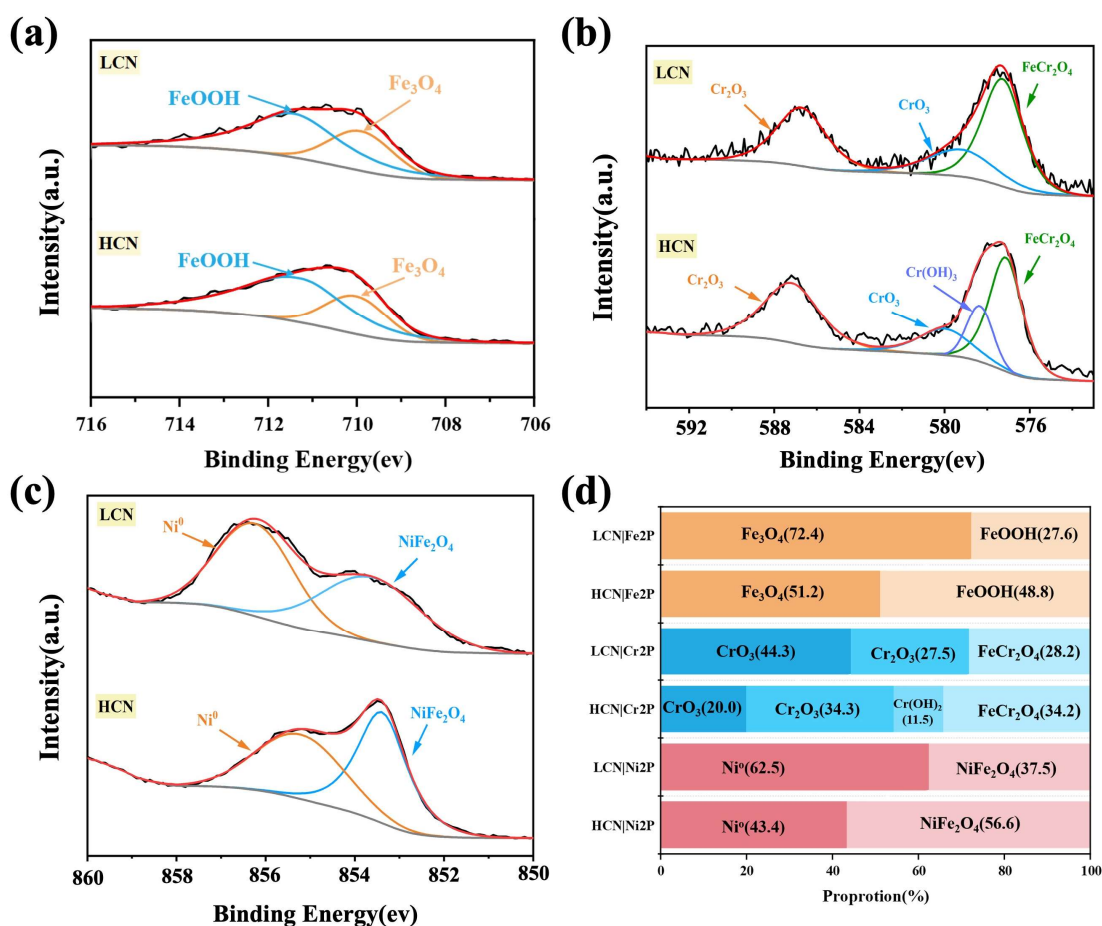


Figure 12. XPS analysis of major alloying elements in the rust layer of Cr–Ni rebar after 504 h of accelerated cyclic wet–dry immersion: (a) Fe $2p_{3/2}$, (b) Cr $2p_{3/2}$, (c) Ni $2p_{3/2}$, (d) phase proportions in the rust layer.

As shown in Figure 12a, the Fe spectrum was deconvoluted into two components at 710.1 and 711.8 eV, which were assigned to Fe_3O_4 and FeOOH, respectively. Semi-quantitative analysis indicated that Fe_3O_4 and FeOOH accounted for 72.4% and 27.6% in the LCN rust layer, whereas in the HCN rust layer Fe_3O_4 decreased to 51.2% and FeOOH increased to 48.8%. This shift suggests that Cr–Ni co-alloying promoted FeOOH forma-

tion/enrichment, consistent with the XRD results. As shown in Figure 12b, Cr species in the LCN rust layer were identified as FeCr_2O_4 (576.4 eV), CrO_3 (578.2 eV), and Cr_2O_3 (587.4 eV), with relative fractions of 28.2%, 44.3%, and 27.5%, respectively. For the HCN steel, the overall Cr signal intensity was markedly higher, and an additional $\text{Cr}(\text{OH})_3$ component at 577.3 eV was detected. The fractions of FeCr_2O_4 , Cr_2O_3 , and $\text{Cr}(\text{OH})_3$ increased to 34.2%, 34.3%, and 11.5%, respectively, whereas CrO_3 decreased to 20.0%. These results indicate that the rust layer on the HCN steel was more compositionally complex and enriched in Cr-bearing species associated with improved corrosion resistance. Previous studies have indicated that the protectiveness of corrosion-product films is closely related to the fraction of Cr-bearing compounds; FeCr_2O_4 , Cr_2O_3 , and $\text{Cr}(\text{OH})_3$ are generally considered beneficial, whereas CrO_3 is relatively unstable and is typically less effective in enhancing corrosion resistance [38]. As shown in Figure 12c, Ni species were resolved into metallic Ni (852.7 eV) and NiFe_2O_4 (855.4 eV). In the LCN rust layer, Ni^0 and NiFe_2O_4 accounted for 62.5% and 37.5%, respectively, whereas in the HCN rust layer Ni^0 decreased to 43.4% and NiFe_2O_4 increased to 56.6%. The higher Ni content in the HCN steel was accompanied by an increased fraction of NiFe_2O_4 , indicating that Ni promoted the formation of additional spinel-type mixed oxides. Together with Cr-bearing corrosion products, these oxides contributed to a denser and more continuous rust layer, thereby providing structural and chemical-state evidence for enhanced rust-layer protectiveness and stability.

To further elucidate the roles of Cr and Ni in the rust layer, the E–pH (Pourbaix) diagram of the Fe–Cr–Ni– H_2O system was constructed at 298.15 K. As shown in Figure 13, the yellow region indicates the E–pH window corresponding to the test solution used in this study. The thermodynamically stable Cr species were dominated by sparingly soluble Cr^{3+} -bearing solid phases, indicating a tendency to form Cr_2O_3 and spinel-type mixed oxides such as FeCr_2O_4 . In this system, Ni was predicted to interact with Fe, thereby favoring the formation of the spinel phase NiFe_2O_4 .

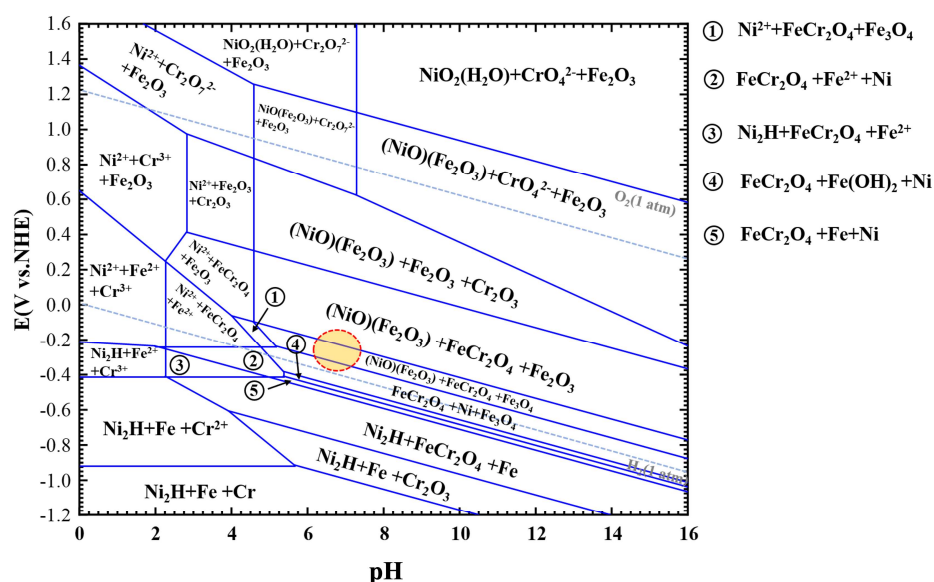


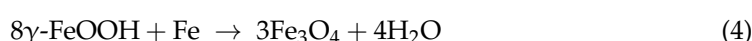
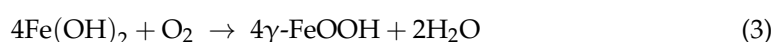
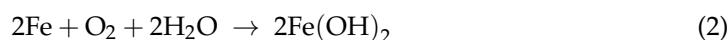
Figure 13. E–pH diagram for the Fe–Cr–Ni– H_2O system.

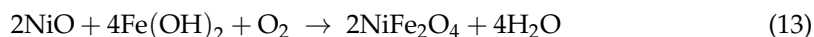
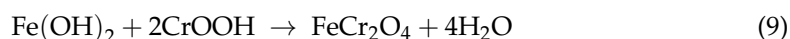
4. Discussion

Based on the results in Sections 3.1–3.5, the HCN steel consistently exhibited lower mass loss and lower corrosion rates than the LCN steel during cyclic exposure in 2 wt.% NaCl, indicating improved corrosion resistance under the present test conditions. It should be emphasized that the two steels differ not only in Cr/Ni contents but also in microstructure; therefore, the respective contributions of alloying chemistry and microstructure

cannot be fully decoupled within this two-material comparison. For the LCN steel, a ferrite–pearlite microstructure was observed. In such a microstructure, cementite (Fe_3C) can form micro-galvanic couples with ferrite, which may accelerate early selective dissolution and facilitate corrosion initiation [39,40]. In contrast, the HCN steel showed a refined and more homogeneous bainitic microstructure, which is expected to reduce micro-galvanic heterogeneity and may weaken the initial driving force for localized attack. This microstructural difference could therefore contribute to the reduced early-stage corrosion tendency of HCN. In parallel, multiple observations support a composition-related improvement associated with Cr–Ni co-alloying and rust-layer evolution. Macroscopically, the more pronounced late-stage decrease in corrosion rate for HCN is consistent with a two-stage process involving an initially porous rust layer followed by development of a denser inner layer at longer times [41]. Electrochemical results align with this trend: at 504 h, i_{corr} of HCN was ~43% of that of LCN, while $|Z|_{0.01\text{Hz}}$ and R_{ct} were higher, implying slower interfacial kinetics and hindered ionic transport. Morphological observations further indicate less severe pit coalescence and reduced pit growth in depth for HCN, consistent with mitigated localized penetration. Regarding rust characteristics, LCN presented more pores/cracks and delayed α -FeOOH formation, whereas abundant needle-like α -FeOOH appeared as early as 168 h on HCN and was associated with pore filling and a more compact barrier-like morphology [42,43], consistent with Cl^- being mainly retained in the outer rust layer. XRD/XPS also indicate a higher α -FeOOH fraction and enrichment of FeCr_2O_4 and NiFe_2O_4 in HCN, which is consistent with enhanced rust stability/compactness and provides a plausible explanation for the lower corrosion rate and reduced pitting tendency under chloride exposure.

Under weekly immersion in 2 wt.% NaCl, the steel substrate underwent anodic dissolution to release Fe^{2+} , which hydrolyzed to form $\text{Fe}(\text{OH})_2$ and was subsequently oxidized to γ -FeOOH [44,45]. Owing to its high electrochemical activity, γ -FeOOH can participate in cathodic processes and promote the formation of Fe_3O_4 , while a fraction of γ -FeOOH is transformed into the thermodynamically more stable α -FeOOH [46] (Equations (2)–(5)). After anodic dissolution, Cr was converted to $\text{Cr}(\text{OH})_3$ and dehydrated to Cr_2O_3 ; meanwhile, Cr-containing products reacted in the solid state with iron oxides to form the stable spinel phase FeCr_2O_4 (Equations (6)–(9)). In this way, Cr oxides provided a physical barrier, and Cr^{3+} , with an ionic radius similar to that of Fe^{3+} , occupied octahedral sites in the spinel lattice to form a Cr-doped structure, thereby enhancing rust layer stability and suppressing unfavorable phase transformations [47]. Ni formed $\text{Ni}(\text{OH})_2$ and NiO and subsequently reacted with iron oxides to produce the spinel phase NiFe_2O_4 (Equations (10)–(13)) [48]. This process can reduce the number of active sites by partially substituting for Fe^{2+} . Moreover, nanoscale NiFe_2O_4 can act as heterogeneous nucleation sites that promote nucleation of $\text{Fe}(\text{O},\text{OH})_6$ structural units, refine the corrosion products, and accelerate the transformation of γ -FeOOH to α -FeOOH [49–51], thereby healing pores and cracks in the rust layer and blocking Cl^- diffusion pathways.





Based on a multidimensional analysis of the experimental results and the mechanisms by which Cr and Ni alloying enhances corrosion resistance, schematic corrosion mechanisms for the LCN and HCN steels in chloride-containing environments were constructed (Figure 14). The schematics contrast the distinct corrosion behaviors of the two steels and illustrate that Cl^- ingress was impeded by improved rust layer compactness and stability. In Figure 14a, the LCN steel, owing to its lower Cr and Ni contents, was unable to form a sufficient amount of the stable $\alpha\text{-FeOOH}$ phase. Under Cl^- attack and wet–dry cycling, the rust layer readily developed through thickness cracks and pores that served as rapid transport pathways for Cl^- to reach the substrate interface, thereby causing localized acidification and accelerating anodic dissolution. As a consequence, rust layer protectiveness was markedly reduced, allowing local Cl^- accumulation and the formation of deep, wide pits. In contrast, in Figure 14b the HCN steel, with higher Cr and Ni contents, formed abundant spinel phases FeCr_2O_4 and NiFe_2O_4 , which further densified the rust layer. FeCr_2O_4 enhanced rust layer stability and filled residual pores, whereas NiFe_2O_4 acted as a heterogeneous nucleation site that promoted rapid transformation of $\gamma\text{-FeOOH}$ to $\alpha\text{-FeOOH}$, thereby increasing the $\alpha\text{-FeOOH}$ fraction. The synergistic effects of chemical modification and densification effectively blocked Cl^- transport pathways, suppressing pit initiation and growth and shifting the corrosion morphology from localized pitting toward a more uniform attack, thereby yielding a substantial improvement in corrosion resistance.

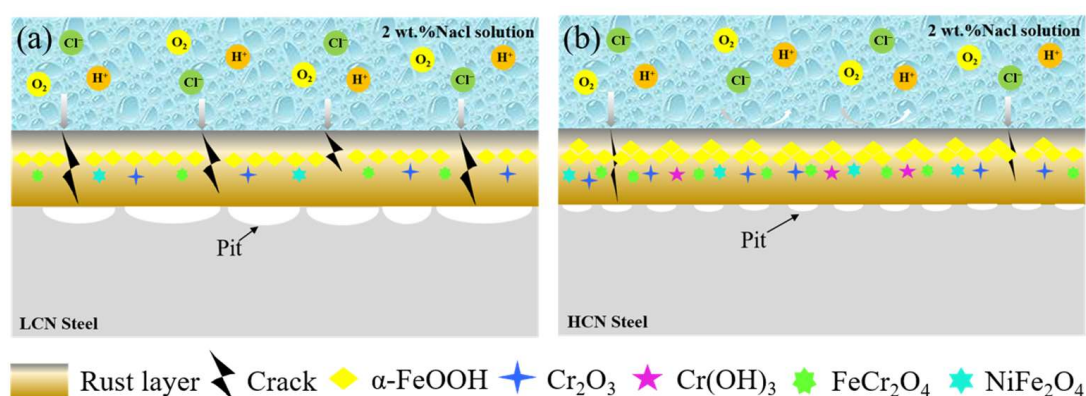


Figure 14. Schematic diagram of corrosion mechanism: (a) LCN steel, (b) HCN steel.

5. Conclusions

Using wet–dry cyclic immersion accelerated corrosion tests, this study systematically elucidated the mechanisms by which combined Cr and Ni additions affect the corrosion behavior and rust-layer evolution of HRB500 rebar in a chloride-containing marine atmospheric environment. The main conclusions are summarized as follows.

1. Increasing Cr and Ni contents increased hardenability and refined the matrix from a ferrite–pearlite structure to a more homogeneous bainitic microstructure; as a result,

microgalvanic heterogeneity was reduced, contributing to lower corrosion susceptibility under the present test conditions.

2. Both gravimetric measurements and electrochemical parameters indicated a two-stage corrosion process, characterized by early acceleration followed by a late-stage decline. Compared with LCN, HCN exhibited lower mass loss and a lower average corrosion rate, and PDP measurements yielded a lower i_{corr} (28.94 vs. 67.53 $\mu\text{A}\cdot\text{cm}^{-2}$ at 504 h).
3. Cr–Ni co-alloying was found to markedly mitigate localized corrosion. At 504 h, HCN reduced the maximum pit depth by approximately 61.8% and shifted the corrosion morphology from deep pitting toward a more uniform attack.
4. Rust-layer analyses show that higher Cr and Ni promote earlier, enriched α -FeOOH formation and a compact Cr/Ni-enriched inner layer containing spinels (FeCr_2O_4 , NiFe_2O_4). These features limit chloride ingress and reduce interfacial charge transfer, enhancing rust-layer protectiveness.

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