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Atmospheric Corrosion Kinetics and QPQ Coating Failure of 30CrMnSiA Steel Under a Deposited Salt Film

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Abstract

Atmospheric corrosion in sand dust environments is driven by deposits that bear chloride, which sustain thin electrolyte layers on metal surfaces. We established a laboratory protocol to replicate this by extracting, formulating, and depositing a preliminary layer of mixed salts from natural dust onto samples, with humidity precisely set using the salt's deliquescence behavior. Degradation was tracked with SEM/EDS, 3D profilometry, XRD, and electrochemical analysis. Bare steel showed progressive yet decelerating attack as rust evolved from discrete islands to a lamellar network; while this densification limited transport, its internal cracks and interfacial gaps trapped chlorides, sustaining activity beneath the rust. In contrast, QPQ-treated steel remained largely protected, with damage localized at coating defects as raised rust nodules, while intact regions maintained low electrochemical activity. By coupling salt chemistries derived from the field with humidity control guided by deliquescence and diagnostics across multiple scales, this study provides a reproducible laboratory pathway to predict atmospheric corrosion.



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Keywords: atmospheric corrosion; deposited salts; 30CrMnSi; QPQ-treated steel

1. Introduction

30CrMnSiA is a representative medium carbon Cr–Mn–Si high strength steel. Owing to its combination of high strength, good hardenability, and fatigue resistance, it is widely used in critical components subjected to alternating loads, including aircraft landing gear, gears, fasteners, and most notably, large rolling bearings (rings, journals, raceways) [1–3]. These components frequently operate in coastal or otherwise corrosive atmospheric environments. When airborne salt deposits on their surfaces, condensation readily occurs and a thin electrolyte film can persist on the raceway, initiating atmospheric corrosion [4–7]. Prior studies show that quenched-and-tempered medium carbon steels exposed to thin electrolyte films develop rust layers dominated by goethite and lepidocrocite; the compactness of these layers is governed by alloying element distribution and the prevailing stress/load state [8–11]. In addition, under rolling contact or fretting, repeated cycles of corrosion product spallation/re-deposition can accelerate pit growth and surface spalling, consistent with observations and mechanisms summarized for oscillating rolling bearings and grease-lubricated contacts [12–16].

To enhance surface protection, the quench–polish–quench (QPQ) salt bath nitrocarburizing route (magnetite film + ϵ/γ' compound layer + diffusion zone) is commonly applied to shafts and bearing rings; however, the long-term benefit is highly sensitive to layer continuity/defects that may form occluded cells for Cl^- accumulation [17,18]. Tribocorrosion data further indicate that, while hard nitride layers chiefly resist wear, localized electrochemical breakdown at defects can still occur and couple with fatigue degradation [19–21].

Most studies on the corrosion resistance of 30CrMnSiA and its surface-modified layers rely on short-term immersion, conventional salt spray, or cyclic accelerated tests. Although expedient for rapid screening, these methods seldom regulate salt deposition load, electrolyte-film thickness, or constant humidity, and therefore do not faithfully reproduce the long-duration moisture/thin-electrolyte regime typical of bearing service [22–25]. The literature also tends to examine corrosion from a single vantage point (mass loss, electrochemistry, or morphology) rather than within an integrated framework that links macroscopic kinetics with microstructural evolution, phase transformation, and electrochemical response [26–29]. Closing these gaps is essential for optimizing QPQ processing and enabling predictive maintenance of bearing components operating in a sand dust environment.

Accordingly, this study quantitatively characterizes the corrosion kinetics of bare and QPQ-treated specimens under deposited salt-film conditions, elucidates the time-dependent evolution of rust/coating morphology and phase composition, correlates electrochemical parameters with the protective effectiveness of rust/coating layers to clarify shifts in rate-controlling steps, and provides practical guidance for surface-engineering optimization and service maintenance of critical bearing components.

2. Materials and Methods

In this work, commercial 30CrMnSiA steel (chemical composition in Table 1) was machined into rectangular coupons ($100 \times 50 \times 2$ mm). Two surface conditions were investigated: (i) bare steel, and (ii) QPQ-treated steel: it was performed by salt bath nitrocarburizing at 570 °C for 90 min in an alkali cyanate melt, followed by quenching in an oxidizing nitrate/nitrite salt at 420 °C for 20 min to form Fe_3O_4 , light polishing to remove approximately 2 to 5 μm , a second oxidizing quench at 420 °C for 20 min, and final sealing in hot oil at 120 °C for 30 min. In addition, we determined the nitrided layer depth by Vickers microhardness (HV0.1) along a line normal to the surface following GB/T 11354-2005 [30] (ISO 18203 [31]). The base hardness is ~ 340 HV0.1. Using the standard criterion of base + 50 HV (≈ 390 HV0.1), the case depth is ~ 0.17 mm. Additionally, cross-section SEM EDS mapping and line profiles indicate a compound layer thickness of approximately 7 μm for the QPQ-treated surface.

Table 1. Chemical composition of 30CrMnSiA steel.

Element	C	Si	Mn	Cr	Ni	P	S	Fe
Composition(wt.%)	0.32	0.95	0.98	1.00	0.20	≤ 0.04	≤ 0.04	Bal.

The indoor accelerated corrosion exposure used in this study was a constant temperature–humidity (isothermal–isohumidity) protocol with pre-deposited salts. The salt mixture was extracted from sand and dust collected in western China. The ion composition and concentration are shown in Table 2, and the bulk pH was 4.5. The deposit was prepared in three steps—dissolving the constituent salts, adjusting the solution pH to 4.5, and freeze-drying—followed by dry-powder spraying onto the specimens to achieve a surface loading of $10 \text{ g}\cdot\text{m}^{-2}$ ($1.0 \text{ mg}\cdot\text{cm}^{-2}$). Deliquescence–efflorescence characterization at 20 °C yielded a deliquescence relative humidity (DRH) of 60% and an efflorescence relative

humidity (ERH) of 52.5%. Accordingly, the accelerated tests were run at 20 °C and 75% RH, i.e., above the DRH, to ensure a continuous electrolyte layer throughout exposure. The test durations were 1, 2, and 6 months. Compared with conventional neutral salt spray and full immersion tests, our protocol reproduces deposit-driven thin-film conditions. We use salts extracted from field dust, deposit a known mass per unit area, and set the relative humidity at the deliquescence or efflorescence point of the mixture. These steps maintain a micrometer scale moisture film on the surface and avoid artifacts caused by rinsing, which allows a direct link between deposit composition, humidity, and damage.

Table 2. Salt content.

ion	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
Concentration (mg·L ^{−1})	406.0	21.8	303.0	51.4
ion	Cl [−]	SO ₄ ^{2−}	SO ₃ ^{2−}	HCO ₃ [−]
Concentration (mg·L ^{−1})	386.5	518.5	195.0	295.7

Corrosion products were removed using a combined mechanical–chemical procedure in accordance with GB/T 16545-2015 [32] (ISO 8407:2009 [33]). An inhibited hydrochloric acid cleaning solution was prepared by dissolving 3.5 g hexamethylenetetramine and 500 mL HCl in 500 mL deionized water and making up to 1000 mL. After each exposure period, loose rust was gently brushed off, and specimens were immersed in the solution and ultrasonically agitated at room temperature for 10–15 min (or until visible products were fully removed). The cleaned coupons were then rinsed sequentially with deionized water and absolute ethanol, blow-dried, placed in a drying oven for 24 h, and weighed on an analytical balance (± 0.1 mg). An unexposed control (“blank”) coupon underwent the same cleaning to correct for any base-metal dissolution during pickling. For each condition, $n = 3$ parallel specimens were measured and the arithmetic mean reported.

For QPQ-treated coupons, strongly adherent products can yield an apparent mass gain after cleaning. In such cases, the mass change $\Delta m = m_{\text{before}} - m_{\text{after}}$ was recorded with sign; when thorough acid removal risked damaging the coating, only loose deposits were brushed/rinsed off, and the resulting net mass change (often a small gain) was used. The corrosion rate was calculated as

$$r = \frac{\Delta m}{A t \rho}$$

where A is the exposed area, t the exposure time, and ρ the steel density.

Overall rust coverage, blistering, and spallation after each exposure were documented by digital photography. Surface and cross-sectional morphologies of the corrosion-product layers on specimens exposed to different environments were examined by field-emission scanning electron microscopy (SEM, Merlin Compact, Carl Zeiss Microscopy GmbH, Jena, Germany) equipped with energy-dispersive X-ray spectroscopy (EDS). Cross-sections were cold-mounted in epoxy, ground sequentially to #2000 grit, polished, ultrasonically cleaned in ethanol, and sputter-coated with gold prior to observation. Surface topography—including areal roughness parameters (S_a , S_q), 2D/3D morphologies, and pit-depth distributions—was quantified using a 3D laser confocal microscope (OLS5100; Olympus Corporation, Tokyo, Japan).

Phase compositions of the corrosion products were characterized by X-ray diffraction (XRD). Measurements were performed on a Bruker D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany, Cu $K\alpha$) operating at 40 kV and 40 mA, with a 2θ range of 20–90°, step size of 0.02°, scan speed of 5°·min^{−1}, and a detector–sample distance of 280 mm. For bare steel, rust layers formed at each exposure time were carefully scraped, ground to

powders, and analyzed; for QPQ specimens, 1 cm × 1 cm coupons were sectioned and scanned directly without powdering.

Electrochemical characterization was performed at room temperature using an electrolyte cell connected to a Gamry Reference 600+ workstation (Gamry Instruments, Warminster, PA, USA) with a standard three-electrode configuration: a saturated calomel electrode (SCE) as reference, a 2 cm × 2 cm Pt plate as counter, and the corroded specimen sealed to expose 1 cm² as the working electrode. The electrolyte, designed to simulate the dominant ions in the mixed-salt deposit, consisted of 0.4 mol·L^{−1} NaCl + 0.2 mol·L^{−1} Na₂SO₄. Prior to measurements, specimens were immersed until the open-circuit potential (OCP) stabilized. Electrochemical impedance spectroscopy (EIS) was then conducted by applying a ±10 mV sinusoidal perturbation (vs. OCP) over a frequency range of 10⁵–10^{−2} Hz, and Nyquist/Bode plots were fitted with appropriate equivalent circuits to extract *R*_s, *R*_f, *R*_{ct}, and diffusion-related elements. Potentiodynamic polarization curves were subsequently recorded from −0.3 V (vs. OCP) to +0.8 V (vs. OCP) at a scan rate of 0.5 mV·s^{−1}, with *E*_{corr} and *I*_{corr} determined via Tafel extrapolation.

3. Results

3.1. Mass Change and Kinetic Trend

As shown in Figure 1a, after 1, 2, and 6 months of exposure at 20 °C and 75% RH with an initial mixed-salt loading of 10 g·m^{−2}, bare 30CrMnSiA steel exhibited cumulative mass losses of −97.49, −171.92, and −259.13 g·m^{−2}, respectively, whereas QPQ-treated specimens showed small net gains of +2.20, +3.37, and +6.29 g·m^{−2} attributable to adherent corrosion products retained on the surface. Consistent with these cumulative trends, Figure 1b shows that the instantaneous corrosion rate of bare steel decreases with exposure time, indicating decelerating kinetics associated with the progressive development of a partially protective rust layer [34].

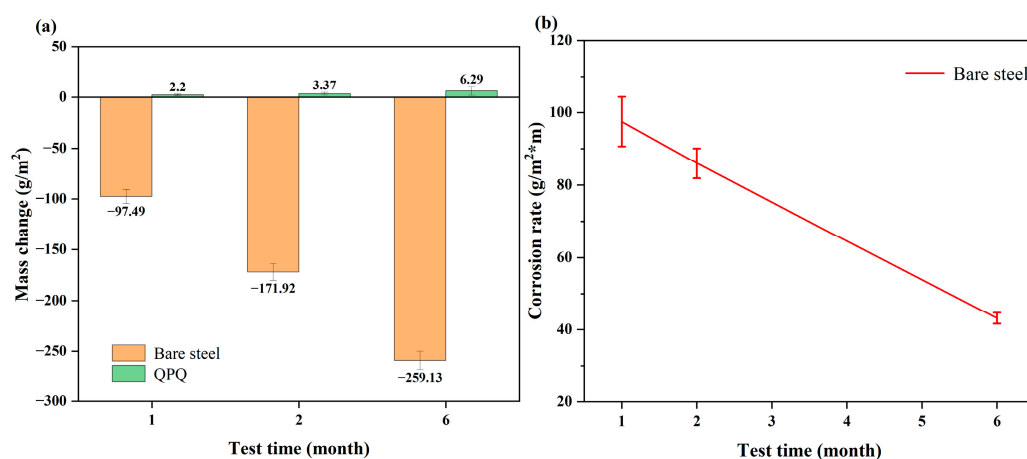


Figure 1. The mass changes in bare steel and QPQ-treated steel after 1, 2, and 6 months (a). The evolution of bare steel corrosion rate with corrosion time (b).

To quantify the kinetics, the mass-loss data for bare steel were fit to a power-law relation, $\Delta m = kt^n$. The fitted exponent was sub-unity ($n \approx 0.63$), indicating decelerating kinetics characteristic of thin-electrolyte-layer corrosion, where progressive rust densification impedes ionic transport. The high coefficient of determination ($R^2 > 0.95$) indicates that this single-stage empirical model captures the overall trend, despite local microstructural heterogeneity [35].

3.2. Macro-Scale Appearance Evolution

As shown in Figure 2, the bare steel surfaces evolved from sparse rust islands after 1 month to an almost continuous reddish-brown layer by 6 months. The color deepened and the texture coarsened, with occasional edge-adjacent spallation, related to densification of the rust. In contrast, QPQ coupons largely retained the dark-gray compound layer, and corrosion remained localized: numerous fine spots and shallow rust nodules were evident at 1 month, giving way to fewer but larger nodules by 2–6 months. This indicates that the corrosion of the QPQ-protected specimens was localized, which may be related to the pre-existing weak points in the QPQ layer. These qualitative observations accord with Figure 1—progressive mass loss on bare steel versus small net mass gains on QPQ due to adherent, rust nodules retained products—indicating uniform rust growth for the former and defect-controlled, localized attack for the latter.

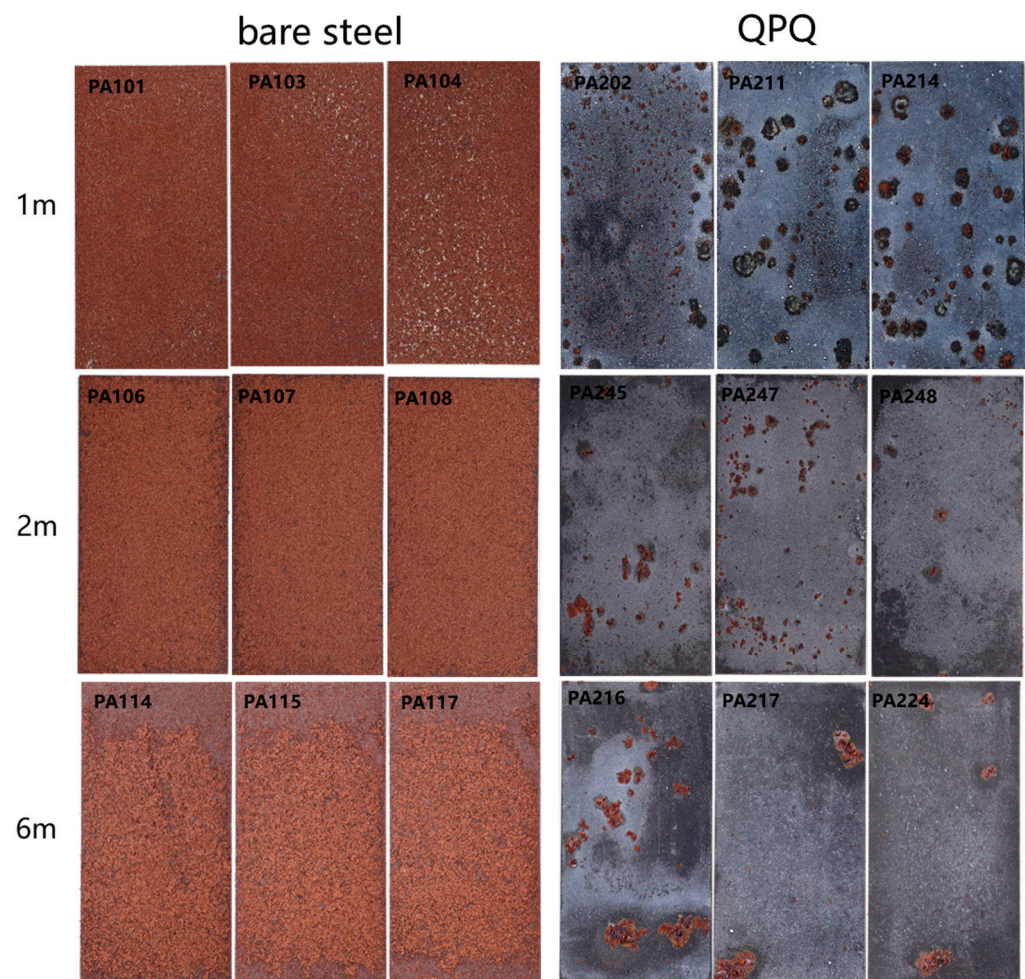


Figure 2. The macro-scale appearance evolution of bare steel and QPQ-treated steel after 1, 2, and 6 months.

3.3. Micro-Morphology (SEM/EDS) and 3D Profilometry

As shown in Figure 3, the rust on bare steel evolves from porous, defect-anchored features to a more compact lamellar network with time. After 1 month (a1–a3), the surface exhibits rust nodule domes and cauliflower-type granules embedded in a highly porous matrix, intersected by long cracks. By 2 months (b1–b3), interwoven lamellar/needle-like crystallites spread between nodular colonies and begin to bridge adjacent areas, although shrinkage cracks persist at colony edges. After 6 months (c1–c3), these lamellae thicken and interlock into a more continuous crust, yet fissures remain along prior boundaries,

indicating incomplete sealing of transport paths. Spot EDS at the marked sites is dominated by Fe and O, with persistent Cl and minor Si/Na/Al, evidencing chloride-bearing residues concentrated near crack rims and pit perimeters. This progression—from granular to interlocking lamellae with chloride retention in crevices—explains the decelerating yet sustained corrosion kinetics inferred from Figure 1.

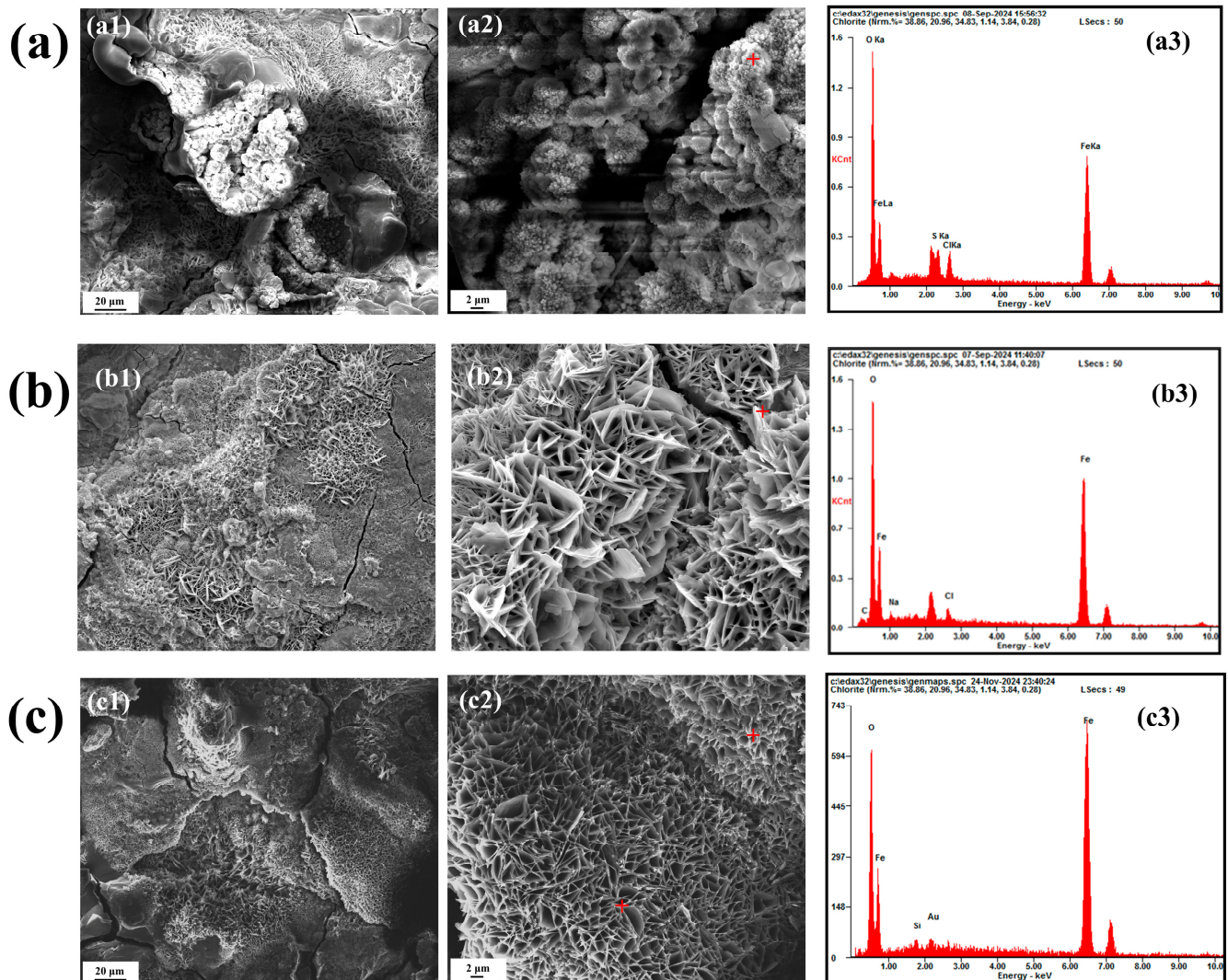


Figure 3. Microstructure and composition of corrosion products on bare steel as a function of corrosion time: (a,a1–a3) 1 month, (b,b1–b3) 2 months, (c,c1–c3) 6 months. Columns 1 and 2 show low- and high-magnification SEM images (scale bars 20 μm and 2 μm, respectively); column 3 presents the corresponding point-EDS spectra at the marked sites.

As corroborated by the macroscopic images, corrosion on the QPQ-treated steel remains localized to discrete rust nodules, while most of the dark-gray compound layer stays intact. SEM/EDS in Figure 4 shows that after 1 month (a1–a3), the products are thin lamellar/needle-like crystals anchored at scattered coating defects. By 2 months (b1–b3), these sites develop into cauliflower-like agglomerates with a porous substructure, indicating under-film growth and local lifting of the compound layer. After 6 months (c1–c3), the nodules coarsen and partially coalesce, and microcracks appear around their perimeters, but unaffected regions between nodules remain largely bare. Point-EDS is dominated by Fe and O, with persistent Cl at nodule rims and crack mouths, consistent with electrolyte entrapment at defects and defect-controlled, under-film corrosion rather than uniform rusting.

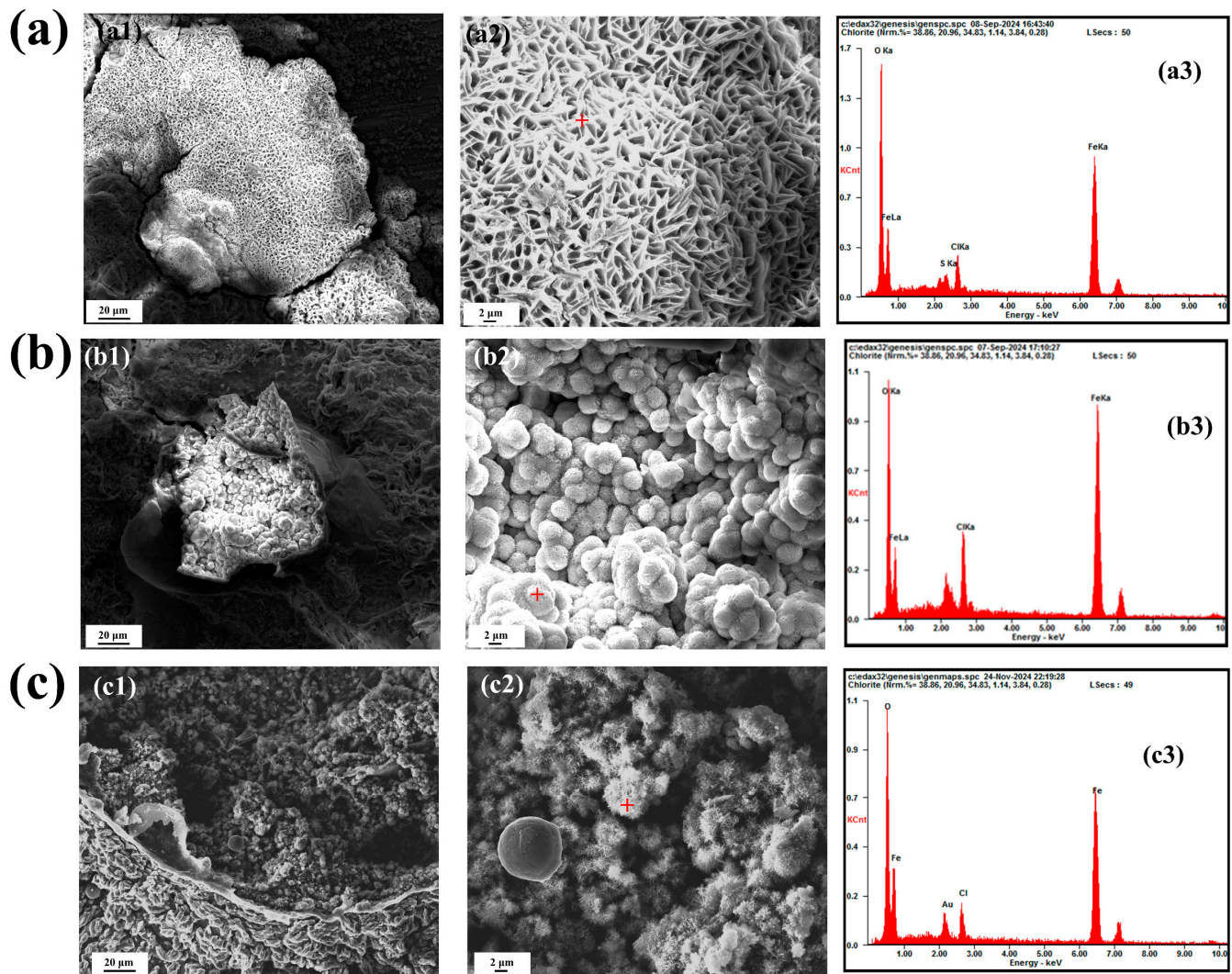


Figure 4. Microstructure and composition of corrosion products on QPQ-treated steel as a function of corrosion time: (a,a1–a3) 1 month, (b,b1–b3) 2 months, (c,c1–c3) 6 months. Columns 1 and 2 show low- and high-magnification SEM images (scale bars 20 μm and 2 μm , respectively); column 3 presents the corresponding point-EDS spectra at the marked sites.

As shown in Figure 5, optical images (a1, b1, c1) and the corresponding 3D laser confocal maps (a2, b2, c2) document a clear coarsening of the bare steel surface with exposure time. After 1 month, corrosion products form discrete nodules separated by shallow inter island valleys. By 2 months, these nodules coalesce into a more continuous carpet with a higher relief and more frequent peaks, yielding an appreciable increase in areal roughness. After 6 months, the relief remains high but appears more compact: valleys are partly infilled and peak edges are rounded, indicating densification of the rust layer. The height maps show the maximum at 2 months, suggesting that roughness (S_a , S_q) increases from 1 to 2 months and then approaches a quasi-steady level by 6 months. This topographic evolution is consistent with the SEM observations and with the decelerating mass-loss kinetics.

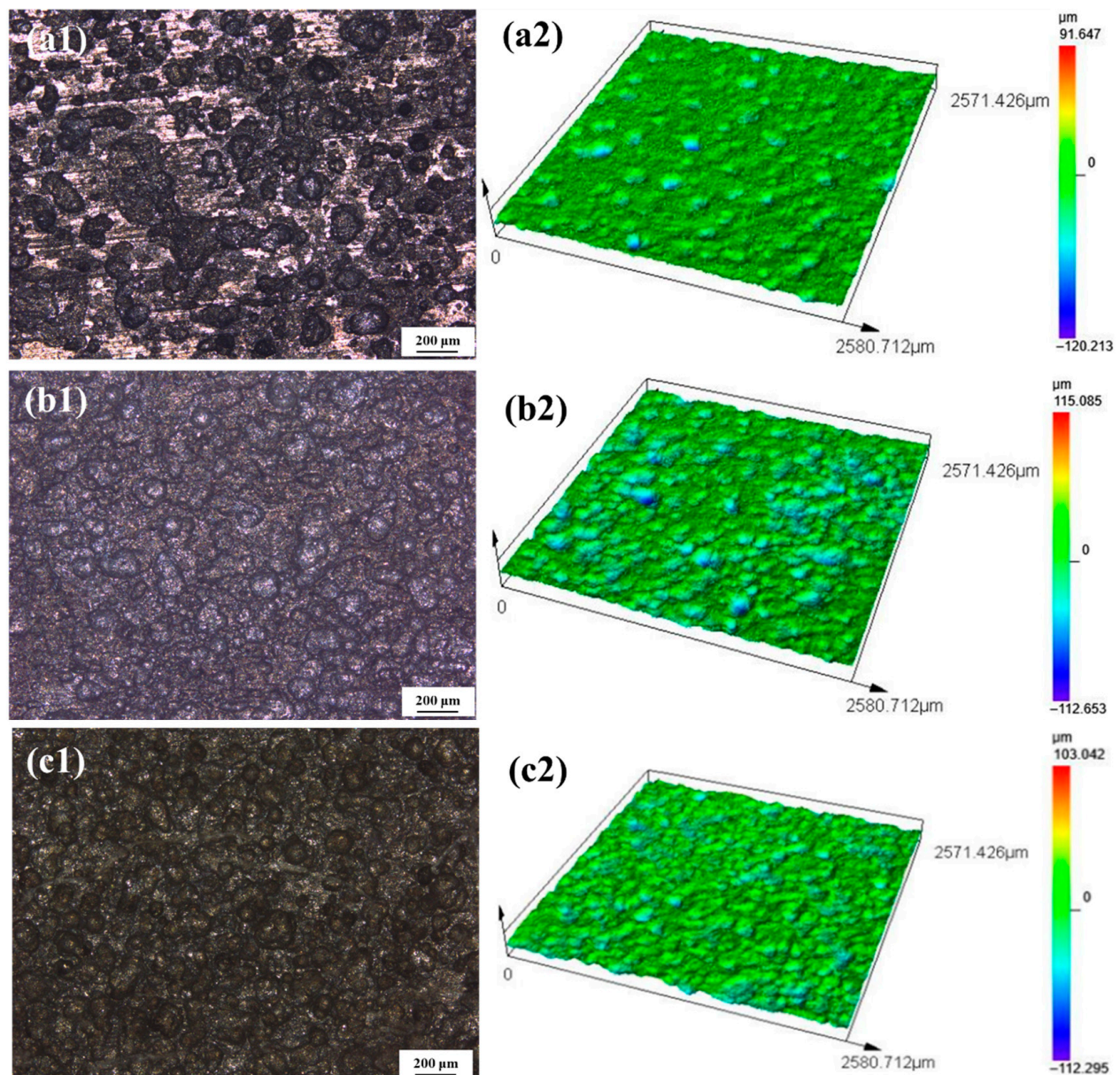


Figure 5. Three-dimensional laser surface profiling on bare steel as a function of corrosion time: (a1,a2) 1 month, (b1,b2) 2 months, (c1,c2) 6 months. Column 1 shows morphology under light microscope; column 2 presents the corresponding 3D morphology.

As shown in Figure 6, corrosion products formed and accumulated at discrete sites on the QPQ surface, whereas the surrounding matrix remained relatively smooth and dark gray. After 1 month (a1–a2), isolated rust nodules protruded with mound-shaped profiles and peak-to-valley relief of $\sim 100\text{--}300\text{ }\mu\text{m}$. By 2 months (b1–b2), these features expanded laterally and vertically, reaching the largest relief (up to $\sim 400\text{ }\mu\text{m}$) and developing uplifted rims and micro-cracked caps—morphologies consistent with under-film product buildup and osmotic/volumetric swelling. After 6 months (c1–c2), multiple nodules coexisted; some coalesced while others partially collapsed into flattened mesas bordered by annular depressions, producing a slight decrease in local relief even as the affected area increased. Overall, the areal roughness (S_a , S_q) rose only modestly compared with bare steel because attack was defect-controlled and spatially confined, whereas the local amplitude (S_z) within individual nodules remained high. Taken together, these observations indicate that corrosion on QPQ-treated steel is localized rather than a uniform material loss process.

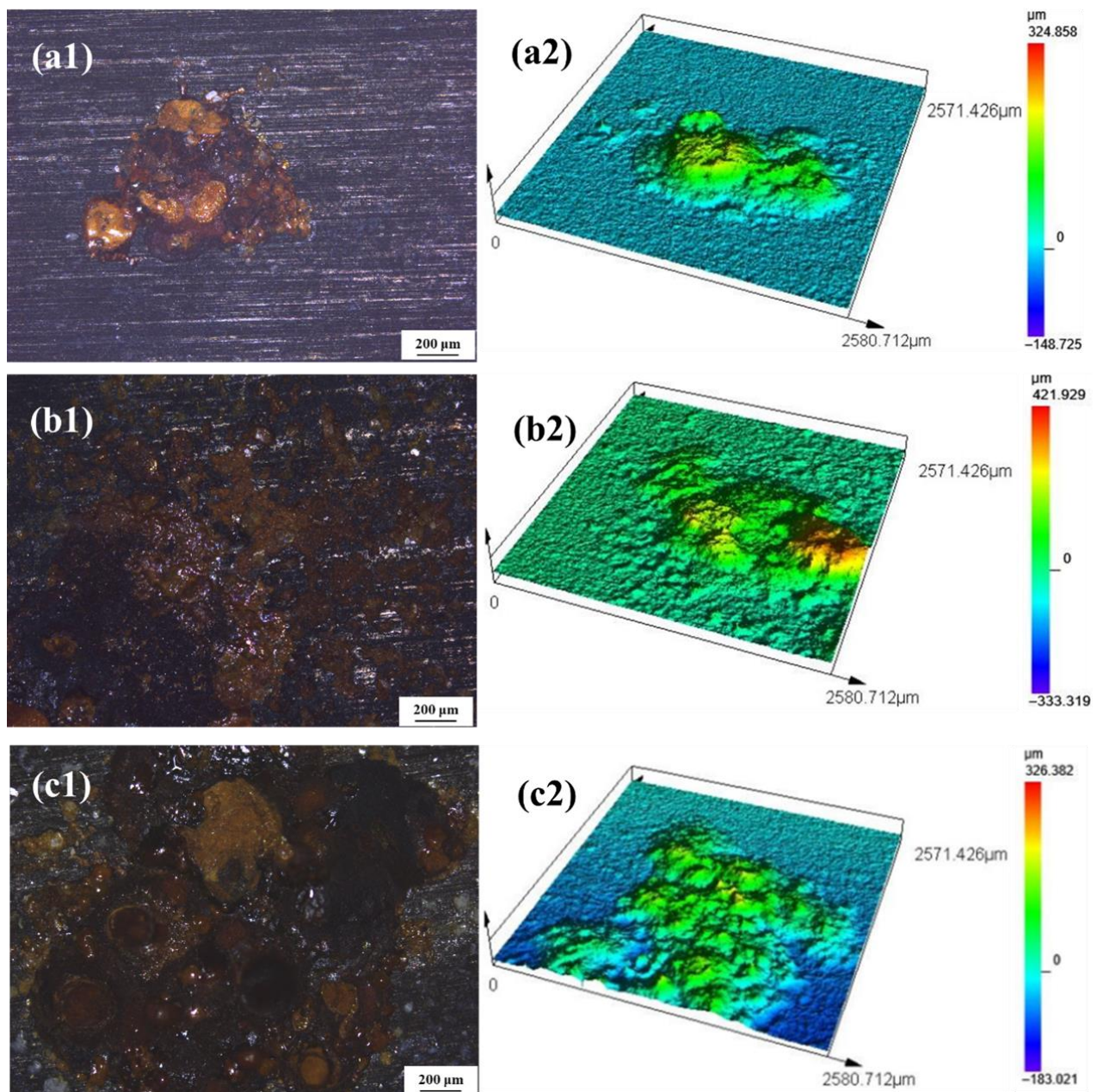


Figure 6. Three-dimensional laser surface profiling on QPQ-treated steel as a function of corrosion time: (a1,a2) 1 month, (b1,b2) 2 months, (c1,c2) 6 months. Column 1 shows morphology under light microscope; column 2 presents the corresponding 3D morphology.

3.4. Phase Composition

As revealed by the XRD patterns in Figure 7, the corrosion products on bare steel and on QPQ-treated steel evolve along different paths. For bare steel (Figure 7a), the 0 m spectrum is dominated by substrate α -Fe. After 1 month, reflections of γ -FeOOH (lepidocrocite) appear together with β -FeOOH (akaganeite)—the latter indicative of Cl^- -stabilized rust—along with minor $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$. By 2 months, α -Fe peaks are attenuated while α -FeOOH (goethite) and Fe_3O_4 intensities increase, consistent with aging and densification of the rust [36]. At 6 months, broadened/weak reflections riding on an elevated background suggest more poorly crystalline product layer composed of intergrown goethite/hematite/magnetite, in agreement with the SEM evidence of a compact lamellar network and with the observed deceleration in mass-loss kinetics.

For QPQ-treated steel (Figure 7b), the 0 m pattern shows the nitrated compound layer ($\epsilon\text{-Fe}_2\text{-}_3\text{N}$) together with the post-oxidation Fe_3O_4 . After 1 month, rust reflections of $\gamma\text{-}/\beta\text{-FeOOH}$ emerge at discrete sites on top of the intact compound layer. By 2 months, $\alpha\text{-FeOOH}$ and Fe_2O_3 become evident, while the nitride reflections remain but are reduced in relative intensity. At 6 months, peaks are superimposed on a diffuse background similar to bare steel, indicating fine-grained, partially amorphous products; however, the persistence of nitride/ Fe_3O_4 signatures underscores that corrosion remains largely under-film and localized, rather than uniform [37]. The recurrent detection of $\beta\text{-FeOOH}$ across both series is consistent with the chloride-rich deposit identified in the environmental survey.

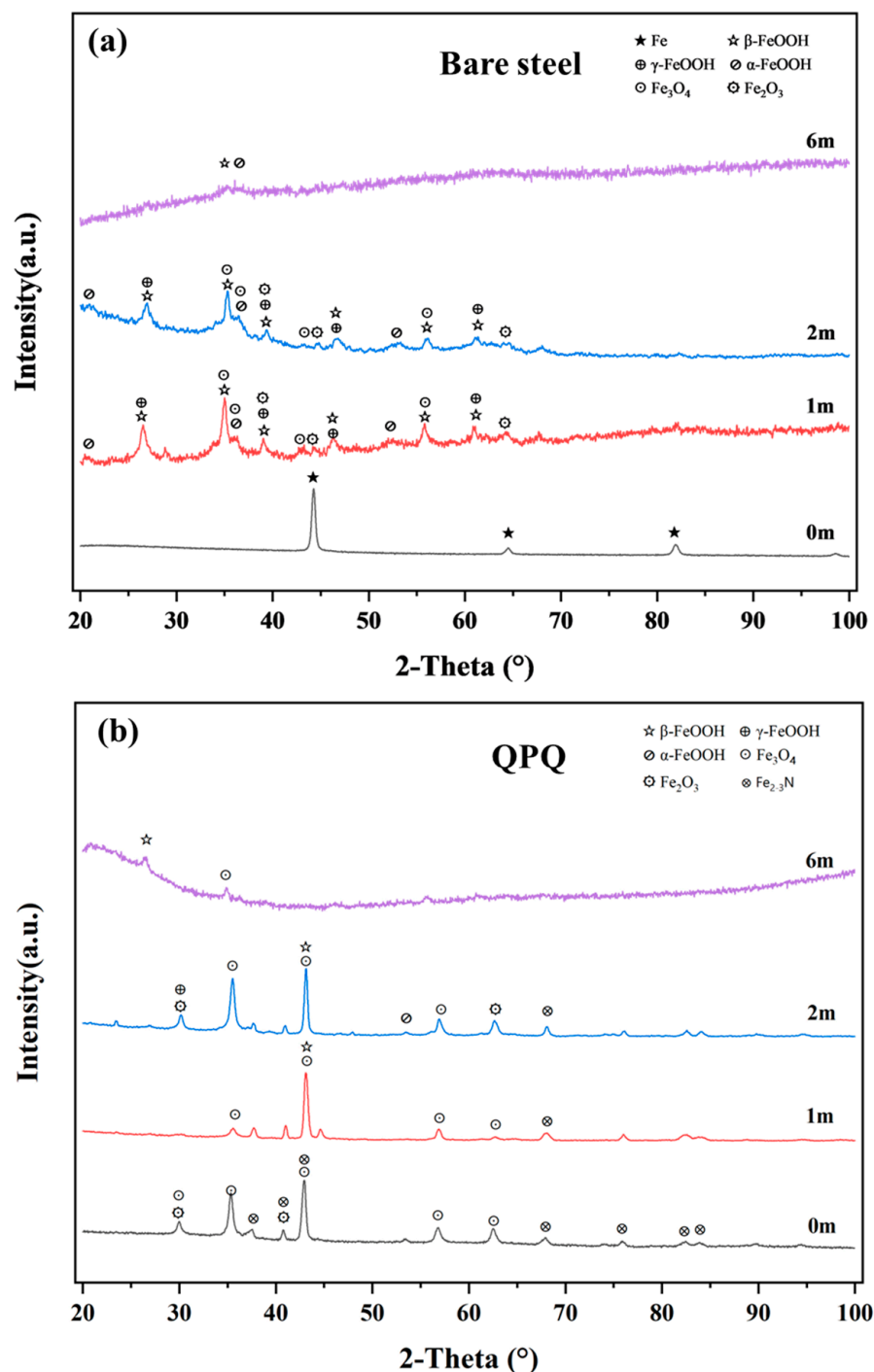


Figure 7. XRD patterns for bare steel (a) and QPQ-treated (b) steel after 0 month, 1 month, 2 months, and 6 months of corrosion.

3.5. Electrochemical Behavior (Polarization and EIS)

Figure 8 presents the potentiodynamic polarization curves measured in $0.4 \text{ mol}\cdot\text{L}^{-1} \text{ NaCl} + 0.2 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_4$, and Table 3 lists the corresponding E_{corr} and I_{corr} values extracted by Tafel analysis. Viewed together, they show the following trends.

For bare steel, before exposure, $E_{\text{corr}} = -0.698 \text{ V}$ (vs. SCE) and $I_{\text{corr}} = 1.57 \times 10^{-5} \text{ A}\cdot\text{cm}^{-2}$. After 1/2/6 months, E_{corr} becomes $-0.726/-0.717/-0.657 \text{ V}$ (overall ennoblement ending at -0.657 V), while I_{corr} increases to $8.98 \times 10^{-5}/1.15 \times 10^{-4}/9.81 \times 10^{-5} \text{ A}\cdot\text{cm}^{-2}$ (peaking at 2 months, then slightly decreasing). The polarization curves exhibit a suppressed anodic branch and a cathodic branch tending toward transport limitation, consistent with a thickening, partially conductive rust layer that both raises transport/charge-transfer resistance and enlarges the effective cathodic area [2,38].

For QPQ-treated steel, in the unexposed state, $E_{\text{corr}} = -0.099 \text{ V}$ and $I_{\text{corr}} = 4.35 \times 10^{-7} \text{ A}\cdot\text{cm}^{-2}$, indicating a more noble and less active surface. After 1/2/6 months, E_{corr} shifts to $-0.591/-0.435/-0.563 \text{ V}$ and I_{corr} increases to $4.77 \times 10^{-6}/3.76 \times 10^{-6}/1.44 \times 10^{-5} \text{ A}\cdot\text{cm}^{-2}$. Small inflections on the anodic branches in Figure 8b are consistent with metastable pit events at coating defects. Even so, I_{corr} for QPQ remains approximately $19\times$, $31\times$, and $7\times$ lower than bare steel at the corresponding times, indicating defect-controlled, localized activation rather than uniform dissolution.

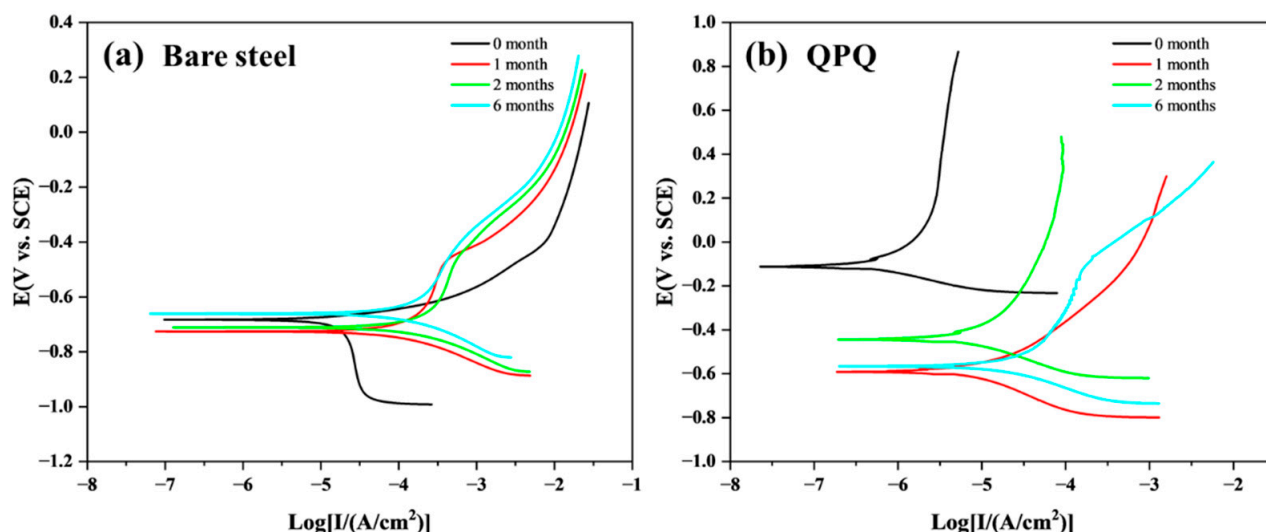


Figure 8. Potentiodynamic polarization curves for bare steel (a) and QPQ-treated (b) steel after 0 month, 1 month, 2 months, and 6 months of corrosion.

Table 3. Fitting values of E_{corr} (V) and I_{corr} ($\text{A}\cdot\text{cm}^{-2}$) from the potentiodynamic polarization curves.

Sample	Time	E_{corr} (V)	I_{corr} ($\text{A}\cdot\text{cm}^{-2}$)
Bare steel	0 month	-0.698	1.57×10^{-5}
	1 month	-0.726	8.98×10^{-5}
	2 months	-0.717	1.15×10^{-4}
	6 months	-0.657	9.81×10^{-5}
QPQ-treated	0 month	-0.099	4.35×10^{-7}
	1 month	-0.591	4.77×10^{-6}
	2 months	-0.435	3.76×10^{-6}
	6 months	-0.563	1.44×10^{-5}

The EIS spectra were interpreted with the equivalent circuits in Figure 9. For pristine bare steel, we used $R_s(Q_{\text{dl}}||R_t)$ circuit with a small low-frequency inductive branch (R_L/L). The clockwise loop is taken as a kinetic inductive response of the interface. It reflects either

adsorption or activation of intermediates in the chloride-containing thin film or a film or defect relaxation beneath rust [39,40]. For corroded bare steel, the response was described by $R_s(Q_f \parallel R_f)(Q_{dl} \parallel R_t)W_0$, where R_s is the solution resistance, Q_f and R_f describe the non-ideal film capacitance and film resistance of the rust, Q_{dl} and R_t describe the double layer and the charge transfer at the interface. Diffusion is represented by a finite length Warburg W_0 which gives a 45° region at intermediate frequency and a low-frequency plateau that are characteristic of finite diffusion paths in a porous rust or interfacial electrolyte.

For QPQ-treated steel, the compact nitride/oxide compound layer and the interfacial process at sparse defects were captured by $R_s(Q_f \parallel R_f)(Q_{dl} \parallel R_t)$. Any diffusion contribution was weak and only occasionally required a minor W_0 . In all cases, Q denotes a constant-phase element (CPE) to account for non-ideal capacitive behavior [41]. Tables 4–6 present, respectively, the fitted parameters for pristine bare steel, exposed bare steel (1, 2, and 6 months), and QPQ-treated steel, according to the equivalent-circuit models in Figure 9.

Within this framework, the qualitative evolution of the fitted elements is consistent with the spectra in Figure 10. On bare steel, R_s is essentially constant, R_f grows with exposure time, and R_{ct} increases as the film forms and becomes denser. The film element shows an early rise in effective capacitance with higher $Y_{0,f}$ and lower n_f for fresh porous rust, then shifts toward lower $Y_{0,f}$ and higher n_f as the film compacts. A weak W_0 appears and gradually strengthens at the lowest frequencies, which indicates an increasing role of diffusion through the rust and electrolyte composite. The very low exponents, $n_f \approx 0.32$ and $n_{dl} \approx 0.34$, point to strong dispersion caused by surface heterogeneity, mixed porosity, and roughness at the interface, and nonuniform current distribution under a thin electrolyte [42–44].

For QPQ-treated steel, the pristine state exhibits a very high R_f and an extremely large R_t , consistent with an intact barrier layer; upon exposure, R_f declines as defects activate and under-film electrolyte accumulates, while R_t drops strongly from the pristine state and then varies non-monotonically (partial recovery when corrosion products occlude defects, followed by renewed decrease as defects coalesce). The interfacial CPEs (Q_f , Q_{dl}) become more dispersive (n decreases) as heterogeneity grows and then partially recover as nodules thicken and choke transport paths. The absence of a pronounced W_0 term throughout the QPQ series further supports a defect-controlled, localized corrosion mechanism rather than diffusion-controlled uniform attack.

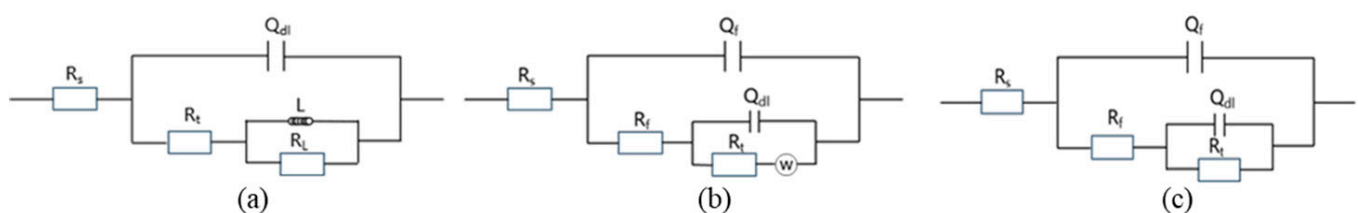


Figure 9. Equivalent-circuit model corresponding to EIS, (a) is the bare steel before corrosion, (b) is the bare steel after corrosion, (c) is the QPQ-treated steel.

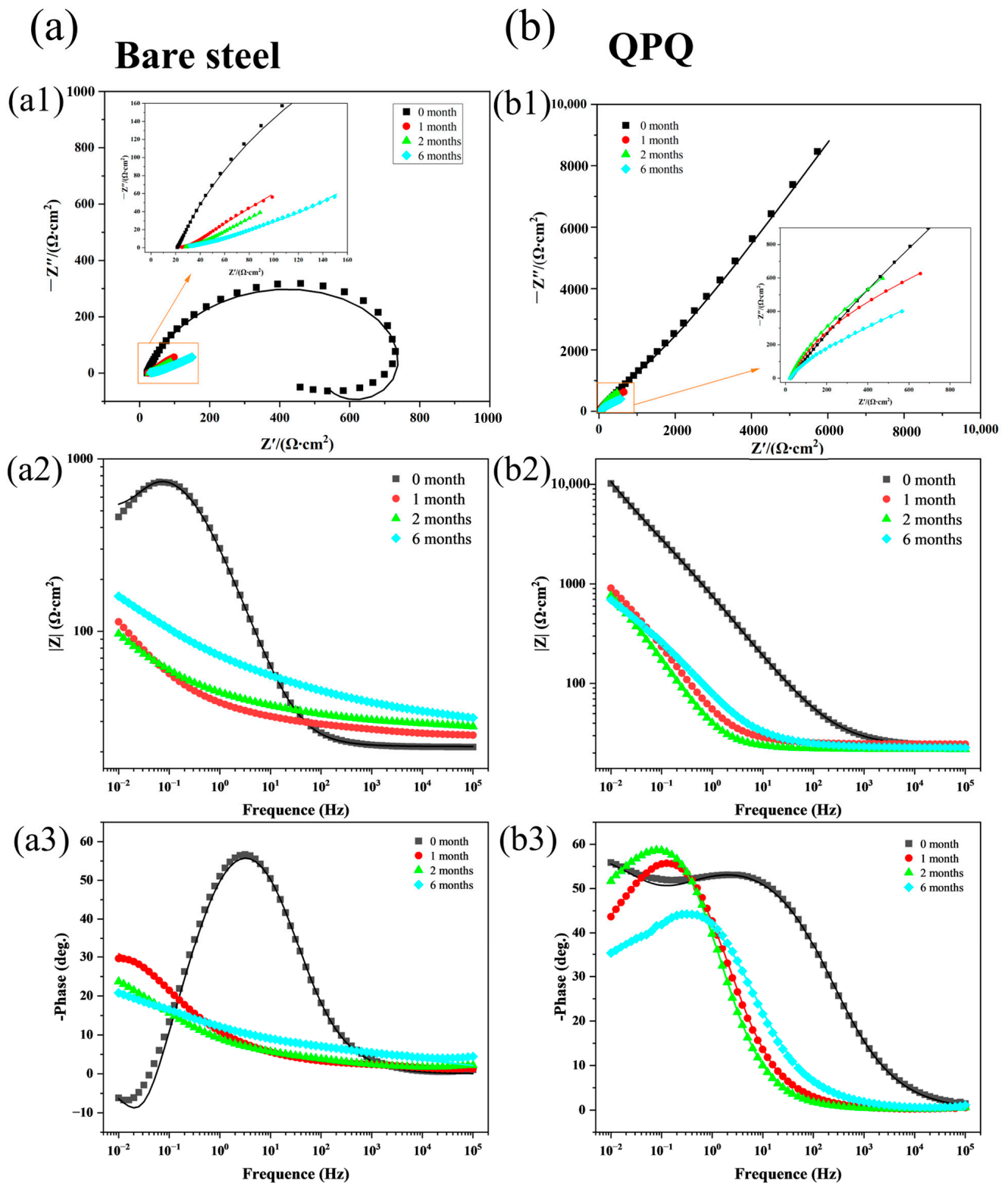


Figure 10. EIS for bare steel (a) and QPQ-treated (b) steel after 0 month, 1 month, 2 months, and 6 months of corrosion. (a1,b1) is the Nyquist plot, (a2,b2) is the $|Z|$ –frequency curve of Bode plot, (a3,b3) is the phase–frequency curve of Bode plot.

Table 4. Equivalent-circuit fit parameters for pristine bare steel, values extracted from the EIS in Figure 10a.

Sample	$R_s/(\Omega \cdot \text{cm}^2)$	$R_t/(\Omega \cdot \text{cm}^2)$	Q_{dl}		$R_L/(\Omega \cdot \text{cm}^2)$	$L/(\text{H} \cdot \text{cm}^2)$
			$Y_0/(\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2})$	n_f		
Before corrosion	21.48	501.1	6.81×10^{-4}	0.80	330.9	1381

Table 5. Equivalent-circuit fit parameters for bare steel (after 1, 2, and 6 months of corrosion), values extracted from the EIS in Figure 10a.

Sample	$R_s/(\Omega \cdot \text{cm}^2)$	$R_f/(\Omega \cdot \text{cm}^2)$	Q_f		$R_t/(\Omega \cdot \text{cm}^2)$	Q_{dl}		W_0
			$Y_{0,f}/(\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2})$	n_f		$Y_{0,dl}/(\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2})$	n_{dl}	
1 month	24.13	8.92	1.13×10^{-2}	0.34	7.78	7.17×10^{-3}	0.66	2.24×10^{-2}
2 months	21.59	6.89	1.88×10^{-5}	0.55	32.97	2.14×10^{-2}	0.32	2.28×10^{-2}
6 months	29.6	41.11	5.08×10^{-3}	0.32	120.7	9.47×10^{-3}	0.49	2.84×10^{-2}

Table 6. Equivalent-circuit fit parameters for QPQ-treated steel (after 0, 1, 2, and 6 months of corrosion), values extracted from the EIS in Figure 10b.

Sample	$R_s/(\Omega \cdot \text{cm}^2)$	$R_f/(\Omega \cdot \text{cm}^2)$	Q_f		$R_t/(\Omega \cdot \text{cm}^2)$	Q_{dl}	
			$Y_{0,f}/(\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2})$	n_f		$Y_{0,dl}/(\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2})$	n_{dl}
0 month	23.5	8735	3.91×10^{-4}	0.64	2.59×10^{12}	2.32×10^{-4}	0.71
1 month	24.79	1664	6.03×10^{-3}	0.75	856.7	3.23×10^{-2}	1
2 months	21.97	1220	8.43×10^{-3}	0.79	3439	6.86×10^{-3}	0.69
6 months	22.95	765.4	4.42×10^{-3}	0.66	1229	1.25×10^{-2}	0.75

3.6. Cross-Section Microstructure and EDS Mapping

Figure 11 shows the cross-sectional SEM morphology and EDS elemental maps of bare steel after 6 months at 20 °C and 75% RH with an initial mixed-salt loading of $10 \text{ g} \cdot \text{m}^{-2}$. At low magnification, (a) a multilayer rust band is visible with through-thickness cracks and local separation from the substrate; higher magnification (b) reveals intergrown lamellar and compact sublayers with wedge-shaped voids along the metal/rust interface. The C map (c) outlines resin intrusion along open cracks and the interface, O (d) is enriched across the entire rust band, Fe (e) is depleted in the rust and uniform in the substrate. The Cl map (f) indicates relative enrichment along interfacial cracks and within inner rust filaments that coincide with sites of delamination. A faint, field-wide Cl signal inside the substrate represents background level counts from the mapping auto scale and is not interpreted as chlorine in the bulk steel. The maps are used qualitatively to indicate distributions rather than absolute O or Cl contents.

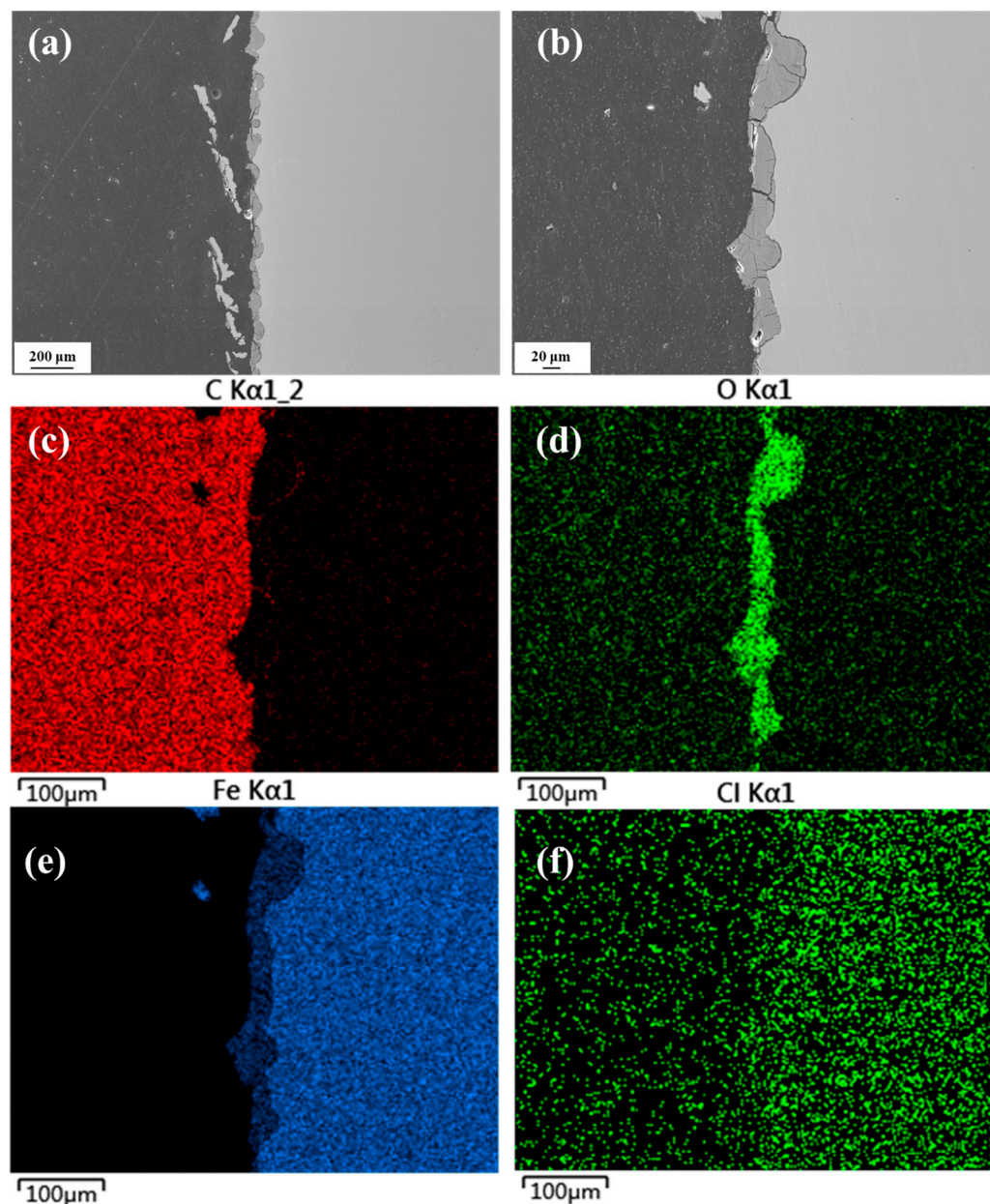


Figure 11. Cross-sectional morphology of bare steel after 6 months of corrosion. (a) Low-magnification SEM. (b) Higher-magnification SEM. (c) C K α map. (d) O K α map. (e) Fe K α map. (f) Cl K α map.

Figure 12 shows the cross-section of the QPQ-treated steel before exposure. A continuous, compact surface layer is evident, consisting of the post-oxidized top film and the underlying nitride compound layer. The N map is strongly enriched at the surface and decays into the substrate, while the O map highlights the thin oxide overlayer. The Fe signal is correspondingly depleted within this compound zone and uniform in the substrate. The C map mainly outlines the mounting resin at the free surface/pores rather than a metallic constituent, confirming that the near-surface layer is dense and well bonded prior to corrosion.

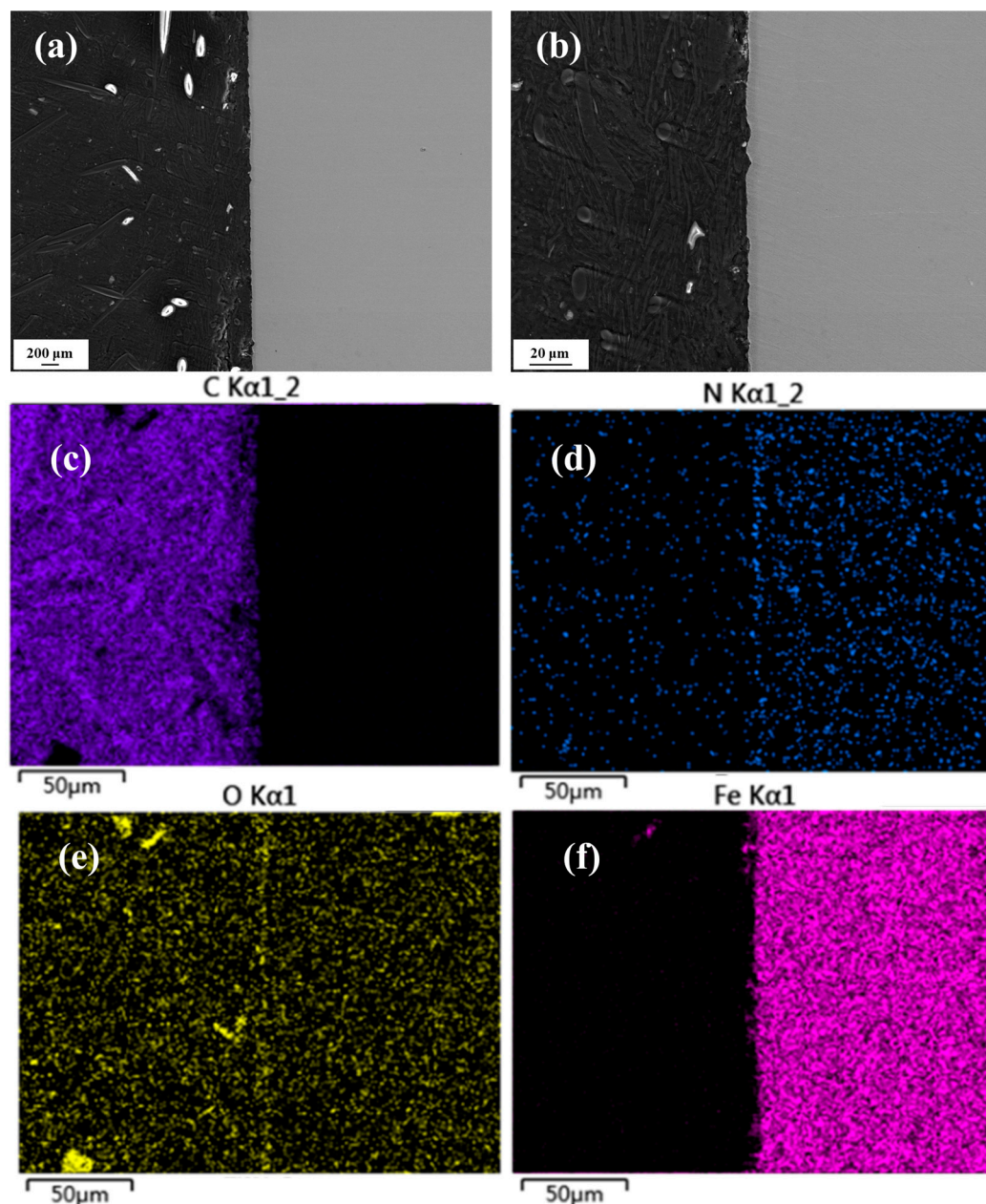


Figure 12. Cross-sectional morphology of QPQ-treated steel before corrosion. (a) Low-magnification SEM. (b) Higher-magnification SEM. (c) C K α map. (d) N K α map. (e) O K α map. (f) Fe K α map.

Figure 13 presents the cross-section after six months. Corrosion remains localized to discrete sites where the compound layer is disrupted; a rust nodule penetrates the surface film and opens a narrow interfacial gap. Chlorine is concentrated along the crack/interfacial cavity and within the inner rust, whereas nitrogen remains continuous in adjacent intact regions, indicating that most of the nitride layer still functions as a barrier away from the defect. Oxygen is enriched throughout the nodule and Fe is depleted there, consistent with hydrated iron oxyhydroxides occupying the defect zone.

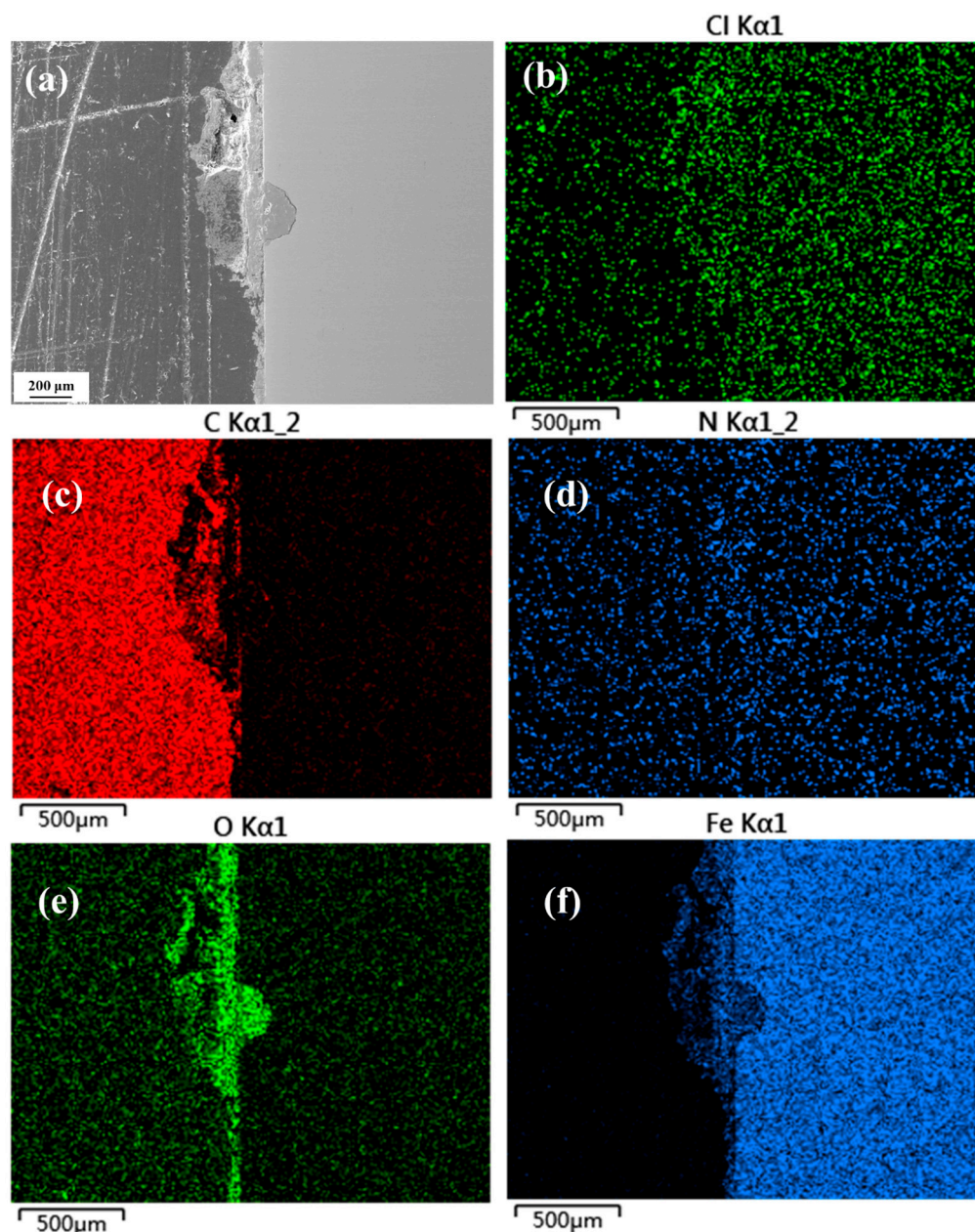
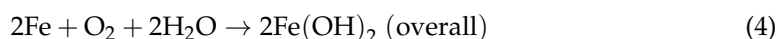
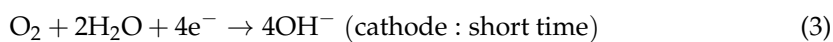


Figure 13. Cross-sectional morphology of QPQ-treated steel after 6 months of corrosion. (a) Low-magnification SEM. (b) Cl K α map. (c) C K α map. (d) N K α map. (e) O K α map. (f) Fe K α map.

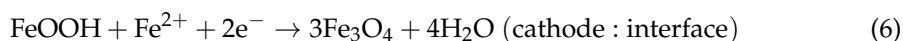
4. Discussion

As shown in Figure 14, taken together with the preceding results, these features indicate a corrosion mechanism governed by a persistently wet salt deposit. Operating above the measured DRH/ERH of the mixed salts at 20 °C keeps a thin electrolyte on the surface (mixture DRH $\approx$ 60%, ERH $\approx$ 52.5%), so the deposit acts as a reservoir of chloride and establishes differential aeration and transport-limited kinetics [45]. Because the mixed salt contains bisulfate, the hydrolysis of HSO_4^- renders the thin electrolyte initially acidic; under these conditions, the anodic process is dominated by iron dissolution and the cathodic process by oxygen reduction. The rapid consumption of H^+ during ORR quickly raises the pH of the thin film. The elementary reactions are as follows:





The ferrous hydroxide is then oxidized to FeOOH polymorphs: γ -FeOOH forms first and β -FeOOH appears in the presence of chloride; with time, aging and partial transformation toward α -FeOOH/Fe₃O₄/Fe₂O₃ densify the layer (XRD, Figure 7; cross-section SEM, Figure 11) [1,46,47]. Under thin-film conditions, an Evans-type redox cycle operates at Fe₃O₄/FeOOH interfaces:



Chloride stabilizes akaganeite (β -FeOOH) and is retained within pores and cracks, so Cl[−] migrates inward to the metal/rust interface and sustains localized anodic dissolution, while oxygen reduction proceeds on outer rust and exposed cathodic areas—i.e., local differential-aeration cells [1,46,47].

Electrochemically, EIS evolves from a single capacitive loop to two time constants, plus a weak diffusion feature (Figure 10), and polarization curves show a suppressed anodic branch with near-constant i_{corr} at $\sim 10^{-5}$ A·cm^{−2} (Figure 10). Together with the power-law fit of mass loss ($n \approx 0.63$), these results indicate decelerating, transport-limited kinetics as the rust layer thickens and partially blocks ion movement. Nevertheless, the persistent interfacial cracks and delamination observed in cross-section provide preferential pathways that retain chloride and moisture, maintaining localized anodic activity beneath the rust (Figure 11). In summary, bare steel under deposited mixed salts at constant humidity undergoes thin-electrolyte corrosion governed by (i) sustained wetting/deliquescence of the salt layer, (ii) inward chloride migration and interfacial attack, and (iii) progressive rust densification that slows the global rate while allowing localized under-rust corrosion to continue along cracks and separation fronts (synthesis of Figures 7 and 9–11).

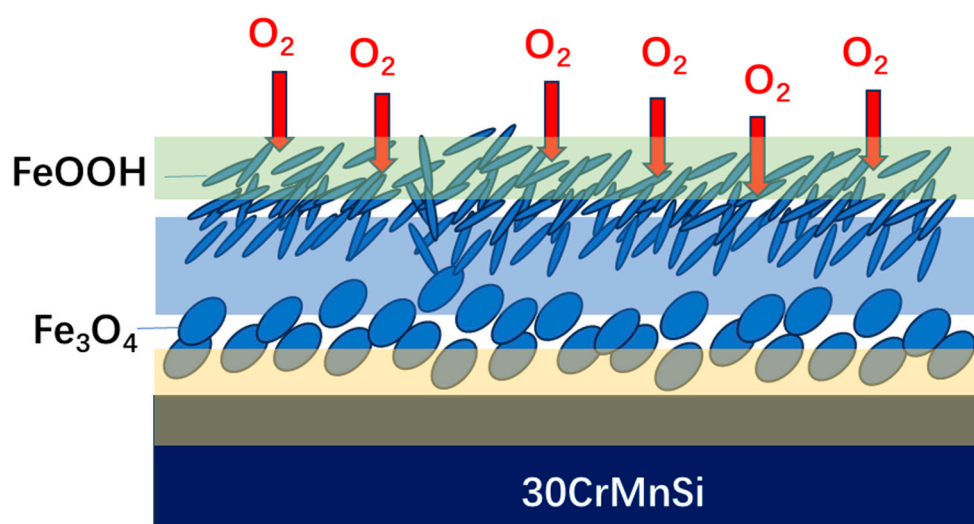


Figure 14. Schematic diagram of the corrosion mechanism of bare steel.

Guided by the schematic in Figure 15, taken together with the macroscopic observations (discrete rust mounds on QPQ), 3D profilometry (high local Sz but modest global roughness), XRD (γ -/ β -FeOOH appearing early and evolving toward α -FeOOH/Fe₃O₄/Fe₂O₃), polarization and EIS, the corrosion mechanism of QPQ-treated steel is defect-controlled under-film corrosion (Figures 6–10). In the intact, state the nitride/oxide bilayer blocks

uniform dissolution and the surface remains largely passive. When RH exceeds the deposit's DRH, a thin electrolyte wets the surface and wicks into pre-existing microdefects such as polishing scratches, pores, or inclusions. Chloride and oxygen reach the substrate at the defect, local anodic dissolution starts beneath the film, and β -FeOOH stabilizes in the occluded site, while hydrolysis of Fe^{2+} lowers the local pH, establishing a differential-aeration cell [48,49]. Corrosion products then accumulate and swell, which lifts the film to create a rust nodule and opens interfacial gaps; nearby defects can activate and coalesce as the process repeats [50,51]. As nodules thicken, some sites become partly occluded and currents diminish, so the average rate stays low while growth concentrates at defects. The impedance is dominated by the compact-layer and charge-transfer responses with only a weak diffusion contribution, and polarization shows low i_{corr} with small anodic kinks, consistent with localized activity confined to defective spots (Figures 6–10), and matches known behavior of nitrocarburized plus post-oxidized layers [52].

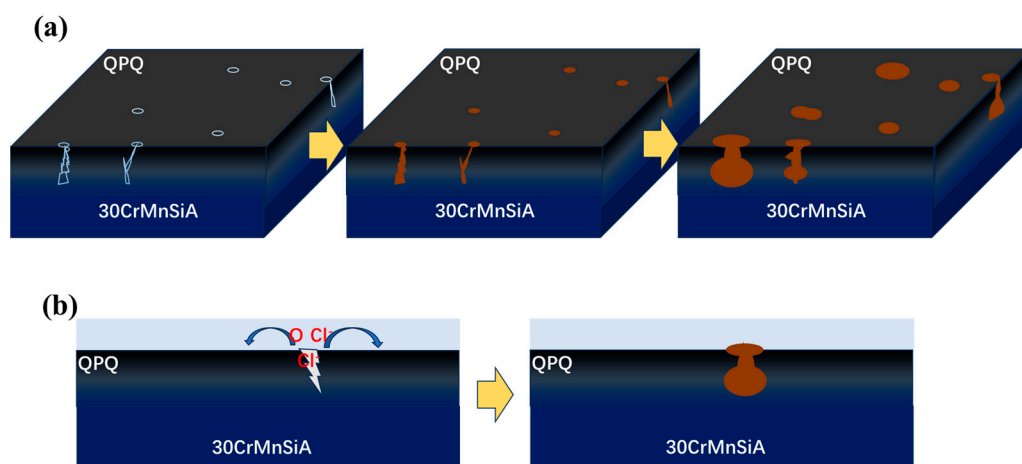


Figure 15. Schematic diagram of the corrosion mechanism of QPQ-treated steel. (a) Three-dimensional. (b) Two-dimensional cross-section.

For design and maintenance, this implies that QPQ alone suppresses uniform corrosion but must be paired with defect management: finishing that minimizes and rounds surface features, strict quality control on compound layer continuity, and post-QPQ sealing (e.g., sol-gel/organic clear coats) to close residual porosity. Geometry should avoid dust-collecting ledges and blind crevices and favor drainage; operationally, simple rinsing after dust events and keeping standby/storage RH below ~50% reduces time above DRH. Inspection should focus on defect-prone lines (grinding traces, edges, fastener holes), where localized swelling or gloss loss signals early under-film activity. In short, the field environment promotes electrolyte cycling that activates only defective sites on QPQ; engineering measures that limit salt retention, reduce defect density, and cap the compound layer will convert this behavior into low-rate, localized, and manageable corrosion over service life.

5. Conclusions

We established a reproducible protocol using salts extracted from field dust and a dry-powder pre-deposit of $10 \text{ g}\cdot\text{m}^{-2}$; at 20°C and 75% relative humidity, a stable thin electrolyte is sustained (mixture DRH $\approx 60\%$, ERH $\approx 52.5\%$). Bare 30CrMnSiA steel shows progressive but slowing corrosion consistent with $\Delta m = kt^n$ ($n \approx 0.63$), with mass loss of -97.49 , -171.92 , and $-259.13 \text{ g}\cdot\text{m}^{-2}$ at 1, 2, and 6 months, while rust evolves from γ/β -FeOOH toward α -FeOOH/ $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ and chloride migrates inward to maintain interfacial anodic sites. The electrochemical test results show that the anodic reaction is suppressed, which is a transport-limited deceleration kinetic process. QPQ largely protects

the surface and the corrosion mechanism of QPQ-treated steel is defect-controlled under-film corrosion. The nitride/oxide bilayer blocks uniform dissolution, yet brine enters microdefects. Iron then dissolves beneath the film, hydrolysis acidifies the occluded site, and retained chloride stabilizes β -FeOOH. Corrosion products expand and lift the coating, forming rust nodules and interfacial gaps, whereas intact regions remain passive. The impedance and polarization responses are consistent with a compact nitride and oxide layer. Overall, chloride deposits drive thin electrolyte corrosion. For dust-laden service, minimize coating defects and control salt retention via surface finishing, sealing, and designs that shed dust.

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