

Available online at www.sciencedirect.com

jmr&t
Journal of Materials Research and Technology
www.jmrt.com.br



Original Article

Corrosion behavior and surface analysis of 690 MPa-grade offshore steels in chloride media

Wei-Hsuan Huang^a, Hung-Wei Yen^b, Yueh-Lien Lee^{a,*}^a Department of Engineering Science and Ocean Engineering, National Taiwan University, 1 Roosevelt Road, Section 4, Taipei 106, Taiwan^b Department of Materials Science and Engineering, National Taiwan University, 1 Roosevelt Road, Section 4, Taipei 106, Taiwan

ARTICLE INFO

Article history:

Received 22 August 2018

Accepted 11 November 2018

Available online 4 December 2018

Keywords:

High-strength low-alloy steel

Corrosion resistance

Polarization curve

Rust

X-ray photoelectron spectroscopy

Electron probe microanalyzer

ABSTRACT

High-strength low-alloy steels have been used prevalently in marine engineering and the defense industry because of their superior yield strength, toughness, and weldability. Although these materials have excellent mechanical properties, the corrosion resistance of high-strength low-alloy steels is a crucial problem, particularly when they are used in a marine environment. In this study, the corrosion behavior of a newly designed NiCu-containing low-carbon steel (NiCu steel) and conventional S690Q alloy steel (S690Q steel) was investigated and compared. Potentiodynamic polarization results indicated that for NiCu steel, current densities are apparently reduced in the anodic region. Surface analyses indicated that NiCu steel created a thick and uniform inner rust layer after it was immersed in NaCl solution for 7 days. Furthermore, a high-density Cr-rich region was observed in the NiCu inner rust layer after an immersion test. Electrochemical impedance spectroscopy results suggested that NiCu steel exhibits higher corrosion resistance than S690Q steel in NaCl solution.

© 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

In order to reduce weight of structure and cost of construction, advanced high-strength steels are used for structural and construction engineering applications, such as oil and gas pipelines, pressure vessels and tubing, ship plates, and automotive components. Tempered martensitic steels have ultrahigh strength and excellent toughness, and several variants of tempered martensitic steel have been used for offshore applications. For example, S690Q offshore steel, which has

yield strength of over 690 MPa, the candidate for replacing the prevalently S460Q steel in offshore structure. However, materials toughness and corrosion resistance are especially crucial when light-weighting is achieved by reducing the thickness of structure. Recently, embrittlement due to high-temperature tempering was found in S690Q steel [1]. To overcome this issue, a tempered martensitic steel, named NiCu steel, has been developed by reducing carbon content and increasing Ni and Cu contents. The NiCu steel has yield strength of over 690 MPa, toughness superior to S690Q, and better weldability [1]. Actually, the NiCu steel is similar to the HSLA-100 steel, which is a classic tempered martensitic steel for marine environments [2].

Steels used in marine environments are susceptible to corrosion, which greatly degrades their properties. Therefore,

* Corresponding author.

E-mail: yuehlien@ntu.edu.tw (Y. Lee).<https://doi.org/10.1016/j.jmrt.2018.11.002>2238-7854/© 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

corrosion resistance of steels is one of the most crucial factors to be considered for real-world applications. Hao et al. [3] studied E690 high-strength steel electrochemical characterization in wet-dry cyclic marine environments. The rust layer in E690 high-strength steel initially promoted corrosion and then inhibited general corrosion after 1440 h of testing, indicating the occurrence of localized corrosion, which increases because of the thickness and intensification of the rust layer. They further reported that corrosion product layers primarily comprise Fe_3O_4 , $\alpha\text{-FeOOH}$, $\beta\text{-FeOOH}$, $\gamma\text{-FeOOH}$, FeOCl , and many amorphous compounds. Wu et al. [4] studied the corrosion behavior and mechanism of E690 high-strength low-alloy steel in a marine environment with different pH values. The corrosion current density of E690 high-strength steel gradually increased with decreasing pH values. After long-term tests under alternating wet-dry marine environments at different pH, uniform corrosion occurred on E690 steel. The rust layer primarily comprised $\alpha\text{-FeOOH}$, $\beta\text{-FeOOH}$, $\gamma\text{-FeOOH}$, Fe_3O_4 , and Fe_2O_3 . The composition of corrosion products slightly differed with pH. Li et al. [5] analyzed the effect of nanosized NbC precipitations on the electrochemical corrosion behavior of high-strength low-alloy steel in 3.5% NaCl solution. NbC precipitations considerably enhanced the corrosion resistance of the H-containing steel. The abundant and highly dispersed nanosized NbC particles, which act as massive and effective hydrogen traps, are crucial for resistance to hydrogen-activated corrosion. Yang et al. [6] studied the effect of hydrostatic pressure on the corrosion behavior of Ni–Cr–Mo–V high-strength steel. They found that the corrosion resistance deteriorated with increasing hydrostatic pressure, which was attributed to the increase of the anodic reaction rate. The increasing hydrostatic pressure accelerated the initiation rate and decreased the growth probability of metastable pitting, which increased the uniform corrosion susceptibility of Ni–Cr–Mo–V high-strength steel. The aforementioned literature listed two cases of corrosion study on two steels of 690-MPa grade. Moreover, the studied materials in this paper, namely S690Q steel and NiCu steel, are designed to reach a grade of 690 MPa for the offshore construction demand. The mechanical properties of S690Q steel and NiCu steel have been studied in relevant literature [7]. However, the corrosion resistances between these two steels have not been compared, even though they are both used in marine environments.

The current work aims at investigating the corrosion behaviors of both S690Q steel and NiCu steel in 3.5 wt% NaCl solution. The electrochemical properties of two types of steel were studied through potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Surface analyses, including scanning electron microscopy (SEM) and focused ion beams (FIBs), were performed for microstructure analysis. In addition, compositions and distributions of

elements in the rust layer of two types of steel were analyzed through X-ray photoelectron spectroscopy (XPS) and an electron probe microanalyzer (EPMA), respectively. The present study will be beneficial to the future applications of high-strength steels, particularly in the harsh marine environment.

2. Experimental

2.1. Sample preparation

Table 1 presents the chemical compositions of S690Q and newly designed NiCu steels. Both of the steel samples were produced through vacuum-induction melting. Square plates ($1\text{ cm} \times 1\text{ cm} \times 0.1\text{ cm}$) with a testing area of 1 cm^2 were prepared for following heat treatment processes and electrochemical tests. S690Q and NiCu samples were tempered at 600°C and 660°C for 1 h, respectively, and were used in this study because of their superior mechanical properties according to our previous results [1]. After heat treatment, all the samples were mechanically ground using emery paper of 80–1200 grit, which was rinsed with deionized water and then washed with alcohol in an ultrasonic bath.

2.2. Electrochemical measurements

Potentiodynamic polarization curves and EIS were conducted in 3.5 wt% NaCl solution using a potentiostat (Gamry Reference 600) to evaluate corrosion performance. A standard three-electrode system comprising a graphite counter electrode and saturated calomel electrode as a reference electrode was used in all electrochemical tests. Potentiodynamic polarization curve measurements were obtained by sweeping the potential from -200 to 300 mV versus OCP at a scan rate of 1 mV/s . EIS measurements were recorded at open circuit potential in a frequency range of 10^{-2} to 10^5 Hz with an alternating current amplitude of 10 mV . Corrosion potential (E_{corr}) and current density (I_{corr}) were determined through Tafel extrapolation. The tested area on the steel samples for all electrochemical tests was 1 cm^2 . Aerated experiments were performed in naturally-aerated solution. In the deaerated experiments, the test solutions were bubbled with pure nitrogen for 30 min in the cell prior to each measurement.

2.3. Microstructure characterization and corrosion product analysis

The surface morphology of the corroded samples was studied through SEM (JEOL JSM6510). Moreover, after the 7 day

Table 1 – Chemical compositions of two types of steel samples (wt%).

	Fe	C	Si	Mn	Cr	Ni	Mo	Cu	Al	Ti + Nb	N
S690Q	Bal.	0.08–0.16	0.2–0.4	0.9–1.0	<0.65	0.8–1.0	<0.5	0.1–0.4	<0.08	<0.04	<0.009
NiCu	Bal.	0.04–0.08	0.2–0.4	0.9–1.0	<0.65	2.5–3.5	<0.5	1.0–2.0	<0.08	<0.06	<0.009

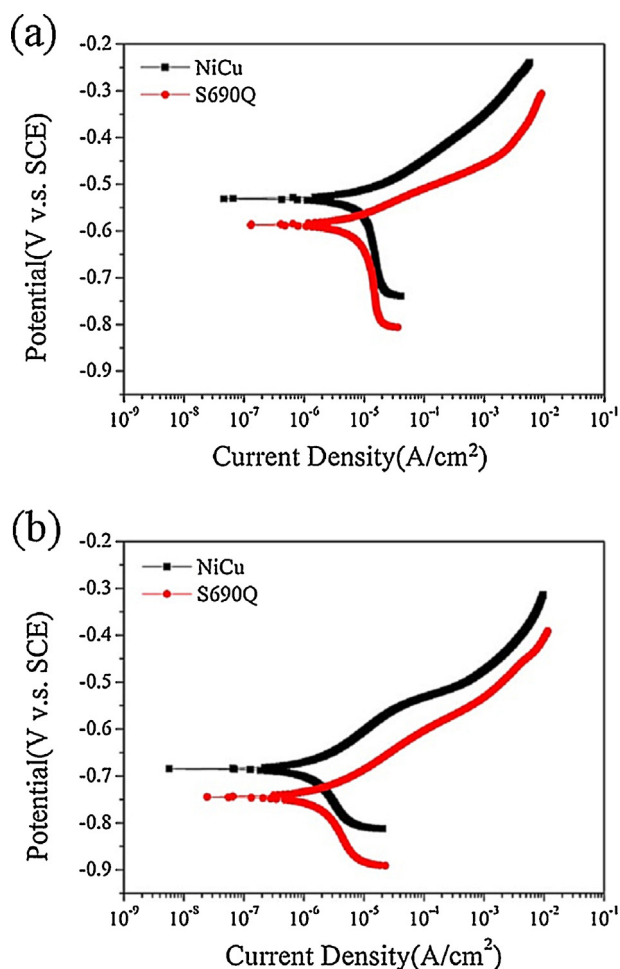


Fig. 1 – Potentiodynamic polarization curve of NiCu and S690Q steel samples in (a) aerated and (b) deaerated 3.5 wt% NaCl solution.

immersion test, some corroded samples were investigated through the FIB (Helios 600i) method to prepare a cross-section and further studied through SEM. X-ray diffraction (XRD) was employed to identify the phases of rust layers. XRD was performed using a Rigaku-TTRAX III diffractometer using Cu-K α radiation at 50 kV/300 mA. The full XRD patterns were recorded at 10–80° 2 θ with a scanning rate of 4°/min. XPS (VGS Thermo K-Alpha) analyses were performed to obtain the compositional information and chemical state of corrosion products generated on the samples after the 7 day immersion test. An Al K α anode of 1400 eV was used as an X-ray source. Survey spectra were recorded for the samples at a kinetic energy of 0–1350 eV at an interval of 1 eV, whereas high-resolution scans with an interval of 0.1 eV were conducted for Fe 2p and Cu 2p. The analyzer pass energy was 50 eV. Base pressure in the experimental chamber was approximately 2×10^{-7} mbar. The spectrum obtained was referred to the C 1s peak (284.5 eV) of carbon. The distributions of several crucial elements in the cross-sections of rust layers were detected by an EPMA (JEOL JXA-8200) at an accelerated voltage of 15 kV and sample current of 0.05 μ A.

Table 2 – E_{corr} and I_{corr} values extracted from polarization curves for NiCu and S690Q steel samples in 3.5 wt% NaCl solution (a) aerated and (b) deaerated.

Sample	E_{corr} (mV vs. SCE)	I_{corr} (μ A/cm 2)
(a) NiCu	-527.3 ± 3.2	7.3 ± 3.1
(a) S690Q	-566.3 ± 19.6	8.3 ± 3.4
(b) NiCu	-676.7 ± 23.8	1.1 ± 0.3
(b) S690Q	-730.0 ± 4.0	1.6 ± 0.5

3. Results and discussion

3.1. Corrosion resistance

Because the nature of marine environment can differ widely from normal to low dissolved oxygen zones, potentiodynamic polarization curves of NiCu and S690Q steel samples in both aerated and deaerated NaCl solutions were studied. As shown in Fig. 1, both of the steel samples were characterized by an increase of current density with increasing potential in the anodic region, indicating their active corrosion behavior without passivation in aerated and deaerated NaCl solutions. In the presence of dissolved oxygen, no pronounced change was observed in a cathodic region; however, an apparent reduction was observed in current densities in the anodic region for NiCu steel sample (Fig. 1a), which indicated the suppression of anodic metal dissolution reactions. This change indicates that the effect of adding a high amount of Cu and Ni was more pronounced on the anodic reaction than on the cathodic reaction. The retardation of the anodic reaction in NiCu steel sample generated more positive E_{corr} and lower I_{corr} than in S690Q steel samples. Moreover, these features are consistent with potentiodynamic polarization curves measured in the absence of dissolved oxygen. Fig. 1b presents a similar trend; however, lower I_{corr} for NiCu and S690Q steel samples was evaluated in the deaerated solution. In addition, no evident limiting diffusive current density was observed in the cathodic region, which was anticipated for both steel samples. The overall results indicate that a high amount of Cu and Ni in the ferrous alloy may affect the anodic dissolution rate. Table 2 summarizes corrosion potential (E_{corr}) and corrosion current density (I_{corr}) extracted from polarization curves were summarized in. Table 2 indicates that NiCu steel sample has a lower iron dissolution rate in both aerated and deaerated NaCl solutions.

To further study the evolution of corrosion resistance during immersion, EIS measurements of NiCu and S690Q steel samples immersed in aerated NaCl solution for different periods were taken. Fig. 2 shows the impedance spectrums of two steel samples as a function of immersion time. Fig. 2a and c presents Nyquist plots from the EIS results for the two steel samples. Both figures display similar features, with only one depressed capacitive semicircle. This type of diagram is usually interpreted as a mechanism of charge transfer on an inhomogeneous surface [7]. The diameters of capacitive semicircles in Nyquist plots decreased with immersion time for both steel samples. It is worthwhile to emphasize the diameter of the capacitive semicircle for the NiCu steel sample was slightly higher than that of the S690Q steel sample for the entire immersion time. On the other hand, during the first

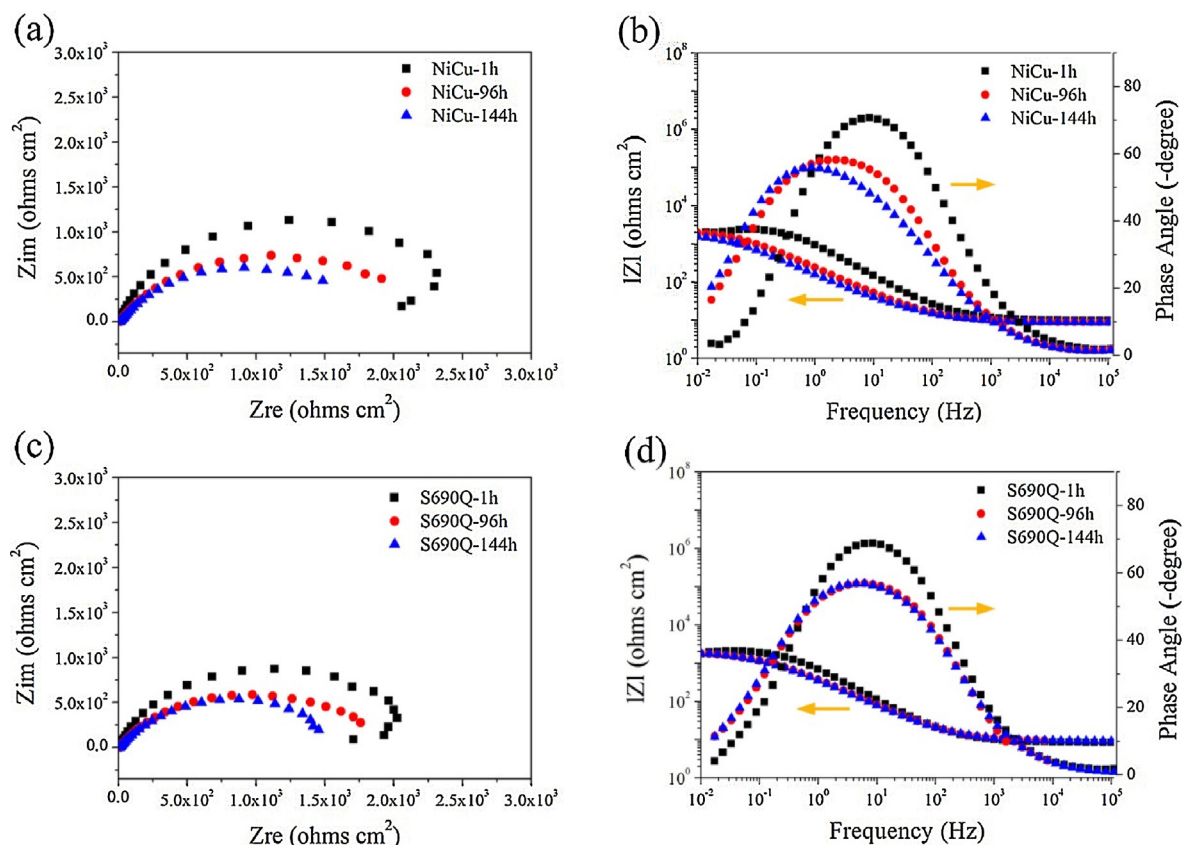


Fig. 2 – Nyquist and Bode plots for (a, b) NiCu (c, d) S690Q steel samples immersed in 3.5 wt% NaCl solution for different durations.

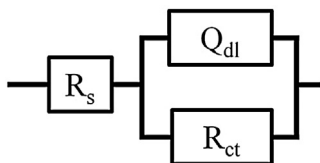


Fig. 3 – Equivalent circuits used to fit experimental impedance spectra.

144 h immersion, the Bode plots of two steel samples showed only one time constant as in Fig. 2b and d.

To describe the impedance response of the corrosion behavior in chloride environments, the equivalent circuit analysis was performed using ZSimpWin software. The equivalent circuit model from the literature [8–10] was used for the EIS results (Fig. 3). In the circuits, R_s and R_{ct} indicate solution resistance and charge transfer resistance of the electrolyte–substrate interface, respectively. The constant phase element (Q_{dl}) is associated with the capacitance of the electrochemical double layer. Table 3 summarizes the fitting result of different electric elements. Although the R_{ct} values of two steel samples decreased with increasing immersion time (Table 3), the R_{ct} values of the NiCu steel sample were always higher than that of S690Q for the entire immersion test. In general, R_{ct} , which is inversely proportional to the corrosion rate of a given metal, is a valuable parameter

Table 3 – Fitted electrochemical parameters for NiCu and S690Q steel samples during 144 h of immersion in 3.5 wt% NaCl solution.

Sample	Q_{dl} ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$)	n	R_{ct} ($\Omega \text{ cm}^2$)	Error (%)
NiCu 1 h	2.11×10^{-4}	0.83	2904	5.0
NiCu 96 h	1.08×10^{-4}	0.71	2367	2.1
NiCu 144 h	1.73×10^{-4}	0.67	2219	4.8
S690Q 1 h	2.96×10^{-4}	0.82	2329	3.4
S690Q 96 h	7.04×10^{-4}	0.70	1937	0.8
S690Q 144 h	8.08×10^{-4}	0.69	1715	1.6

used to evaluate the corrosion resistance of metallic substrates [11,12]. The larger diameter of the Nyquist capacitive semicircle accompanying the higher R_{ct} value indicates that NiCu steel had superior anticorrosion performance in NaCl solution.

3.2. Microstructure observation after corrosion

Fig. 4 shows the surface morphology of as polished and a series of micrographs of NiCu and S690Q steel samples after different immersion times in aerated NaCl solution. To observe the initial formation of the rust layers, planview SEM images of the steel samples were taken after 5 and 60 min of immersion in 3.5 wt% NaCl. The morphologies of rust layers gradually evolved with increasing exposure time. After 5 min of immersion time (Fig. 4b and f), some corroded area covered with the

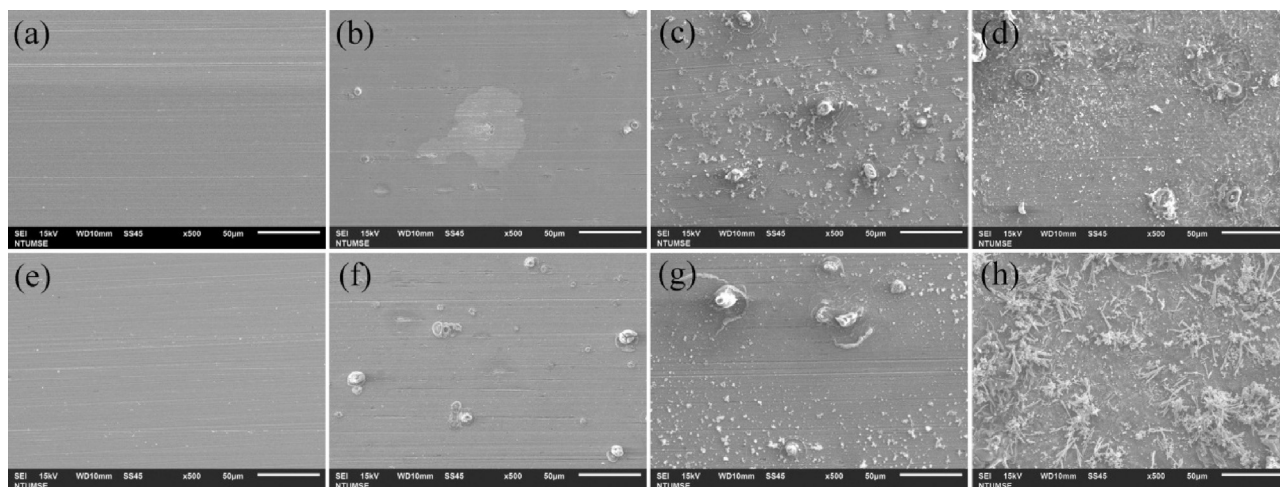


Fig. 4 – SEM images after different immersion times in 3.5 wt% NaCl solution; (a) NiCu as polished; (b) NiCu at 5 min; (c) NiCu at 60 min; (d) NiCu at 7 days; (e) S690Q as polished; (f) S690Q at 5 min; (g) S690Q at 60 min; (h) S690Q at 7 days.

corrosion product was observed in all steel samples. However, the size and density of the local corrosion region on the S690Q steel sample were larger than those on the NiCu sample, which is in agreement with the high anodic dissolution rate obtained in previous polarization measurements. Some snowflake-like particles deposited upon the dark rust layer were observed on all steel samples after 60 min of immersion time (Fig. 4c and g), indicating that the rust layer comprises two parts: loose outer and dense inner layers. After 7 days of immersion (Fig. 4d and h), ground grooves caused by polishing were not distinguishable on the surface of the two steel samples, suggesting that the rust layer was thick. In addition, different amounts of snowflake-like corrosion product were deposited on each surface. Compared with the NiCu steel sample, the S690Q sample showed high surface coverage by snowflake-like corrosion in SEM.

The rust layers were further analyzed using FIB cross-section SEM images. Fig. 5 shows the cross-sectional morphologies of the rust layer on NiCu and S690Q steel samples formed after 7 days of immersion. A rust layer can be observed in all cases, which indicates that the outer rust layer observed in the SEM images fell off when the FIB samples were prepared and rinsed with distilled water. This observation indicates that the outer loose rust layer can be easily removed from the substrate, indicating less protection for the steel substrate. By contrast, the compact rust layer in contact with the substrate remained attached to the surface, exhibiting appropriate protection for the substrate. The layer can be considered the primary barrier for reducing the permeation of corrosive species. The average thickness of this inner rust layer for the NiCu and S690Q steel samples was 1750 and 900 nm, respectively. The reduction in the thickness of the inner rust layer (Fig. 5b) can be probably attributed to the high anodic dissolution rate and numerous oxygen reduction reactions on the S690Q steel sample. Intensive O_2 bubbling facilitates the transport of dissolution ions (e.g., Fe^{2+} ions) away from the surface and obstructs rust layer deposition. Therefore, the precipitation speed of the corrosion product is reduced, resulting in thinner rust layers.

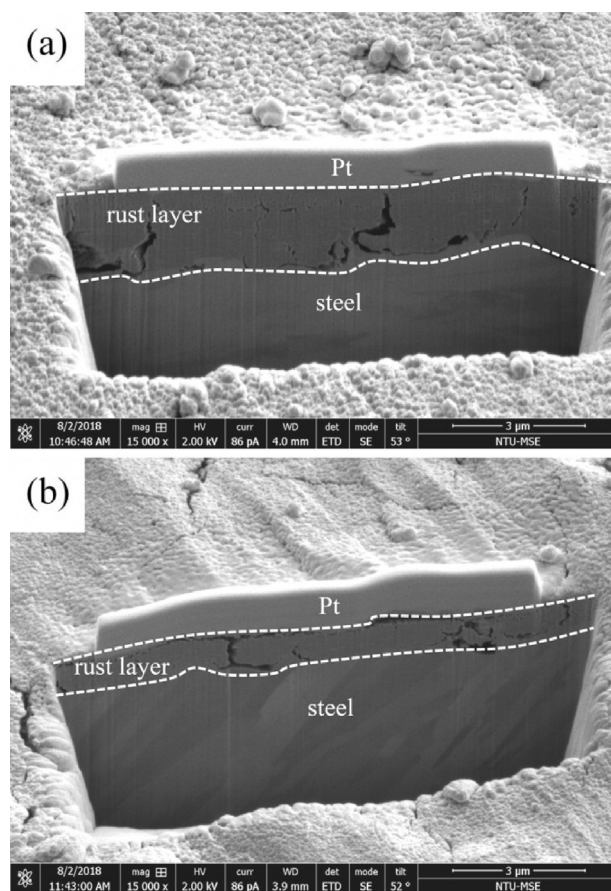


Fig. 5 – FIB cross-section SEM images of the rust layer on (a) NiCu and (b) S690Q steel samples formed after 7 days of immersion.

3.3. Rust characterization

To determine the distributions of elements in the rust layer on the two steel samples, rust layer cross-sections were

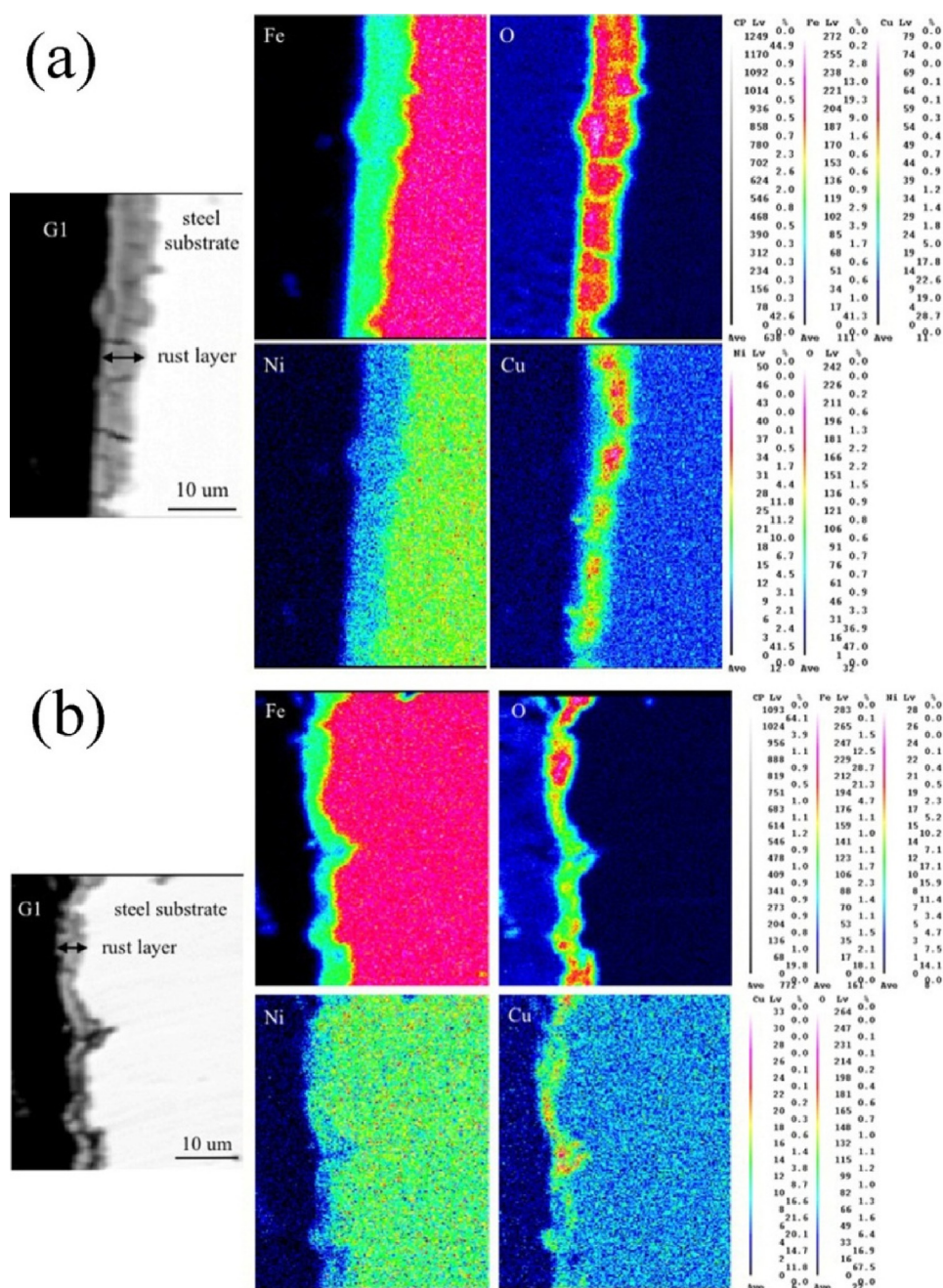


Fig. 6 – EPMA mapping of alloying elements in the rust layer formed on the steel samples after 7 days of immersion; (a) NiCu (b) S690Q.

examined using an EPMA. Fig. 6 shows the results. Firstly, it can be seen that the S690Q steel sample was unevenly corroded. The rust layer of the S690Q steel sample was rougher than that of the NiCu sample, which corresponds to the differences in their dissolution rates. Fig. 6 shows the EPMA mapping results of alloying elements, revealing the enrichment of Cu in the region of the inner rust layer in all samples. Fig. 6a indicates that the NiCu steel sample exhibited a high-density Cr-rich region in the inner rust layer. The inner rust layer of the alloying samples was not enriched in Ni, which may be attributed to the short immersion time; thus, less Ni compound was observed in this study.

Figs. 7 and 8 show the results of XPS analyses on the rust layer on the two steel samples after 7 days of immersion. Figs. 7a and 8a show the overall spectra of the specimens. No considerable difference was found for Fe, O, or C; however, the Cu signal was slightly intensified on the spectrum for the NiCu steel sample. The Ni signal was not detected in the rust layer through XPS, because less Ni compound was observed. Figs. 7b and 8b show the Fe 2p spectrum of the two steel samples. Three overlapping peaks at 709.6, 710.8, and 711.8 eV corresponding to $\text{Fe}_{\text{ox}}^{2+}$, $\text{Fe}_{\text{hy}}^{3+}$, and $\text{Fe}_{\text{ox}}^{3+}$, respectively, were detected which indicated that Fe_3O_4 , Fe_2O_3 , and FeOOH coexisted in the rust layer. For the Cu 2p spectrum (Figs. 7c and 8c),

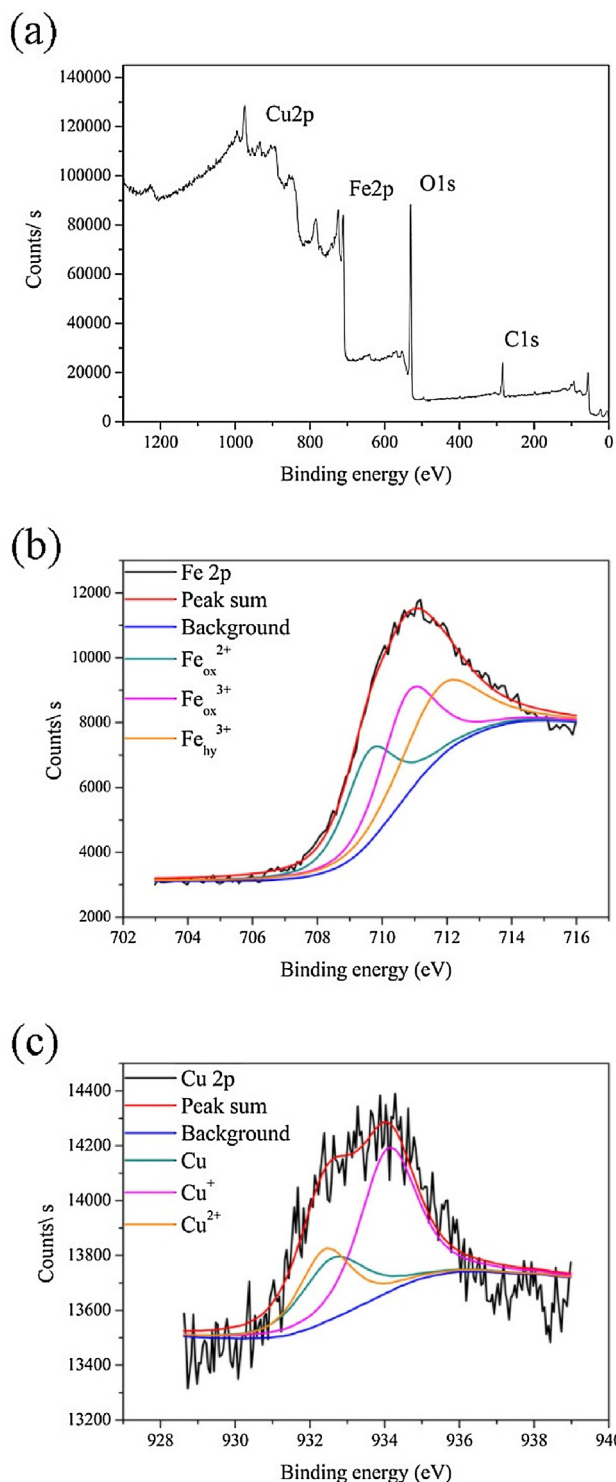


Fig. 7 – (a) Overall XPS spectra of NiCu steel sample after 7 days of immersion in 3.5 wt% NaCl solution; high-resolution XPS spectra for (b) Fe 2p and (c) Cu 2p.

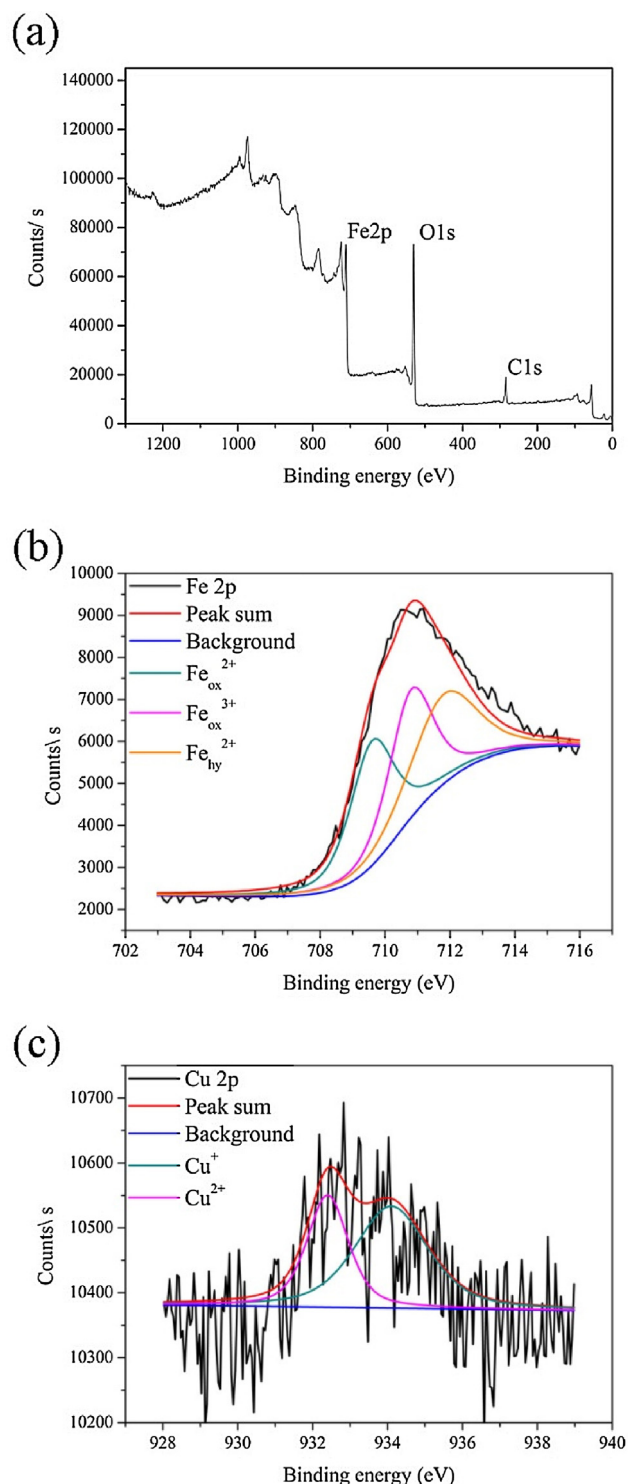


Fig. 8 – (a) Overall XPS spectra of S690Q steel sample after 7 days of immersion in 3.5 wt% NaCl solution; high-resolution XPS spectra for (b) Fe 2p and (c) Cu 2p.

both the NiCu and S690 spectra presented three overlapping peaks at 932.6, 934.1, and 932.4 eV corresponding to Cu⁰, Cu¹⁺, and Cu²⁺, respectively. XPS results indicated the precipitation of Cu and Cu oxides (CuO and Cu₂O) on the surface of the steel samples. However, compared with the NiCu steel

sample, Cu signals were less intense for the S690Q sample after 7 days of immersion. This observation is consistent with the previous EPMA result, which indicated that the low density of the Cr-rich region in the inner rust layer on the S690Q steel sample.

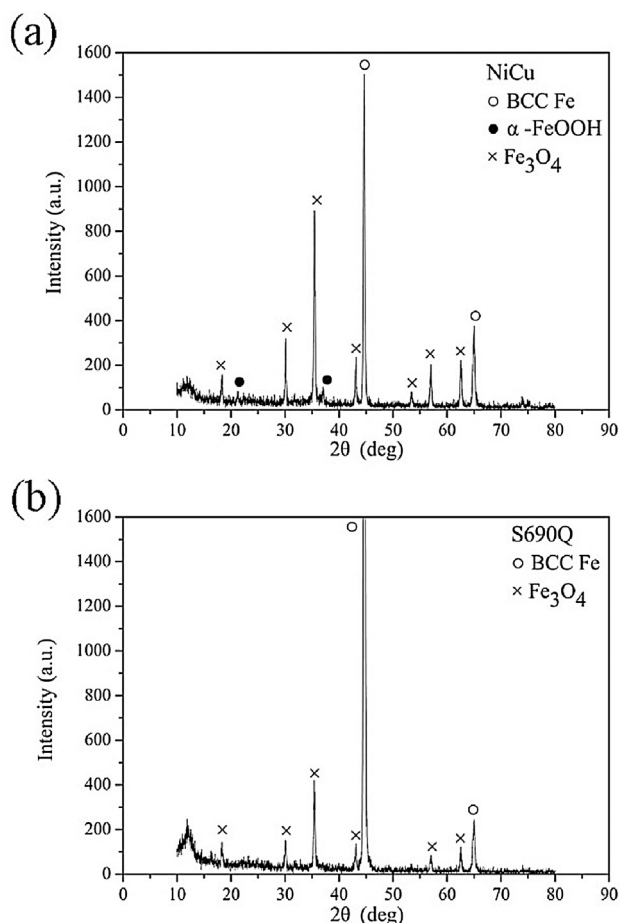


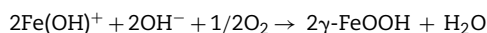
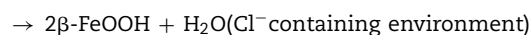
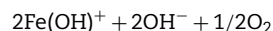
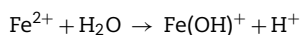
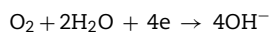
Fig. 9 – XRD pattern of (a) NiCu and (b) S690Q steel samples after 7 days of immersion test.

Because of weldability concerns, the C content of newly designed NiCu alloy steel has been restricted. To compensate for the reduction in strength with the decreasing C concentration, more Cu was added to NiCu steel for precipitation strengthening. Apart from increasing hardenability, Cu has been added to steels to improve corrosion resistance [13–16]. For example, Hong et al. [14] analyzed the effect of Cu addition on the corrosion resistance of low-alloy steel in sulfuric acid. The Cu-containing steel provides considerably lower corrosion rates than Cu-free steel in a sulfuric acid solution. In addition, they also observed that the accumulated Cu compound on the surface, which primarily comprised Cu and Cu oxides associated with FeOOH, improved the corrosion resistance of the low-alloy steel by reducing the active dissolution of the substrate. Ujiro et al. [15] explained that alloying Cu on the corrosion resistance for both ferritic and austenitic stainless steels is beneficial because of the stability of the deposited Cu on the anodic surface. Xi et al. [16] studied the effect of adding different amounts of Cu on the corrosion resistance of 316L austenitic stainless steel. Their results indicated that the pitting and protective potential of 316L–Cu stainless steel increased with increasing Cu content in the solution state. In general, in the research regarding Cu-bearing steels, the copper layer formed on the steel surface suppressed the anodic dissolution rate of the steel through blocking and screening

mechanisms [14–17]. Therefore, the lower anodic dissolution rate on the NiCu steel sample can be partially attributed to the formation of a more protective rust layer containing larger copper compounds.

The rust layers formed on the surface were identified through XRD. Fig. 9 shows the XRD spectra of the two steel samples after the 7 day immersion test. In addition to the peaks of bcc iron, Fe₃O₄ is identified as a corrosion product formed on all steel samples in an XRD pattern. Furthermore, peaks of α-FeOOH were detected on the NiCu steel sample because Cu accelerates the transformation of ferric oxyhydroxide into α-FeOOH [18–21].

Several studies have demonstrated that rust formed on steel primarily comprises ferric oxyhydroxides (FeOOH), including goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), and magnetite (Fe₃O₄), and many X-ray amorphous compounds [22–24]. Among these corrosion products, β-FeOOH can be preferentially formed in the rust layer on steel exposed to chloride-ion environments [25–30]. The irreversible formation of β-FeOOH and γ-FeOOH under oxidizing conditions are as follows [31]:



At a later corrosion stage, these metastable phases, such as β-FeOOH and γ-FeOOH, gradually transform into a thermodynamically stable phase of α-FeOOH [24,31–34]. Therefore, the lower anodic dissolution rate on the NiCu sample can be partially attributed to the presence of the more stable and protective structure of α-FeOOH in the rust layer.

4. Conclusion

In our previous study, the mechanical properties of a newly designed NiCu steel and conventional S690Q steel were systematically investigated; NiCu steel had higher yield strength and superior toughness. In this study, the corrosion behavior and properties of the rust layer of the two alloy steels in a Cl[−]-containing environment were further evaluated and characterized. The preliminary results of this study are summarized as follows:

1. Potentiodynamic polarization results indicated that the NiCu steel exhibited an apparent reduction in current densities in the anodic region.
2. The NiCu steel had higher R_{ct} values than the S690Q steel sample for the entire immersion time up to 144 h,

indicating that the NiCu steel is more resistant to corrosion than the S690Q steel in NaCl solution.

3. Surface analyses indicated that a higher Cu content in the alloy steel (NiCu) created a thicker and more uniform inner rust layer after 7 days of immersion in NaCl solution.
4. The higher density of the Cr-rich region in the NiCu inner rust layer was observed through the EPMA and XPS analysis. The accumulated Cu compound, which primarily comprised Cu and Cu oxides, improved the corrosion resistance of the low-alloy steel by suppressing the anodic dissolution rate.
5. The XRD results indicated that the higher Cu content in the alloy steel (NiCu) improved the passivity by facilitating the formation of a more protective and stable phase of α -FeOOH.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

This work was sponsored by the Ministry of Science and Technology, R.O.C., under Grant No. MOST 107-2221-E-002-085. We acknowledge Mr. Meng-Hsuan Chiang for providing technical assistance and valuable contributions.

REFERENCES

- [1] Yen HW, Chiang MH, Lin YC, Chen D, Huang CY, Lin HC. High-temperature tempered martensite embrittlement in quenched-and-tempered offshore steels. *Metals* 2017;7(7):253–65.
- [2] Mujahid M, Lis AK, Garcia CI, DeArdo AJ. HSLA-100 steels: Influence of aging heat treatment on microstructure and properties. *J Mater Eng Perform* 1998;7:247–57.
- [3] Hao W, Liu Z, Wu W, Li X, Du C, Zhang D. Electrochemical characterization and stress corrosion cracking of E690 high strength steel in wet-dry cyclic marine environments. *Mater Sci Eng A* 2018;710:318–28.
- [4] Wu W, Hao WK, Liu ZY, Li XG, Du CW, Liao WJ. Corrosion behavior of E690 high-strength steel in alternating wet-dry marine environment with different pH values. *J Mater Eng Perform* 2015;24(12):4636–46.
- [5] Li J, Wu J, Wang Z, Zhang S, Wu X, Huang Y, et al. The effect of nanosized NbC precipitates on electrochemical corrosion behavior of high-strength low-alloy steel in 3.5%NaCl solution. *Int J Hydrogen Energy* 2017;42(34):22175–84.
- [6] Yang Y, Zhang T, Shao Y, Meng G, Wang F. Effect of hydrostatic pressure on the corrosion behaviour of Ni–Cr–Mo–V high strength steel. *Corros Sci* 2010;52(8):2697–706.
- [7] Shi Y, Yang B, Xie X, Brechtel J, Dahmen KA, Liaw PK. Corrosion of $\text{Al}_x\text{CoCrFeNi}$ high-entropy alloys: Al-content and potential scan rate dependent pitting behavior. *Corros Sci* 2017;119:33–45.
- [8] Lopez DA, Simison SN, de Sanchez SR. The influence of steel microstructure on CO_2 corrosion. EIS studies on the inhibition efficiency of benzimidazole. *Electrochim Acta* 2003;48(7):845–54.
- [9] Popova A, Christov M, Vasilev A. Inhibitive properties of quaternary ammonium bromides of N-containing heterocycles on acid mild steel corrosion. Part II: EIS results. *Corros Sci* 2007;49(8):3290–302.
- [10] Kissi M, Bouklah M, Hammouti B, Benkaddour M. Establishment of equivalent circuits from electrochemical impedance spectroscopy study of corrosion inhibition of steel by pyrazine in sulphuric acidic solution. *Appl Surf Sci* 2006;252(12):4190–7.
- [11] Qiu Y, Thomas S, Gibson MA, Fraser HL, Pohl K, Birbilis N. Microstructure and corrosion properties of the low-density single-phase compositionally complex alloy AlTiVCr. *Corros Sci* 2018;133:386–96.
- [12] Hassan HH, Abdelghani E, Amin MA. Inhibition of mild steel corrosion in hydrochloric acid solution by triazole derivatives: Part I. Polarization and EIS studies. *Electrochim Acta* 2007;52(22):6359–66.
- [13] Kato C, Grabke HJ, Egert B, Panzner G. Electrochemical and surface analytical studies on hydrogen permeation with Fe–Cu alloys in sulfuric acid with and without H_2S . *Corros Sci* 1984;24(7):591–611.
- [14] Hong JH, Lee SH, Kim JG, Yoon JB. Corrosion behaviour of copper containing low alloy steels in sulphuric acid. *Corros Sci* 2012;54:174–82.
- [15] Ujiro T, Satoh S, Staehle RW, Smyrl WH. Effect of alloying Cu on the corrosion resistance of stainless steels in chloride media. *Corros Sci* 2001;43(11):2185–200.
- [16] Xi T, Shahzad MB, Xu D, Sun Z, Zhao J, Yang C, et al. Effect of copper addition on mechanical properties, corrosion resistance and antibacterial property of 316L stainless steel. *Mater Sci Eng C* 2017;71:1079–85.
- [17] Hao L, Zhang S, Dong J, Ke W. A study of the evolution of rust on Mo–Cu-bearing fire-resistant steel submitted to simulated atmospheric corrosion. *Corros Sci* 2012;54:244–50.
- [18] Chen AH, Xu JQ, Li R, Li HL. Corrosion resistance of high performance weathering steel for bridge building applications. *J Iron Steel Res Int* 2012;19(6):59–63.
- [19] Yamashita M, Miyuki H, Matsuda Y, Nagano H, Misawa T. The long term growth of the protective rust layer formed on weathering steel by atmospheric corrosion during a quarter of a century. *Corros Sci* 1994;36(2):283–99.
- [20] Stratmann M, Bohnenkamp K, Ramchandran T. The influence of copper upon the atmospheric corrosion of iron. *Corros Sci* 1987;27(9):905–26.
- [21] Zhang QC, Wu JS, Wang JJ, Chen JG, Li AB. Corrosion behavior of weathering steel in marine atmosphere. *Mater Chem Phys* 2002;77(2):603–8.
- [22] Diaz I, Cano H, de la Fuente D, Chico B, Vega JM, Morcillo M. Atmospheric corrosion of Ni-advanced weathering steels in marine atmospheres of moderate salinity. *Corros Sci* 2013;76:348–60.
- [23] Cano H, Neff D, Morcillo M, Dillmann P, Diaz I, de la Fuente D. Characterization of corrosion products formed on Ni 2.4 wt%–Cu 0.5 wt%–Cr 0.5 wt% weathering steel exposed in marine atmospheres. *Corros Sci* 2014;87:438–51.
- [24] Hao L, Zhang S, Dong J, Ke W. Evolution of corrosion of MnCuP weathering steel submitted to wet/dry cyclic tests in a simulated coastal atmosphere. *Corros Sci* 2012;58:175–80.
- [25] Ma Y, Li Y, Wang F. Corrosion of low carbon steel in atmospheric environments of different chloride content. *Corros Sci* 2009;51(5):997–1006.
- [26] Morcillo M, de la Fuente D, Diaz I, Cano H. Atmospheric corrosion of mild steel. *Rev Metal Madrid* 2011;47(5):426–44.
- [27] Singh AK, Ericsson T, Häggström L, Gullman J. Mössbauer and X-ray diffraction phase analysis of rusts from atmospheric test sites with different environments in Sweden. *Corros Sci* 1985;25(10):931–45.
- [28] Misawa T, Hashimoto K, Shimodaira S. The mechanism of formation of iron oxide and oxy-hydroxides in aqueous solutions at room temperature. *Corros Sci* 1974;14(2):131–49.

-
- [29] Antunes RA, Costa I, Araujo DL. Characterization of atmospheric corrosion products formed on steels. *Mater Res* 2003;6(3):403–8.
- [30] Misawa T, Asami K, Hashimoto K, Shimodaira S. The mechanism of atmospheric rusting and the protective amorphous rust on low alloy steel. *Corros Sci* 1974;14(4):279–89.
- [31] Zhou Y, Chen J, Xu Y, Liu Z. Effects of Cr, Ni and Cu on the corrosion behavior of low carbon microalloying steel in a Cl⁻ containing environment. *Mater Sci Technol* 2013;29(2):168–74.
- [32] Oh SJ, Cook DC, Townsend HE. Atmospheric corrosion of different steels in marine, rural and industrial environments. *Corros Sci* 1999;41(9):1687–702.
- [33] Hiller JE. Phasenumwandlungen im Rost. *Mater Corros* 1966;17(11):943–51.
- [34] Keller P. Quantitative, röntgenographische Phasenanalyse verschiedener Rosttypen. *Mater Corros* 1967;18(10):865–78.