Corrosion Behavior of NiCu Low-Alloy Steel in Deoxygenated NaHCO3 Solution Containing Cl- (Postprint)

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Abstract

The evolution of open-circuit potential curves and impedance spectra of NiCu low-alloy steel was monitored in-situ under long-term immersion conditions in a simulated deep groundwater environment, namely deoxygenated 0.1 mol/L $NaHCO_3$ + 0.1 mol/L NaCl solution, to investigate the corrosion evolution mechanism on the electrode surface, and compared with the corrosion behavior of low-carbon steel under identical conditions. The results demonstrate that the corrosion resistance of NiCu low-alloy steel in the experimental solution is significantly superior to that of low-carbon steel, particularly regarding its resistance to localized corrosion. The alloying element Ni enriches in the inner rust layer, possibly existing as $NiFe_2O_4$, whereas the enrichment of Cu is not pronounced, with a possible existence form of $CuFeO_2$.

Full Text

Preamble

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Corrosion Behavior of NiCu Low Alloy Steel in a Deaerated $NaHCO_3$ Solution Containing Cl^- Ions

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Abstract The corrosion evolution of NiCu low alloy steel was investigated in a simulated deep groundwater environment (deaerated 0.1 mol/L $NaHCO_3$ + 0.1 mol/L NaCl solution) through in-situ monitoring of open-circuit potential variations and impedance spectra evolution during long-term immersion, with results compared to those of low carbon steel under identical conditions. The findings demonstrate that NiCu low alloy steel exhibits significantly superior corrosion resistance to low carbon steel, particularly in terms of localized corrosion resistance. The alloying element Ni enriches in the inner rust layer, likely existing as $NiFe_2O_4$, while Cu enrichment is less pronounced, possibly present as $CuFeO_2$.

Keywords low alloy steel, rust layer, HCO_3^-, Cl^-

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THE CORROSION BEHAVIOUR OF NiCu LOW ALLOY STEEL IN A DEAERATED BICARBONATE SOLUTION CONTAINING Cl^- IONS

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ABSTRACT The corrosion behaviour of low alloy steel containing Ni and Cu was studied because it is a promising candidate canister material for the disposal of high-level radioactive waste (HLW) in China. Due to the intensely radioactive nature of HLW, the waste has to be prevented from reaching the biosphere for many tens of thousands of years. Deep geological disposal is now considered to be the most preferable option for isolating HLW and it relies on series of natural and engineered barriers, e.g. a metallic canister. However, as soon as the waste package is settled, groundwater would seep back slowly through the outer barriers and ultimately arrive at the surface of the canister. Accordingly, there comes the groundwater-induced dissolution of the canister and subsequent transport of radionuclides through the barriers. That is to say, the effectiveness of radionuclide retention and isolation depends mostly and finally on the corrosion resistance of metallic canisters in deep groundwater environments.

In this work, the test solution is deaerated 0.1 mol/L $NaHCO_3$+0.1 mol/L NaCl, simulating the deep groundwater environment. The evolution of corrosion of

NiCu low alloy steel in the test solution was investigated by electrochemical measurements. XRD was used to illustrate the composition of formed corrosion products. SEM was used to observe the electrode surface morphology and the cross section of the rust layer. The electrochemical results showed that low alloy steel has a lower corrosion rate and is less prone to localized corrosion than low carbon steel.

In order to understand the mechanism of alloying elements, EDS and EPMA were used to analyse the distribution of alloying elements cross-sectional. XPS and E-pH diagram were used to estimate the possible existence form of alloying elements. By means of EDS and EPMA, it was founded that Ni is concentrated in the inner rust layer while the enrichment of Cu is not so obvious. XRD, XPS and E-pH results indicated that Ni and Cu are existed in the form of $NiFe_2O_4$ and $CuFeO_2$ respectively.

KEY WORDS low alloy steel, rust, HCO_3^-, Cl^-

Introduction

Deep geological disposal is currently the internationally preferred approach for permanent management of high-level radioactive waste, and China intends to adopt this strategy. In this scheme, metallic canisters serve as the first engineered barrier for storing vitrified high-level waste. Consequently, whether these canisters can achieve their required service life represents a critical factor determining the success of high-level waste disposal. During long-term geological disposal, groundwater will gradually diffuse to the canister surface, causing corrosion and eventual failure. Various metallic materials including low carbon steel, Cu, titanium alloys, and nickel-based alloys have been evaluated for service life under different geological disposal conditions worldwide.

Low carbon steel is considered a quasi-corrosion-resistant metal that exhibits a certain corrosion rate but low susceptibility to localized corrosion, enabling service life predictions under disposal conditions. However, studies have revealed that in groundwater environments, low carbon steel exists in a reactivated state following passivation, resulting in relatively high corrosion rates. When the solution contains SO_4^{2-} ions, the metal surface shows uniform corrosion morphology, whereas Cl^- ions induce localized corrosion morphology. This indicates that in actual disposal scenarios, low carbon steel canisters would have high corrosion rates due to their reactivated state, and when groundwater contains aggressive ions, they could suffer localized corrosion perforation or stress corrosion cracking, failing to meet design lifetime requirements. Therefore, from both economic and safety perspectives, it is necessary to investigate improving low carbon steel corrosion resistance through alloying—adding alloying elements that enhance corrosion resistance in groundwater environments.

Nishimura et al. studied the atmospheric corrosion resistance of low alloy steels containing Co or Ni, finding that Co likely exists in trivalent form within FeOOH, helping the rust layer block aggressive anions like Cl^-, though this effect was only significant in early stages. Ni likely exists in divalent form within Fe_3O_4, increasing inner rust layer density with more pronounced effects in later stages. Wang et al. obtained corrosion rate curves over 5 years for weathering steel containing Cr, Cu, P, and Ni versus carbon steel in three atmospheric environments, attributing the lower corrosion rate of weathering steel to alloying element enrichment in the rust layer. Cao et al. compared the pitting corrosion resistance of Ni-Cu-P steel, Cu-containing low alloy steel, and carbon steel in seawater splash zones, demonstrating that Ni-Cu-P steel exhibited superior uniform and pitting corrosion resistance compared to carbon steel. In fact, Ni-Cu-P series low alloy steel was commercially produced in the United States as early as 1964 as a steel grade with excellent corrosion resistance in seawater splash zones. Additionally, NiCu low alloy steel has seen significant development in Japan in recent years, primarily for use in areas with high Cl^- content such as marine atmospheric environments. However, no reports exist on the applicability of such steels to high-level radioactive waste geological disposal environments. Therefore, this work selected NiCu low alloy steel as a candidate canister material for high-level radioactive waste geological disposal, investigating its corrosion behavior in deaerated Cl^--containing $NaHCO_3$ solution and comparing it with low carbon steel under identical conditions.

Experimental

A three-electrode system was employed. The electrolyte solution was 0.1 mol/L $NaHCO_3$ + 0.1 mol/L NaCl. The test samples were bulk specimens of NiCu low alloy steel and Q235 low carbon steel with chemical compositions shown in , each measuring 10 mm × 10 mm × 3 mm. The working electrode area was 100 mm^2, with remaining surfaces sealed with epoxy resin. The reference electrode was saturated calomel electrode (SCE) and the counter electrode was Pt sheet. For long-term immersion tests of NiCu low alloy steel, in addition to one working electrode sample, three additional bulk samples were prepared in the same container for subsequent analysis. All samples were ground sequentially with sandpaper to 800 grit, then rinsed with deionized water, degreased with ethanol, and dried.

Prior to experiments, high-purity N_2 (99.999%) was continuously purged into the sealed electrolytic cell containing electrolyte solution for deoxygenation. Simultaneously, samples were lightly polished with 800-grit sandpaper in the same electrolyte solution to remove surface films before immediate immersion into the cell. After 30 minutes of continued gas purging, experiments commenced, with a water-sealed bottle maintaining high-purity N_2 in the cell headspace throughout testing. Polarization curves were measured using a PARSTAT 2273 electrochemical workstation. After the working electrode' s open-circuit potential stabilized, scanning was performed from -1.0 V to 0.4 V at 10 mV/min. Long-term in-situ corrosion potential monitoring was conducted using an HA-151A potentiostat, pausing only when impedance measurements were required. All potentials were measured relative to SCE. Electrochemical impedance spectra were measured using a PARSTAT 2273 workstation over a frequency range of 0.01 Hz to 100 kHz. After NiCu low alloy steel immersion testing, three bulk samples were removed from the sealed cell, dried under high-purity N_2 flow, and sealed for storage.

A Shimadzu XD-5A X-ray diffractometer (XRD) was used to analyze corrosion products on one sample (No.1). The corrosion products were then removed using pickling solution (20 g $(CH_2)_6N_4$ + 500 mL HCl + 500 mL H_2O), and surface corrosion morphology was observed using an FEI XL-30FEG scanning electron microscope (SEM). Another sample (No.2) was entirely encapsulated in epoxy resin, slowly ground to polish with 400-grit sandpaper to prepare a cross-sectional sample, then rinsed with deionized water, degreased with ethanol, and dried. Cross-sectional corrosion morphology was observed using FEI XL-30FEG SEM, and element line scanning across the rust layer cross-section was performed using energy dispersive spectroscopy (EDS). A Shimadzu EPMA-1610 electron probe microanalyzer (EPMA) was then used for element mapping of the rust layer cross-section. The final sample (No.3) had its loose outer rust layer removed with stainless steel foil, and inner rust layer alloying element valence states were analyzed using a Thermo ESCALAB250 X-ray photoelectron spectroscope (XPS).

Results and Discussion

2.1 Comparison of Corrosion Resistance Between NiCu Low Alloy Steel and Low Carbon Steel

The dashed line in [Figure 1: see original paper]a shows the polarization curve of NiCu low alloy steel in deaerated $NaHCO_3$ solution containing Cl^-. The corrosion potential of NiCu steel in the test solution is approximately -0.780 V, with hydrogen evolution as the cathodic reaction and anodic behavior describable as active, passivation, passive, and reactivation regions. In the active region (-0.78 to -0.63 V), anodic corrosion current density increases rapidly with positive potential scanning. In the passivation region (-0.63 to -0.48 V), anodic corrosion current density decreases significantly with positive potential scanning, indicating formation of protective product films on the substrate surface with gradually increasing protective capability. In the passive region (-0.48 to -0.20 V), anodic corrosion current density fluctuates around 2.7 mA/cm^2 rather than showing monotonic increase or decrease, with maximum and minimum values of 4.5 mA/cm^2 and 1.25 mA/cm^2 respectively. These fluctuations likely result from competitive adsorption between aggressive Cl^- and protective species. When scanning potential exceeds -0.20 V, the sample enters the reactivation region, where anodic corrosion current density increases exponentially with positive potential scanning, eventually reaching the anodic limiting diffusion current density.

Under identical experimental conditions, low carbon steel polarization curve results are shown as the dashed line in [Figure 1: see original paper]b. Comparison with NiCu low alloy steel reveals that low carbon steel' s corrosion potential is approximately -0.810 V, more negative than NiCu low alloy steel' s, with both cathodic regions dominated by hydrogen evolution. In the anodic region, low carbon steel' s passivation potential is approximately -0.658 V, also more negative than NiCu low alloy steel' s. After the passivation region, low carbon steel does not enter a passive interval like NiCu low alloy steel but rapidly transitions to reactivation (pitting) state. Furthermore, the minimum anodic current density achieved before entering the reactivation region is 13.44 mA/cm^2, nearly an order of magnitude higher than NiCu low alloy steel' s passive region current density. These results demonstrate that NiCu low alloy steel exhibits superior corrosion resistance in the test solution; passive films form more readily on NiCu low alloy steel substrate and remain more stable; and NiCu low alloy steel' s corrosion rate is nearly an order of magnitude lower than low carbon steel' s before entering the reactivation region.

The solid line in [Figure 1: see original paper]a shows NiCu low alloy steel electrode' s open-circuit potential versus time during 28 days of immersion in deaerated $NaHCO_3$ solution containing Cl^-. This curve can be divided into three stages: low-potential region before transition, high-potential transition region after transition, and high-potential stable region after transition. During the first 3 days of stage one, NiCu low alloy steel' s open-circuit potential stabilizes around -0.77 V, close to the corrosion potential in the polarization curve, indicating no protective corrosion product film coverage on the electrode surface in early immersion. After day 3, the open-circuit potential begins slowly shifting positive with fluctuations, indicating gradual formation of protective corrosion products on the electrode surface. By day 11, the open-circuit potential has risen to approximately -0.70 V. Within half a day, NiCu low alloy steel' s open-circuit potential undergoes abrupt change, steeply rising from -0.70 V to approximately -0.50 V, indicating fundamental changes in the corrosion products covering the electrode surface. Comparison with polarization curves suggests the electrode surface is likely in the passivation region, meaning the protective capability of the surface corrosion product film is relatively good at this time. In stage two (days 11-20), NiCu low alloy steel electrode surface open-circuit potential exhibits oscillation after climbing, with maximum oscillation value of -0.45 V (stable passivation region according to polarization curves) and minimum of -0.58 V (passivation region). This indicates simultaneous rupture and repair processes of protective corrosion product films on NiCu low alloy steel electrode surface, showing instability. In stage three (after 20 days), NiCu low alloy steel' s open-circuit potential in the test solution stabilizes at approximately -0.52 V. Referring to corresponding polarization curves, NiCu low alloy steel electrode surface is considered to be stably near the Flade potential after 28 days of immersion, approaching a passive state.

Low carbon steel' s open-circuit potential versus time during 35 days of immersion in the test solution is shown as the solid line in [Figure 1: see original paper]b. Results indicate that low carbon steel surface electrode potential changes can be simply divided into two stages. In stage one (first 20 days), open-circuit potential slowly rises from -0.81 V to approximately -0.76 V. Subsequently, potential transition completes rapidly, entering stage two. In stage two (after 20 days), low carbon steel' s open-circuit potential shifts positive, reaching a maximum value of approximately -0.48 V. Based on corresponding polarization curve results, low carbon steel electrode surface should be in a reactivated (pitting) state, with surface corrosion product films beginning to change and protective effects declining. Subsequently, open-circuit potential shifts slightly negative to approximately -0.52 V, indicating the electrode surface is at the boundary between passivation and pitting, with unstable surface corrosion product films. After this, open-circuit potential shows a slowly rising trend, with electrode surface gradually developing toward reactivation state and protective capability of corrosion product films declining. Meanwhile, during stage two, open-circuit potential occasionally shows potential drops during its rising process, with minimum drop values around -0.56 V, indicating transition toward passivation state according to polarization curve results. These are all manifestations of unstable corrosion products on electrode surface. These results demonstrate that in the same deaerated $NaHCO_3$ solution containing Cl^-, NiCu low alloy steel' s open-circuit potential ultimately stabilizes in the later passivation region with better protective corrosion product films and lower corrosion rates, while low carbon steel's open-circuit potential ultimately stabilizes in the post-passivation reactivation (pitting) region, with corrosion product films beginning to lose protectiveness and higher corrosion rates.

To further investigate changes in electrode surface corrosion resistance during immersion, electrochemical impedance spectra of both electrodes after different immersion times are shown in [Figure 2: see original paper].

As seen in [Figure 2: see original paper]a, during stage one (first 11 days) of immersion, NiCu low alloy steel' s Bode phase angle plots exhibit a single phase angle peak. With prolonged immersion time, the phase angle peak shifts toward low frequency region, with peak frequency decreasing from approximately 6 Hz to 1 Hz. Phase angle peak values increase slightly from 65° to approximately 70°. Additionally, phase angle peaks show certain diffusion characteristics in low frequency region, which weaken with immersion time. Bode impedance plots correspondingly show impedance reduction, with low-frequency (10 mHz) impedance decreasing from 3250 $\Omega \cdot cm^2$ to approximately 1783 $\Omega \cdot cm^2$, and high-frequency (10 kHz) impedance decreasing from 17.4 $\Omega \cdot cm^2$ to approximately 10.1 $\Omega \cdot cm^2$. In stage one, corrosion processes become easier with prolonged immersion time, and low alloy steel corrosion rates increase. This indicates that corrosion products formed on NiCu low alloy steel in stage one are not protective but may accelerate substrate corrosion through galvanic effects. In stages two and three after potential mutation (after day 11), sample Bode phase angle plots change significantly, no longer showing single symmetric phase angle peaks. This phenomenon is typically attributed to superposition of multiple time constants. In high frequency region (100 Hz-10 kHz), Bode phase angle plots show a weak phase angle peak; while in low and medium frequency regions (<100 Hz), Bode phase angle plots show an extremely asymmetric broad phase angle peak resulting from superposition of two time constants. In this work, the test solution uses mixed $NaHCO_3$ and NaCl solution, so when HCO_3^- and Cl^- accumulate in different locations on electrode surface, different corrosion modes (uniform corrosion, pitting, etc.) occur in different regions, leading to superposition of multiple time constants. Bode impedance plots after potential mutation show certain degree of overlap, especially in high frequency region (>100 Hz) where impedances are similar. Low-frequency impedance increases slightly with immersion time, possibly because protective corrosion product films have formed on electrode surface in later stage three, reducing corrosion rates to some extent.

Low carbon steel electrochemical impedance spectra ([Figure 2: see original paper]c) show that in stage one (first 20 days), Bode phase angle plots also present as single phase angle peaks, which shift slightly toward low frequency with prolonged immersion time, with peak frequency decreasing from approximately 4.6 Hz to 2.4 Hz. Phase angle peak values show little variation, basically maintaining around 63°. Phase angle curves also show weak diffusion characteristics in low frequency region, weakening with immersion time. Additionally, certain degree of high-frequency phase shift was detected in these experimental results, but this is generally considered experimental error. Bode impedance plot results show that three curves measured in stage one basically overlap. In stage two after potential mutation (after day 20), both phase angle and impedance curves show obvious changes. Similar to low alloy steel results, sample Bode phase angle plots no longer show single symmetric phase angle peaks but rather superposition of multiple time constants. A weak phase angle peak appears in high frequency region (>10 Hz), with phase angle peak values increasing with immersion time. A broad asymmetric peak appears in medium-low frequency region (<10 Hz), showing superposition of at least two time constants, with phase angle peak values decreasing with immersion time. Bode impedance plots show that impedance increases with immersion time except at lowest frequency values.

To better analyze measured impedance spectra curves, two corresponding equivalent circuits were selected for fitting, as shown in [Figure 3: see original paper]. [Figure 3: see original paper]a is used to fit electrochemical impedance spectra data obtained during stage one before open-circuit potential mutation. Where R is solution resistance; Q is double layer capacitance; R is charge transfer resistance; W is Warburg impedance; Q is high-frequency capacitance, which only appears in low carbon steel electrochemical impedance spectra data and was not measured in low alloy steel data, thus component Q is connected with dashed lines in [Figure 3: see original paper]a. [Figure 3: see original paper]b is the equivalent circuit corresponding to electrochemical impedance spectra measured after open-circuit potential transition. Where Q and R are capacitance and resistance of precipitated corrosion products layer respectively, Q and R are capacitance and resistance of pitted area respectively, Q and R are capacitance and resistance of passive area respectively. Q is also connected with dashed lines in [Figure 3: see original paper]b because it appears in later low carbon steel electrochemical impedance spectra data but was never measured in low alloy steel data. Fitting results for these two circuits are listed in Tables 2 and 3 respectively. For constant phase element (CPE), Q , Q , Q , Q and Q , impedance Z depends on angular frequency ω: $Z = Y_0{}^{-1}(j\omega)^{-n}$. Therefore equivalent component Q has two parameters: Y_0 with dimensions $S \cdot s^n \cdot cm^{-2}$, and dimensionless exponent n. Depending on n value, CPE can represent inductance (n = -1), resistance (n = 0), Warburg impedance (n = 0.5), and pure capacitance (n = 1).

Table 2 shows that both R and R of low alloy steel decrease with immersion time, indicating easier corrosion processes. Correspondingly, Y_0, increases with immersion time, with n above 0.8, possibly related to corrosion product deposition on electrode surface. These newly deposited corrosion products are mostly non-protective and loosely structured, thus increasing interface capacitance. Low carbon steel results show no obvious rising or falling trends for R , R or Y_0, , indicating stable corrosion during stage one immersion. Both materials are in uniform corrosion state at this time. After potential mutation, corrosion behavior of both samples changes significantly. As shown in [Figure 3: see original paper] and Table 3, a corrosion product layer precipitates on the electrode surface exterior, with detected capacitance and resistance denoted as Q and R respectively. Fitting results in Table 3 show that low alloy steel has larger Y_0, and smaller R , while low carbon steel has larger R and smaller Y_0, , with n close to 0.8. These results indicate that in later immersion stage, low alloy steel' s outer product layer structure may be more porous and non-protective than low carbon steel' s. At the interface between corrosion products and substrate, both materials' corrosion behavior changes significantly compared to early immersion, no longer maintaining uniform corrosion but transitioning to composite states of two corrosion behaviors (pitting and passivation). Table 3 shows that low alloy steel' s R , Y_0, and n remain basically stable with little variation. In contrast, low carbon steel shows large differences between two data sets: after 24 days immersion, Y_0, and R are both large, while after 32 days immersion, both Y_0, and R decrease significantly, possibly indicating pitting behavior occurrence. In passivation regions, low alloy steel' s Y_0, remains basically stable, with n close to 0.5, indicating that corrosion products here have blocking effects on reactant or product diffusion. R increases from stage two to stage three, indicating that in later immersion stage, low alloy steel corrosion rates in passivation regions decrease to some extent. For low carbon steel, Y_0, remains low, increasing with immersion time, while R decreases with immersion time, indicating that low carbon steel corrosion rates in passivation regions increase to some extent in later immersion stage.

Previous work has presented surface corrosion morphology of low carbon steel after 30 days immersion in the test solution, showing obvious corrosion pits. [Figure 4: see original paper] shows surface corrosion morphology of NiCu low alloy steel after rust layer removal with pickling solution. [Figure 4: see original paper]a shows the same magnification as low carbon steel surface morphology in literature, but NiCu low alloy steel sample surface exhibits uniform corrosion morphology, while low carbon steel surface shows localized corrosion morphology. At 5000× magnification, as shown in [Figure 4: see original paper]b, fine voids can be observed on the sample surface, preliminarily identified as metastable pitting cavities, mostly located at weak grain boundary regions. This indicates that under identical experimental conditions, low carbon steel undergoes pitting after immersion for some time, while NiCu low alloy steel still mainly shows uniform corrosion, with only fine metastable pitting cavities observed at high magnification. This demonstrates that Ni and Cu alloying elements added to low carbon steel can suppress localized corrosion and promote uniform corrosion development.

2.2 Mechanism of Alloying Elements

[Figure 5: see original paper] shows XRD pattern of NiCu low alloy steel products after 28 days immersion in the test solution. The corrosion products after 28 days immersion mainly consist of α-FeOOH, Fe_3O_4 and $Fe_6(OH)_{12}CO_3$, with no detection of Ni or Cu.

To further detect whether Ni and Cu exist in corrosion products, EDS and EPMA were used for rust layer cross-sectional analysis of NiCu low alloy steel, with results shown in [Figure 6: see original paper]. [Figure 6: see original paper]a shows SEM cross-sectional corrosion morphology of NiCu low alloy steel, where the lightest color is metal substrate, the darkest is epoxy resin, and the corrosion product film lies between them. The rust layer can be divided into inner and outer rust layers: the outer rust layer is loose and easily detached with poor protective performance, while the inner rust layer is relatively dense. [Figure 6: see original paper]b and c show line scan results along the line in [Figure 6: see original paper]a, with [Figure 6: see original paper]b showing Ni element analysis and [Figure 6: see original paper]c showing Cu element analysis. [Figure 6: see original paper]b shows that Ni content in the inner rust layer is higher than in substrate, showing obvious enrichment, while Ni content in outer rust layer decreases significantly with distance from substrate. [Figure 6: see original paper]c shows that Cu content in inner rust layer differs little from that in metal substrate, decreasing slightly with distance from substrate in outer rust layer. [Figure 6: see original paper]d is a partially enlarged image of [Figure 6: see original paper]a, with [Figure 6: see original paper]e and f showing EPMA mapping results for Ni and Cu elements respectively. EPMA results are consistent with EDS results: Ni shows obvious enrichment in inner rust layer, while Cu content in substrate and inner rust layer is higher than in outer rust layer, but no obvious enrichment in inner rust layer was detected. Since Cu content in this low alloy steel is relatively low, EDS and EPMA methods have difficulty resolving distribution differences between corrosion product film layers and substrate. Literature indicates that alloying element enrichment in inner rust layer helps form dense inner rust layers, thereby improving metal corrosion resistance.

[Figure 7: see original paper] shows XPS detection results for alloying elements Ni and Cu in inner rust layer of corrosion product film. [Figure 7: see original paper]a shows Ni $2p_3/_2$ peak at (855.8\$±0.1)$eV, close to NiO peak in databases, though NiO was not detected in XRD$

forms when Ni substitutes Fe in Fe_3O_4 crystal, and since Ni and Fe atomic radii differ little, discrimination through lattice structure differences is difficult. However, $NiFe_2O_4$ has higher thermodynamic and electrochemical stability than Fe_3O_4, and $NiFe_2O_4$ is a negatively charged structure that can effectively block aggressive anions, thereby reducing substrate corrosion. Therefore, $NiFe_2O_4$ presence in inner rust layer is beneficial for improving metal material corrosion resistance in Cl^--containing solutions. [Figure 7: see original paper]b shows Cu $2p_3/_2$ peak at (932.7$±0.1)*eV*, *indicatingCulikelyexistsasmonovalentCu*(*I*), *suchasCuFeO*_{2}$, though its low content prevents XRD detection.

[Figure 8: see original paper] shows the potential-pH diagram for Fe-Ni-Cu-H_2O system at 25 °C. Under long-term immersion conditions, $NaHCO_3$ buffer solution pH can still maintain around 8.33, so within the potential range studied in this system, the most likely existence forms of Ni and Cu are $NiFe_2O_4$ and $CuFeO_2$ respectively. As shown in [Figure 8: see original paper], thermodynamically calculated stable regions of $NiFe_2O_4$, $CuFeO_2$ and Fe_3O_4 have overlapping portions in this potential-pH diagram, indicating these three Fe oxides can coexist stably under certain conditions. Based on solution pH and open-circuit potential fluctuations in stages two and three, electrode surface potential and solution pH fluctuate within the small shaded box in [Figure 8: see original paper], which lies exactly within the overlapping thermodynamic stability region of these three substances. This proves that $NiFe_2O_4$, $CuFeO_2$ and Fe_3O_4 very likely coexist in rust layer, especially in inner rust layer, thereby providing certain protection to metal substrate.

Conclusions

1. Compared with low carbon steel, NiCu low alloy steel’ s final electrode surface state stabilizes in the later passivation region rather than pitting activation region after long-term immersion, with lower corrosion rates and uniform corrosion morphology rather than localized corrosion.
2. Alloying elements Ni and Cu exist in inner rust layer as $NiFe_2O_4$ and $CuFeO_2$ respectively, thereby improving metal material corrosion resistance.

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