Synergistic effect of sulfur dioxide and chloride on the corrosion of 3.55 wt% Ni weathering steel

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Abstract

In this paper, we studied the synergistic effect of sulfur dioxide and chloride on the corrosion of weathering steel containing 3.55 wt% Ni. The weight loss and the rusts formed on weathering steel in atmosphere containing chloride, and a mixture of sulfur dioxide and chloride were studied by wet/dry cyclic corrosion tests. The results showed that in a chloride containing atmosphere, the rust presented a bi-layer structure, with a loose outer layer with chloride clustered and a dense inner layer containing goethite. Due to the synergistic effect of sulfur dioxide and chloride, the sample corrosion was accelerated, which changed the rust structure and phase distribution. Goethite formed in the outer rust layer with a shell-like morphology, which limited the volume changes causing crack formation. Chloride passed through the cracks to corrode the substrate and akaganeite formed in the inner rust layer, which eliminated the cation selectivity.

1. Introduction

The good anti-corrosion property of weathering steel is attributed to the addition of weathering element such as Cu, Cr, Ni and Mo, which helps the homogeneous and adherent rust layer to form on the steel surface during corrosion [1–5]. Among these alloying elements, Ni has an outstanding overall anti-corrosion performance especially in marine atmosphere [6–12]. Diaz et al [8] believed that the presence of Ni in weathering steel increased the content of nano-phasic (super-paramagnetic) goethite (α-FeOOH) in the inner side of the rust layer, which facilitated the formation of a dense rust layer on the steel. This hindered the entry of corrosive media through the cracks and pores. Some researchers [9–12] have also found that Cl− was impeded from entering the inner rust layer in the presence of Fe2NiO4 and fine-grained goethite in the inner rust due to cation selectivity.

An atmospheric corrosion of steels is influenced by both the alloying elements and the atmosphere. Many studies [6–12] have been carried on to determine how Ni element affects the corrosion resistance of weathering steel, especially in a marine atmosphere. It displayed cation selectivity when Ni content exceeded 3 wt%. The atmosphere in coastal cities in developing countries such as China contains SO2 from vehicle and industrial emissions [13, 14]. The presence of both Cl− and SO2 had a significant effect on the corrosion of weathering steel. Researchers [15–19] have paid attentions to corrosion behavior of Ni-containing alloying steel in the atmosphere containing both Cl− and SO2. Li et al [15] studied the effect of Ni on the corrosion resistance of bridge steel in a coastal-industrial atmosphere. Liang et al [16] studied the corrosion of steels exposed for sixteen-year and found that SO2 only evidently deteriorated steels during the initial corrosion stage. Allam et al [17] studied the atmospheric corrosion of steel in the Arabian Gulf, and found that Cl ions were more aggressive than sulfate ions during the initial atmospheric corrosion stage of steels. Singh et al [18] studied the corrosion behavior of low alloy structural steels exposed in different climatic conditions including Chennai (industrial polluted, saline), and indicated that SO2 facilitated the formation of goethite. Chen et al [19] studied the effect of SO2 on the corrosion of a low-alloy steel in simulated coastal industrial atmospheres (SO2 + Cl ions) and indicated that a higher SO2 content promoted the formation of goethite. However, the Ni contents mainly
Table 1. Chemical composition of tested steel (wt%).

| Alloy | C   | Si  | Mn  | P   | S   | Al  | Ni  | Cu  | Nb  | Ti  | Fe  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Content | 0.036 | 0.23 | 0.71 | 0.02 | <0.003 | <0.04 | 3.55 | 0.32 | 0.06 | 0.01 | Bal. |

ranged from 0.01% – 0.6wt% in these studies, and there was no compare with a purely coastal atmosphere (Cl ions). Therefore, further study is needed to understand the synergistic effect of Cl ions and SO2 on the corrosion of weathering steel containing more than 3 wt% Ni by the comparing the rusting evolution.

The aim of this study is to understand of synergistic effect of Cl− and SO2 on the rust evolution and ion selectivity of weathering steel containing 3.55 wt% Ni by comparing the corrosion behavior in atmosphere containing Cl−, and a mixture of Cl− and SO2. SEM, EDS, XRD, and Raman Spectroscopy were used to study the composition and phase distribution of rust.

2. Experimental

2.1. Sample preparation

The experimental steel containing 3.55 wt% Ni was prepared using a 200 kg vacuum induction furnace. The chemical composition of the tested steel is listed in Table 1. A steel ingot was forged to 80 mm × 80 mm × 400 mm billets that were subjected to rolling. The billets were homogenized at 1200 °C for 30 min before rolling. Afterwards, they were rolled above 1000 °C from 80 to 40 mm, followed by rolling between 950 and 810 °C to a final thickness of 12 mm. They were finally cooled to 500 °C by water and cooled to room temperature in air.

The samples were cut into 30 mm × 20 mm × 5 mm and 10 mm × 10 mm × 5 mm, then subjected to weight loss measurement, and rust microstructure and composition analysis. All samples were ground by 800 g silicon carbide papers, dehydrated by alcohol, cleaned with acetone, rinsed with distilled water, and finally dehydrated with anhydrous ethanol. The actual size and weight of the samples were measured with the accuracies of ±0.02 mm and ±0.1 mg, respectively, after drying in a desiccator for 24 h. The weight was recorded as W0.

2.2. Wet/dry cyclic corrosion tests

The corrosion behavior of the tested steel in Cl−, Cl− and SO2 containing atmosphere was studied by an alternative wet/dry cyclic corrosion, using 0.1 mol l−1 NaCl and 0.01 mol l−1 NaHSO3 + 0.1 mol l−1 NaCl solutions as the corrosive media. Hereafter the experimental samples are referred to C and CS, respectively. One cycle lasted 80 min, in which the samples were first immersed into the solutions for 18 min, at 42 °C, and then were dried in 45 °C for 62 min. The drying stage included natural drying for 46 min at RH = 85% and forced drying for 16 min at RH = 38%. The samples were hanged in the chamber, with the equal distance between each sample. The samples were taken out after 2, 4, 6, 10, and 14 days, respectively.

2.3. Weight loss measurement

The rusted samples were scraped until most of the substrate was exposed, then immersed in a solution (500 ml distilled water + 500 ml 38wt% hydrochloric acid, 20 g hexamine) under ultrasonic vibration. The samples were then cleaned with anhydrous alcohol, dried in air, and the net weight was recorded as W1(g).

The corrosion depth of the samples was calculated by equation (1):

\[ d_c = \frac{(W_0 - W_1)}{(\rho S)} \]  

(1)

where \( d_c \) (μm) is the corrosion depth, \( S (\text{cm}^2) \) refers to the surface area of the sample, \( \rho (\text{g cm}^{-3}) \) is the density of the steel, \( W_0 \) is the weight of the sample before corrosion and \( W_1 \) is the weight after corrosion.

The corrosion rate of the samples \( V (\text{mm} \cdot \text{a}^{-1}) \) was determined by equation (2):

\[ V = K \frac{(W_0 - W_1)}{(\rho t S)} \]  

(2)

where \( K \) is 8.76 × 10−1; \((W_0 - W_1)\) is the weight loss, \( g; S, \rho, t \) is same meaning as above.

The surface morphologies of rust layers were characterized by SEM (Ultra Plus), and the cross-sectional distribution maps of alloy elements in rust layers were obtained by EDS (Ultra Plus). The phase composition was obtained by x-ray diffraction (XRD, D/Max 2400) with a Cu target. The scanning speed was set as 2° min−1 and the 2θ angle was set from 10° to 70°. The phase distribution was obtained by Raman spectroscopy (Raman, LabRaman HR 800) by irradiating samples with a He–Ne laser with a 633 nm wavelength. The power of the laser was kept at 17 mW. The locations of the specimens to be studied were focused through an Olympus microscope at 100× magnification.
3. Results and discussion

3.1. Corrosion depth and corrosion rate

Figure 1(a) shows the variations of corrosion depth with time for samples C and CS. As the corrosion time extended, the corrosion depths of the tested steels gradually increased for both C and CS samples. Moreover, the corrosion depth of CS was evidently bigger than C, which became more pronounced as the test time extended. In the early stage (<144 h), the corrosion depths of both C and CS samples rapidly increased, but as corrosion proceeded, the increase in the corrosion depth slowed for both samples and even evidently slowed for sample C (144–336 h). At the early stage, the corrosion was fast because no protective rust had formed yet. Subsequently, the corrosion rate of the C sample declined, since during the late stage a protective rust layer gradually formed on the steel surface. Figure 1(b) shows the corrosion rate curves of specimens C and CS. Generally, the corrosion rate decreased with the corrosion time for both samples. For sample CS, the corrosion rate quickly declined in the early stage (<144 h), then slowly in the late stage (144–336 h), while that of sample C fluctuated in the early stage (<144 h), and subsequently decreased in the late stage (144–336 h).

3.2. Rust analysis

The co-existence of Cl\textsuperscript{−} and SO\textsubscript{2} accelerates the corrosion of steel. Cl\textsuperscript{−} can pass through the rust layer and directly corrode the steel substrate. When it contacts SO\textsubscript{2} and O\textsubscript{2}, the steel substrate is corroded into FeSO\textsubscript{4} which can be oxidized to rust, freeing SO\textsubscript{4}\textsuperscript{2−}, by which more substrate would be corroded, producing fresh FeSO\textsubscript{4}, hence more SO\textsubscript{4}\textsuperscript{2−}, and so on [18, 20, 21]. H\textsubscript{2}SO\textsubscript{4} was produced during this cyclic process, and the rusting process was accelerated. Moreover, as Marcus et al. [22] stated, before the protective rust layer forms, HSO\textsubscript{3}\textsuperscript{−} was more aggressive than Cl\textsuperscript{−}. As a continuous rust layer formed on the steel surface (about 144 h), the superimposed effect was weakened. That explains why the corrosion rate of sample CS was significantly higher than that of sample C in the early corrosion stage. As corrosion proceeded, some corrosive media were hindered by the rust layer, and the corrosion rate decreased. Subsequently, the difference between the corrosion rates of C and CS samples became smaller.
3.3. Rust morphology and elemental distribution

The morphologies of the cross-sectional rust layers on the tested steels were detected by SEM, and elemental maps of Cl and Ni were obtained by EDS (figure 3). The morphologies (figures 3(a) and 3(b)) show that the thickness of the rust layer formed on sample C was much smaller than that on CS. The rust layer of sample C was relatively dense and tightly attached to the substrate, while the outer part was looser, which matches the surface morphology in figure 2(a). Cl clustered at the loose outer rust layer (figure 3(c)), far away from the substrate, indicating that it displayed cation selectivity.

The morphology of the outer rust of sample C is porous (figures 2(a) and 5(a)) which could hardly hinder the entry of the corrosive solution, allowing Cl ions to easily pass through the rust. As a result, Cl ions were enriched in the outer rust layer of sample C (figure 3(c)). In contrast, the inner rust layer of sample C was fine and compact, which impeded the penetration of corrosion media including Cl ions (figure 3(c)), which is corresponding to the investigation done by Wu et al [23]. Our previous study [11] showed that the cation

Figure 3. Morphologies of the cross-sectional rust layer formed on samples (a) C and (b) CS, map scanning result of Cl in rust layer on samples (c) C and (d) CS, and that of Ni (e) C and (f) CS.

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Figure 4. XRD patterns of the rust layers of tested steel samples C and CS.

Figure 5. Micrographs of cross-sectional rust layers on samples (a) C and (b) CS. The right images show the Raman spectra corresponding to the points marked in the left images. L: $\gamma$-FeOOH, G: $\alpha$-FeOOH, A: $\beta$-FeOOH, M: Fe$_3$O$_4$. 
selectivity of the rust is closely related to the structure characteristics, and a fine, compact rust layer restricted the penetration of Cl ions. This result is consistent with former research results that claimed that the rust layers of WS (3 wt% and 4 wt% Ni) presented cation selectivity in a marine atmosphere [9, 12, 24].

For sample CS, the outermost rust layer appeared smooth and the inner layer contained many cracks, which is in good agreement with the surface morphology of sample CS (figure 2(b)). Through these cracks, the corrosive liquid containing Cl ions, whose diameter is only about one-fourth that of a H2O molecule, may pass through the rust layer and further corrode the steel substrate more easily. Then rust nests formed close to the substrate. This assumption is verified by the distribution of Cl and rust nests, as shown in figures 3(b) and (d). Most of Cl was located very close to the substrate and mostly overlapped with the rust nests, which displays the opposite result of the Cl distribution in sample C. Evidently, the presence of SO2 was responsible for the loss in the cation selectivity of sample CS.

Ni was homogeneously located throughout the entire rust layer in sample C (figure 3(e)), which is corresponding to the investigation done by Cano et al [25], who found that Ni was uniformly located in the rusts formed on Ni 2.4 wt% weathering steel exposed to marine environments. Previous studies [3, 26] have proved that Ni in the rust is bivalent and can replace Fe2+ of Fe3O4 to form NiFe2O4 phase [9]. A narrow band of Ni could be observed in the outer rust layer of sample CS (figure 3(f)) where a narrow crack located. This matches our previous study [15], in which Ni was found to accumulate at the cracks where element S clustered as Ni content increased to more than 3 wt%.

3.4. Characterization of the rust

3.4.1. XRD

The crystal phase compositions of the rusts formed on both tested steel samples were analyzed by XRD (figure 4). Both C and CS samples were composed of similar crystal phases, i.e., Fe3O4 (magnetite), γ-FeOOH (lepidocrocite), β-FeOOH (akaganeite), and α-FeOOH (goethite) regardless of the test conditions. Moreover, due to the difference of the corrosive media, the intensities of the diffraction peaks corresponding to goethite increased, whereas those associated with lepidocrocite declined, indicating that the relative content of goethite increased, while that of lepidocrocite decreased. The presence of SO2 in the atmosphere promoted the formation of goethite and hindered the formation of lepidocrocite in the rust layer as corrosion proceeded. This is in agreement with Chen et al [19] who discovered that as the SO2 content increased, the transformation from lepidocrocite to goethite was accelerated during the long-term corrosion.

XRD presents the overall phase composition of the rust, but it does not provide the phase distribution [27]. Moreover, maghemite is usually not easy to distinguish from magnetite when using XRD technique, so the presence of maghemite is often unclear. Therefore, Raman spectroscopy is needed to further investigate the phase composition and their distribution in the cross-sections of the rust layers. The results are shown in figure 5.

3.4.2. Raman spectroscopy

As shown in figure 5(a) and table 2, the rust layer near the substrate of sample C was mainly composed of goethite. Lepidocrocite emerged during the rust formation, namely, at points 3 and 4. As the distance from the substrate increased, the compositions of phases changed to lepidocrocite, magnetite, and akaganeite. The location of akaganeite in the rust formed on sample C was far away from the substrate and was located in the outer part, rather than the inner part of the rust layer. This is consistent with the distribution of Cl in figure 3(c) since it is known that akaganeite is usually closely correlated with the Cl− content [28].

**Table 2. Raman peak positions corresponding to the phases in the C rust, according to the literatures [29–31].**

| Raman peak positions | α-FeOOH | β-FeOOH | γ-FeOOH | Fe3O4 |
|----------------------|---------|---------|---------|-------|
|                      | 203, 244, 300, 387, 399, 415, 650, 1303 | 139, 308, 331, 389, 420, 650, 1303 | 166, 217, 250, 251, 310, 350, 650, 1303 | 306, 538, 663, 666 |
| Standard             | 480, 552, 685, 1002, 1113, 1304 | 499, 539, 609, 720, 1410 | 713, 1303 | 663, 666 |
| 1                    | 205, 300 | —       | —       | —     |
| 2                    | 205     | —       | —       | —     |
| 3                    | 300     | —       | 217     | —     |
| 4                    | 205     | —       | 650, 1303 | —     |
| 5                    | —       | 308     | 217, 1303 | 666   |
| 6                    | —       | 308     | 217     | 660   |

Bold: main peak.
In contrast, the case evidently changes, the rust next to the steel substrate of sample CS was composed of magnetite and akageneite, as illustrated in figure 5(b) and table 3. Then, goethite appeared at point 2, near the substrate. As the distance from the substrate increased, lepidocrocite emerged at point 3. As the distance continued to increase, the phases were similar, i.e., goethite and lepidocrocite. Akaganeite was located in the inner region of the rust layer instead of the outside, which is the opposite of the akaganeite distribution in the rust of sample C. In contrast, akaganeite clustered at the outer side of the rust on C sample, while it distributed in the inner part of the rust formed on sample C and distributed almost all over the rust layer of sample CS. A previous study\cite{9} showed that when $\alpha$-FeOOH was poorly crystallized, some main peaks in the $\alpha$-FeOOH spectrum exhibited broad peak widths and low peak intensities, such as at the points 1–4 of sample C (figure 5(a) and table 2). According to the other papers\cite{32, 33}, this type of $\alpha$-FeOOH requires at least several years or even decades of exposure to form in the rusts of conventional weathering steels. Although Diaz found that Ni accelerated the formation of nano-phase $\alpha$-FeOOH\cite{8} and an increased Ni content enhanced this process, it still required a long time. In our study, an alternative wet/dry cyclic corrosion test was used, which lasted 336 h. A longer time might be required for the

![Image of corrosion process diagrams](image)

**Figure 6.** Corrosion process diagrams of samples (a), (b) C and (c), (d) CS, the initial stage of corrosion (a) C and (c) CS, corrosion processes under the rust (b) C and (d) CS.

**Table 3.** Raman peak positions corresponding to the phases in the CS rust, according to the literatures\cite{29–31}.

| Raman peak positions | Raman band $(\text{cm}^{-1})$ |
|----------------------|-----------------------------|
|                      | $\alpha$-FeOOH | $\beta$-FeOOH | $\gamma$-FeOOH | $\text{Fe}_3\text{O}_4$ |
| Standard             | 203, 244, 300, 387, 399, 415, 480, 552, 685, 1002, 1113, 1304 | 139, 308, 331, 389, 420, 499, 539, 609, 720, 1410 | 166, 217, 250, 251, 310, 350, 379, 525, 529, 713, 1303 | 306, 538, 663, 666 |
| 1                    | —               | 307            | —              | 666 |
| 2                    | 238, 685        | 308            | —              | —   |
| 3                    | 205             | 540            | 716            | —   |
| 4                    | 205             | —              | 524, 711       | —   |
| 5                    | 401             | —              | 525, 712       | —   |
| 6                    | 205, 385        | —              | 522, 717       | —   |

Bold: main peak.
Table 4. Volume expansion rate based on iron of the iron corrosion product [36].

| Expansion rate | Fe₂O₄ | α-FeOOH | γ-FeOOH | β-FeOOH | Fe(OH)₂ | Fe(OH)₃ | Fe(OH)₃ · 3H₂O |
|----------------|-------|---------|---------|---------|---------|---------|----------------|
| 2.29           | 3.21  | 3.49    | 3.81    | 4.14    | 4.57    | 7.07    |

fine crystallization of α-FeOOH. As for sample CS, the main goethite peak appeared at points 5 and 6 (figure 5(b) and table 3), mainly because SO₂ facilitated the formation of goethite [18, 19].

The previous studies [12, 18, 29–31] show that Raman peaks for magnetite and maghemite are quite different. Magnetite was found in the Raman results of samples C and CS, while maghemite (γ-Fe₂O₃) was not evidently found in this study. Thus, maghemite was not a component of the rust layer in samples C and CS.

3.5. Corrosion processes

The corrosion process diagrams of samples C and CS are shown in figure 6. For sample C, in the initial stage, the corrosive medium such as H₂O, O₂, and Cl⁻ arrive at the substrate, the steel substrate can be corroded into Fe³⁺ + Cl⁻ → FeCl₂ + H₂O which can transform into akaganeite (figure 6(a)) [34]. Akaganeite is an active phase that can continue to transform into lepidocrocite and magnetite, meanwhile, the Fe₃(OH)₆ · 4H₂O transformed into lepidocrocite. As corrosion proceeded, more stable goethite formed due to the transition of akaganeite, lepidocrocite and magnetite. The rust layer became thick and compact which hindered the entry of corrosive Cl⁻, especially in the innermost rust layer (figures 5(a) and 3(c)).

For the sample CS, in the initial stage (figure 6(c)), the corrosive media such as SO₂, H₂O, O₂, and Cl⁻ reached the substrate, before the protective rust layer forms, SO₂ is more aggressive than Cl⁻ when pH is lower than 7 [22]. The steel substrate can be corroded into FeSO₄ which was oxidized to form goethite. Previous research has shown that SO₂ could accelerate the formation of a compact surface layer [35] like a ‘shell’ and facilitates the formation of goethite [19]. A shell-like morphology formed (figures 2(b) and 3(b)), and goethite distributed in the outer rust layer (figure 5(b) and table 3). The shell hindered the entry of outside corrosive ions. The corrosive ions already located in the innermost of the rust layer promoted the inner corrosion of the substrate (figure 6(d)). Moreover, during the wet/dry cycles, different phase transformations occurred (e.g., lepidocrocite to goethite) which changed the volume due to the different volume expansion rates of the phases (table 4). Since goethite is an inactive phase, the shell limited both the volume changes and stress relief, thus, it would be broken and cracks formed due to its poor deformability (figure 3(b)). As corrosion proceeded, the phase transformations continued, and cracks formed, which provided channels in the rust layer through which Cl ions could pass. The Cl ions corroded the substrate to form nests containing large amounts of akaganeite (figure 5(b)).

During corrosion, both the phase transitions from active phases such as akaganeite, lepidocrocite, and magnetite to the inactive phase goethite, and the transformation from an active phase to another less active phase, occurred and caused volume changes. The main difference was, the phase distribution is quite different especially in the outer layer. The surface morphology of sample C was porous (figures 2(a), 5(a) and 6(a)), while that of sample CS seemed like shell which is dense (figures 2(b), 5(b) and 6(b)). The latter limited the volume change and stress relief that caused the crack formation (figures 3(b), 6(c) and (d)), while that did not occur in sample C (figures 3(a), 6(a) and 6(b)). That is why in sample CS, akaganeite was found in the innermost rust layer (figure 5(b)) due to the entry of Cl ions through the cracks formed during the phase transition (figures 3(d) and 6(d)).

4. Conclusions

The synergistic effect of sulfur dioxide and chloride on the corrosion of samples was analyzed by weight loss measurements, SEM, EDS, XRD, and Raman spectroscopy. The main conclusions are as follows.

1. In a chloride-containing atmosphere, the rust presented a bi-layer structure, with a loose outer layer where chloride ions clustered and a dense inner part where goethite was located.

2. Due to the synergistic effect of sulfur dioxide and chloride, the sample corrosion was accelerated, and the rust structure and phase distribution changed.

3. Goethite formed in the outer rust layer with a shell-like morphology, which limited the volume changes and caused crack formation. Chloride passed through the cracks to corrode the substrate and form nests with a relatively large amount of akaganeite in the inner rust layer, thus, the cation selectivity was lost.
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