Atmospheric Corrosion Behavior of Weathering Steel in Periodically Changed Environment

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The service environments of weathering steel are periodically various. However, the general accelerated corrosion test cannot effectively simulate the periodic change. In order to investigate the influence of periodic changed environments on corrosion, a low alloy weathering steel was exposed to an indoor air with NaCl and NaHSO₃ aqueous solutions spraying the steel in turns. It was found that both atmospheric corrosion rate and the degree of alloy element enrichment in the inner rust layer were higher when the samples were sprayed with NaCl aqueous solution. Meanwhile, more compact rust layers were formed when the samples were sprayed with NaHSO₃ aqueous solution. Rust layer would stabilize more rapidly by spraying NaCl and NaHSO₃ aqueous solutions in turns than by spraying a single corrosion solution, which can be attributed to a combined advantage of alloy element enrichment and slow corrosion. Stabilization of rust layer is not necessarily derived from enrichment of alloy elements and stabilization of rust layer can produce stronger effect against further corrosion than enrichment of alloy elements.

KEY WORDS: weathering steel; EIS; XRD; rust layer; atmospheric corrosion.

1. Introduction

Weathering steel has been widely used and researched due to its excellent atmospheric corrosion resistance and low price.¹ The steel is committed to bare use, and mainly used in buildings, bridges, container and other structures. Previous study shows that the excellent corrosion resistance of the weathering steel is owing to alloy elements enrichment in the inner rust layer and compactness of the rust layer.²–⁴ On the other hand, the corrosion behavior of weathering steel is greatly influenced by service environments.⁵–⁷ The atmospheric environments are changed periodically. Generally, there are two kinds of periods: (1) short period such as day-night alternation; (2) long period such as seasonal alternation. The widely used accelerated corrosion tests are carried out in the environments of constant corrosion solution, temperature and humidity by wet-dry cycle with short period.⁸,⁹ Thus, these accelerated corrosion tests cannot reflect the corrosion behavior of weathering steel in environment changing with long period.

In this present investigation, we put forward a new accelerated corrosion scheme to solve the above mentioned problem. Samples were divided into two groups (A and B) with the same chemical composition, microstructure and shape, and then subjected to the wet-dry cyclic corrosion test. In the 1st stage, group A was corroded by 0.5%NaCl solution for 1 month, and group B was corroded by 0.5%NaHSO₃ for 1 month. These two stages constitute a whole cycle and were repeated for 2 times. NaHSO₃ solution and NaCl solution were used to tracking the influence of mild and harsh corrosion stage respectively by detect S and Cl in the rust layer. This scheme is advantageous to investigate the effects of long periodic change of environment on corrosion behavior. On the basis of the above scheme, the relationship between alloy elements enrichment and stabilization of the rust layer is meticulously researched.

2. Experimental

2.1. Material

The chemical composition of tested steel is listed in Table 1. The tested steel was cut into two different sizes for wet-dry cyclic corrosion test (CCT). Specimens with dimensions of 40 mm × 40 mm × 4 mm were used for measuring the weight gain in the corrosion process. Specimens with dimensions of 10 mm × 10 mm × 4 mm were used for electrochemical impedance spectroscopy (EIS) measurements. Wires for electrical connections were soldered on the samples. All the specimens were embedded in epoxy resin and only the largest surfaces were exposed for corrosion. The exposed surfaces of each sample were mechanically grinded

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>Cr</th>
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<td>0.064</td>
<td>0.25</td>
<td>1.5</td>
<td>&lt;0.01</td>
<td>&lt;0.005</td>
<td>0.48</td>
<td>0.18</td>
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2.2. Wet/dry Cyclic Corrosion Test (CCT)

After being cleaned with ethanol, the specimens were subjected to the CCT. The setup of the study consist of: (1) weighing the initial sample; (2) wetting the sample surface with 40 μL.cm⁻² corrosive solution. The detailed corrosion process is summarized in Table 2; (3) drying the samples in a chamber maintained at 25°C and 60% RH for 12 h; (4) re-weighing the sample after dried; (5) washing the sample with deionized water to prevent the accumulation of progressive salt; (6) repeating the above steps from (2) to (5).

2.3. Rust Layer Analysis

The rust powder was collected from the surfaces of specimens with dimensions of 40 mm × 40 mm × 4 mm every month. Then the rust powder was subjected to an internal standard X-ray diffraction (XRD) test using a Cu target. The scan speed was 2.0°/min and the 2θ angle ranged from 10° to 50°. ZnO was used as an internal standard. The diffraction intensities of (011) reflection of α-FeOOH, the (110) reflection of β-FeOOH, the (020) reflection of Fe₃O₄ were measured and compared with the (100) reflection of ZnO powder. The ratio of corrosion products to ZnO was 7:3.7)

To observe directly on the morphology of the inner rust layer, the surfaces of the rusted specimens were coated with acrylate adhesive. After solidification of the adhesive, the outer rust layer adhered tightly to the acrylate adhesive. Then, the acrylate adhesive together with the outer rust layer can be completely removed. The surface appearances of the outer rust, inner rust and rust layer cross-section were analyzed by scanning electron microscopy (SEM). Meanwhile, Cr, Cl and S contents in 10 different regions of the outer rust layers and the inner rust layers on each specimen were measured by energy dispersive x-ray spectrometer (EDS). The averaged values were taken for each specimen.

2.4. N₂ Adsorption Test

The N₂ adsorption isotherms of the corrosion products were measured at 78 K using an AUTOSORB-6B. All the N₂ adsorption samples were degassed at 100°C under 10⁻³ Torr for 2 h before tests. The specific surface area (SSA) of the samples was determined by fitting the BET equation to adsorption isotherms using the cross sectional area (0.162 nm²) of the N₂ molecule.

2.5. Electrochemical Impedance Measurements

The electrochemical impedance spectroscopy (EIS) and polarization curves measurements were carried out using a three electrodes cell with platinum as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, and rusted specimens with an exposed area of 1 cm² as the working electrode. All the specimens were tested at room temperature using a Solartron 1255B frequency response analyser in combination with a PAR 1287A potentiostat. The frequency range for EIS was from 10⁵ Hz to 10⁻² Hz with a sinusoidal potential perturbation of 10 mV at open circuit potential. The polarization curves were obtained at a constant scan rate of 5 mV.min⁻¹. The corrosive electrolyte was 0.1 M aqueous NaCl solution. The impedance data were taken after measuring the open circuit potential for 1 800 s, and the change rate of the open circuit potential is less than 0.1 mV/s.

3. Results

3.1. Weight Gain Measurements

The weight gain values of group A and B are shown in Fig. 1. On the 30th day, the weight gain of the weathering steel that exposed to 0.5%NaCl is higher than that exposed to 0.5%NaHSO₃ and the weight gain per unit area of the former is about twice of the latter. As for group A, the weight gain in the following 30 days (30th day–60th day of group A) corroded by NaHSO₃ is about 5 mg.cm⁻². However, when the naked steel is corroded by NaHSO₃ for 30 days (30th day–60th day of group B), the weight gain is about 15 mg.cm⁻². As for group B, the weight gain of the following 30 days (30th day–60th day of group B) corroded by NaCl is about 13 mg.cm⁻². However, when the naked steel is corroded by NaCl for 30 days (30th day–60th day of group A), the weight gain is about 30 mg.cm⁻². The results suggest that a protective rust layer is formed after being exposed to corrosive media for 30 days, this make the corrosion amount decreased in the following corrosion process.

After first cycle with different corrosive media alternate (the initial 60 days), the weight gain curves of group A and B become flat. This indicates that the protection ability of the rust layer had been improved. Besides, the weight gain of group B is significantly lower than that of group A on the 60th day, although these two groups were all corroded by

<table>
<thead>
<tr>
<th>Corrosion order</th>
<th>The 1st month</th>
<th>The 2nd month</th>
<th>The 3rd month</th>
<th>The 4th month</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>0.5%NaCl</td>
<td>0.5%NaHSO₃</td>
<td>0.5%NaCl</td>
<td>0.5%NaHSO₃</td>
</tr>
<tr>
<td></td>
<td>spraying</td>
<td>spraying</td>
<td>spraying</td>
<td>spraying</td>
</tr>
<tr>
<td>B</td>
<td>0.5%NaHSO₃</td>
<td>0.5%NaCl</td>
<td>0.5%NaHSO₃</td>
<td>0.5%NaCl</td>
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<tr>
<td></td>
<td>spraying</td>
<td>spraying</td>
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</tr>
</tbody>
</table>

Fig. 1. Corrosion weight gain results of group A and B.
0.5%NaCl and 0.5%NaHSO₃ for one month separately and the only difference is the corrosion order. When the two groups were corroded for two cycles (120 days), the weight gain of group B is still lower than group A, and the difference value of the weight gain between group A and B is almost unchanged compared with the difference value on the 60th day.

3.2. Scanning Electron Microscopy

The SEM micrographs of the outer and inner rusts of all samples are compared in Figs. 2(a)–2(p). Whether the steel is corroded by 0.5%NaCl or 0.5%NaHSO₃ for 1 month, the structure of the outer rusts are loose and porous (Figs. 2(a) and 2(i)), and the inner rusts are more compact than the outer rusts although there are local cracks existed (Figs. 2(e) and 2(m)). When the two groups are corroded for one cycle with different corrosive media alternate (2 months), the outer rusts are still loose and porous (Figs. 2(b) and 2(j)) while the inner rusts become smooth and compact (Figs. 2(f) and 2(n)). As for group A, partial areas of the compact inner rusts become loose at the 3rd month and the 4th month (Figs. 2(g) and 2(h)). As for group B, the inner rusts are always very compact after 2 months (Figs. 2(o) and 2(p)), and the loose outer rusts become compact at the 4th month (Fig. 2(l)).

The cross-sections of all samples were investigated by SEM (Figs. 3(a)–3(h)). After being exposed to 0.5%NaCl for 1 month, a continuous rust layer is formed and the interface between rust layer and steel substrate is uneven (Fig. 3(a)). However, when the naked steel being exposed to 0.5%NaHSO₃ for 1 month, the connection between rust layers is very poor and some part of the rust layer fall off (Fig. 3(c)). After one cycle of different corrosive media alternate (2 months), the continuous rust layer of group A delaminated, and there is always in existence a large crack between outer and inner rust layer in the following corrosion process.
(Figs. 3(b), 3(c) and 3(d)). As for the samples of group B, the outer rust layer fall off partly after one cycle (2 months), but the connection between outer and inner rust layer is fine (Fig. 3(f)), and the rust layer is intact in the following corrosion process (Figs. 3(g) and 3(h)).

3.3. Element Distribution in the Rust Layers
Chromium is one of the main corrosion-resistant elements in the weathering steel. If the mass ratio of chromium and iron in the rust layer is greater than that in the steel substrate, then we can conclude that the chromium is enriched in the rust layer. Hence, the $D_Cr$ was taken as a measure index to evaluate the enrichment degree of chromium in the rust layer. The definition of $D_Cr$ is: $D_Cr = (Cr/Fe_{rust})/(Cr/Fe_{steel})$, where $Cr/Fe_{rust}$ is the mass ratio of chromium and iron in the rust layer, and $Cr/Fe_{steel}$ is the mass ratio of chromium and iron in the steel substrate. $D_Cr > 1$ imply that the chromium enriched in the rust layer. The greater the $D_Cr$ is the more obvious the enrichment is. Relationships between $D_Cr$ and corrosion time are listed in Fig. 4. As for the group A and B, the chromium is enriched in the inner rust layer, but it is not detected in the outer rust layer. It should be noted that the $D_Cr$ of group A first decrease then increase, and then decrease again. The $D_Cr$ changes of group B is contrary to that of group A. From the corrosion process (Table 2) we can see that the $D_Cr$ is high after weathering steel had been exposed to NaCl for 30 days, while the $D_Cr$ is low after the steel had been exposed to NaHSO$_3$ for 30 days. It means that the enrichment level of alloy element is higher in a harsh corrosion environment than that in a light corrosion environment.

Figure 5 shows the evolution of the contents of S and Cl for group A and B during the whole corrosion process as a function of time. The contents of S and Cl for all specimens in the outer rust layer are always higher than that in the inner rust layer, which can be attributed to that the inner rust layer is more compact than the outer rust layer, and the compact rust layer can resist the penetration of the corrosive media. There is only Cl or S in the rust layer for group A or B on the 30th day, because the steel is corroded by a single corrosive media in the initial 30 days, and the contents of this two elements are very high in the outer and inner rust layers.

After one cycle with different corrosive media alteration, the contents of the corrosive media in the inner rust layer of the two groups decreased, and remain at a low level in the following corrosion process.

3.4. Electrochemical Properties of the Rust Layer
All the Nyquist date were modeled using ZSimpwin software and an equivalent electrical circuit (as shown in Fig. 6) was proposed for the simulation of the electrochemical process of the rusted steel. $R_s$ is the resistance of the solution, $R_r$ is the resistance of the rust layer, $C_r$ is the capacitance of the rust layer, $C_{dl}$ is the double layers, $R_t$ is the charge transfer resistance and $W$ is the Warburg impedance. The $R_r$ is used to evaluate the ability of the rust layer to resist corrosion.11)

Fig. 4. Change in $D_Cr$ value of the inner rust layers as a function of time.

Fig. 5. Change in S and Cl contents of the outer and inner rust layers for group A and B as a function of corrosion time.

Fig. 6. Equivalent electrical circuit for the EIS date of rusted samples.
Figure 7 shows the Nyquist impedance plots and the fitting values of the rust layer resistance ($R_r$) for the rusted samples of group A and B during the whole corrosion process. The impedance spectra of all the samples comprise of a semicircle at high frequency and a diffusion tail at low frequency. The radius of the semicircle stand for the resistance of the rust layer, and the diffusion tail indicates that the electrochemical reaction rate is controlled by diffusion step. In general, for a planar electrode, the Warburg slope is about $45^\circ$. The model is satisfactory for simple reactions on a planar electrode but is not adequate for complicated reactions and porous electrodes. It is worth note that the Warburg slope of some data in Fig. 7(a) are seemed to be less than $45^\circ$. Karumathilaka and Hampson considered that the Warburg slope of a porous electrode is between about $22.5^\circ$ and $45^\circ$ based on characteristic of an electrode with semi-infinite pores. At lower frequencies, linear Warburg portion due to diffusion process can be seen. The Warburg slope is as an empirical parameter related qualitatively rather than quantitatively to the diffusion resistance where a higher slope signifies a slower rate of diffusion and a low slope a more rapid rate of diffusion. Thus the rust layer of group A has a smaller diffusion resistance until on the 120th day. On the 30th day, the $R_r$ of group A and B are both less than 100 $\Omega$, and the $R_r$ of the rusted steel which is corroded by 0.5%NaCl for 30 days is much higher than which is corroded by 0.5%NaHSO$_3$ for 30 days. In the following corrosion process, the $R_r$ of group A is fluctuating obviously while the $R_r$ of group B is constantly increasing. It is deserved to note that for group A, the $R_r$ changes in opposite trend to level of alloy element enrichment $D_C$. However, the $R_r$ of group B constantly increases.

Figure 8 shows the evolutions of the anodic and cathodic tafel slope for group A and B during the whole corrosion process. For every rusted sample, the anodic tafel slope is lower than the cathodic tafel slope, which indicates that the rust layers are protective to the steel substrate. After one cycle of different corrosive media alternate (60th day), the anodic tafel slope of the two groups are almost same and are less than that of 30th day, which indicates that the corrosion tendency of the steel substrate is decreased. After two cycles (120th day), the anodic tafel slope of the two groups are still low. Meanwhile, the anodic tafel slope of group B is lower than that of group A, which implies that the corrosion resistance of group B is higher than that of group A.

3.5. XRD for Rust Layers

Figure 9 shows the phase content of group A and B for various times. The corrosion products of the weathering steel mainly consist of: $\alpha$-FeOOH, $\beta$-FeOOH, $\gamma$-FeOOH, Fe$_3$O$_4$ and large amounts of X-ray amorphous compounds. The contents of $\beta$-FeOOH and $\gamma$-FeOOH of group A at day30 are relatively high due to the NaCl environment in the initial 30 days. The main phase of group B at day30 is $\alpha$-FeOOH due to the effect of NaHSO$_3$ in the initial 30 days. As for group A, the relative contents of corrosion products are changed between the 90th day and the 120th day. However, the corrosion products of group B are little changed during the 90th day to the 120th day. This indicates that corrosion products of group B are more stable than that of group A.

3.6. Results from the N$_2$ Adsorption Test

Figure 10 shows the SSA of the corrosion products for group A and B in the whole corrosion process. In general, the larger the SSA is, the smaller the particle size of the corrosion product is. The SSA of group A reaches the peak

Fig. 7. Evolutions of the EIS results from the rusted samples as a function of the time. A-30 means the sample of group A is corroded for 30 days, the other symbols can be analogized same.

Fig. 8. Changes in tafel slope of anodic and cathodic as a function of time under corrosion order A and B.
value on the 60th day, while at low values on the 30th, the 90th and the 120th day. The value of SSA changes in opposite trend to level of alloy element enrichment D Cr except on the 120th day. However, the SSA of group B constantly increases with time, but the rate of increase significantly reduces on the 120th day.

4. Discussions

The rust layers of group A or group B which formed on the 30th day were influenced by Cl– or HSO₃– separately. After the 30th day, both Cl– and HSO₃– exist in the rust layer of group A and B. These two ions have a common effect on the corrosion products. On the 30th day, the rust layer formed in Cl– environment has a smaller diffusion resistance than that formed in HSO₃– environment. Meanwhile, the crack in the rust layer of group A is larger than that of group B (Figs. 2(e) and 2(m)). What is more, HSO₃– environment is beneficial to the formation of α-FeOOH, while Cl– environment is beneficial to the formation of β-FeOOH.17) It can be seen from the above results that the rust layer formed in HSO₃– environment is more compact and stable than that formed in Cl– environment.

It is generally believe that the rust layer stability is due to the alloy elements enrichment. However, in term of results from the present investigation, it is worth to note that the alloy elements enrichment does not lead directly to a decrease of the corrosion rate before the formation of a protective rust layer. The experimental results show that when the weathering steels were sprayed with 0.5%NaCl, the corrosion rate and the enrichment degree of Cr in the inner rust layer are both higher than that when the steels were sprayed with 0.5%NaHSO₃ (Figs. 1 and 4). This indicates that the extent of alloy elements enrichment is high when the corrosion is serious. On the contrary, the extent of alloy elements enrichment is low when the corrosion rate is slow. Although the enrichment of Cr for group A is very high on the 30th day (Fig. 4), the corrosion rate is also high at the same time (Fig. 1). The results imply that the enrichment of the alloy elements is the result of the corrosion, and the protective effect of the rust layer does not increase necessarily with the enrichment of the alloy elements.

From the experimental results, it is shown that the degree of alloy elements enrichment in a harsh corrosion environment (0.5%NaCl) is higher than that in a light corrosion environment (0.5%NaHSO₃). Meanwhile, the relative content of stable phase (α-FeOOH)17) in a light corrosion environment was higher than that in a harsh corrosion environment (Fig. 9). Therefore, alloy elements enrichment and rust layer stabilization are occurring in different periods in a periodically changed environment. Thus, the periodically changed environment is advantageous to the formation of a protective rust layer. If the corrosion environment is always harsh, the rust layer is not stable although the alloy elements are enriched in the inner rust layer. If the corrosion environment is always light, the rust layer is stable, but the degree of alloy elements enrichment is low. Therefore, in the periodically changed environment, the enrichment of alloy elements and the stabilization of the rust layer are occurring alternately, and these two factors combine to form the excellent protective performance of the rust layer. The above discussions are the reason why the corrosion rates of carbon steel and weathering steel have no obvious change in a single corrosion environment (Fig. 11), but the corrosion rates of weathering steel gradually decrease in the periodically changed environment (Fig. 1).

Compact and stable rust layers of group A and B are formed after one cycle of different corrosive media alternate.
(day60), but the rust layer characters are different between the two groups. As for group A, the SSA exhibits low value on the 120th day. This is because the value of SSA represents the whole rust layer, however, the protection effect is mainly attributed to the thin inner rust layer next to the steel substrate. With prolonged corrosion time, the thickness ratio of inner rust layer to whole rust layer continues to decrease so that SSA of rust layer reduces in the 4th month. As for group B, the R and the SSA increased continuously in the whole corrosion process, and the corrosion degree of group B is lower than that of group A (Fig. 1). The above discussions imply that the order of corrosion has an effect on the formation of the protective rust layer, and the corrosion order B can accelerate the formation of a compact rust layer with a smaller corrosion degree than the opposite corrosion order. The reason for this phenomenon is that the initial corrosion environment of group B is lighter than that of group A, and the rust layer formed in the light environment is more stable than that in the harsh environment. In the following corrosion process, the initial stable rust layer of group B remains stable and the protective ability of the rust layer continuously enhanced. However, the rust layer formed in a harsh environment is not stable despite its higher content of alloy elements. This indicates that stabilization of rust layer is not necessarily derived from enrichment of alloy elements and stabilization of rust layer can produce stronger effect against further corrosion than enrichment of alloy elements.

5. Conclusions

(1) High corrosion rate and high enrichment of alloy elements in inner rust layers can occur simultaneously during atmospheric corrosion of weathering steel, which implies that enrichment of alloy element is the result of the atmospheric corrosion and enrichment of alloy elements does not necessarily slow down atmospheric corrosion.

(2) It takes a long time for weathering steel to form a protective rust layer in an unchanged environment, while in the periodically changed environment, alloy element enrichment and rust layer stabilization occur alternately and the protective rust layer can be quickly formed under the combine action of alloy element enrichment and subsequent slow corrosion.

(3) Stabilization of rust layer is not necessarily derived from the enrichment of alloy elements and stabilization of rust layer can produce stronger effect against further corrosion than enrichment of alloy elements.

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