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Abstract

The effects of pH variation on the corrosion behavior of Q235B steel in simulated industrial-coastal atmosphere were investigated using dry/wet alternating corrosion weight-gain simulation experiments, XRD, and EIS methods. The results show that when the SO2 concentration is low, the effect of pH variation on the corrosion rate of Q235B steel is not significant; when the SO2 concentration is high, there exists an extremum phenomenon in the effect of pH variation on the corrosion rate of Q235B steel, i.e., when the pH value is at a certain value between "high" and "low" , the corrosion rate of Q235B steel reaches a maximum. When the SO2 concentration in the simulated industrial-coastal atmosphere is constant, the effect of pH variation on the phase composition of the rust layer on Q235B steel surface is not significant. Analysis shows that the presence of SO2 in the simulated industrial-coastal atmosphere environment inhibits the formation of b-FeOOH to a certain extent. With the increase of SO2 concentration, the relative contents of b-FeOOH and g-FeOOH in the rust layer decrease, and g-FeOOH may undergo reduction to Fe3O4 or phase transformation to a-FeOOH. With the extension of corrosion time, the evolution of the phase composition of the rust layer shows a similar trend. Furthermore, when the SO2 concentration in the simulated industrial-coastal atmosphere is low, the corrosion of Q235B steel mainly follows the Cl− cycling mechanism, and changing the pH value has no significant effect on the corrosion behavior of the steel; when the SO2 concentration is high, the corrosion of Q235B steel mainly follows the Cl− cycling mechanism in the initial stage, and with the extension of corrosion time, the influence of SO2 on corrosion gradually becomes significant and accelerates the corrosion of steel through H2SO4 regeneration cycling.

Full Text

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Effect of pH Value on the Corrosion Behavior of Q235B Steel in a Simulated Industrial-Coastal Atmosphere*

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Abstract Using a dry/wet cyclic corrosion weight-gain simulation experiment, XRD, EIS, and other methods, the effect of pH variation in a simulated industrial-coastal atmosphere on the corrosion behavior of Q235B steel was studied. The results show that, when the concentration of SO_2 is relatively low, the effect of pH variation on the corrosion rate of Q235B steel is not obvious; when the

concentration of SO_2 is relatively high, the effect of pH variation on the corrosion rate of Q235B steel exhibits an extremum phenomenon, namely: when the pH value is at a certain value between "relatively high" and "relatively low," the corrosion rate of Q235B steel reaches a maximum. When the SO_2 concentration in the simulated industrial-coastal atmosphere is fixed, the effect of pH variation on the phase composition of the rust layer on the surface of Q235B steel is not obvious. Analysis indicates that the presence of SO_2 in the simulated industrial-coastal atmospheric environment suppresses, to a certain extent, the formation of β-FeOOH. As the SO_2 concentration increases, the relative contents of β-FeOOH and γ-FeOOH in the rust layer decrease, and γ-FeOOH may undergo reduction to Fe_3O_4 or phase transformation to α-FeOOH. With increasing corrosion time, the evolution of the rust-layer phase composition shows similar regularity. In addition, when the SO_2 concentration in the simulated industrial-coastal atmosphere is relatively low, the corrosion of Q235B steel mainly follows the cyclic mechanism of Cl^-, and the influence of changing pH on the corrosion behavior of the steel is not obvious; when the SO_2 concentration is relatively high, the initial corrosion of Q235B steel mainly follows the cyclic mechanism of Cl^-, but with increasing corrosion time, the influence of SO_2 on corrosion gradually becomes significant, and the corrosion of the steel is accelerated through the regeneration cycle of H_2SO_4.

Keywords Q235B steel, dry/wet cyclic experiment, industrial-coastal atmospheric corrosion, rust layer

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EFFECT OF pH VALUE ON THE CORROSION EVOLUTION OF Q235B STEEL IN SIMULATED COASTAL-INDUSTRIAL ATMOSPHERES

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ABSTRACT The atmosphere in many cities along the coastal lines such as

Qingdao in China has been polluted with SO_2 due to the development of industry, and the atmosphere therefore has been changed to coastal-industrial atmosphere. The corrosion behavior and mechanism of steels in coastal-industrial atmosphere with the co-existence of SO_2 and Cl^- are different from that in the coastal atmosphere containing only Cl^- or the industrial atmosphere containing only SO_2. In addition, pH value is diverse in different coastal-industrial atmosphere. However, there are only few researches on the effect of pH value on the corrosion evolution of steels in the coastal-industrial atmosphere. Almost all the atmospheric corrosion data of steels were obtained by the field exposure test, which could not reflect the dependence of the atmospheric corrosion evolution of steels on pH value due to the difficulties in

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controlling the field conditions. In this work, the effect of pH value on the corrosion evolution of Q235B steel in the simulated coastal-industrial atmospheres has been investigated by the dry/wet cyclic corrosion test (CCT), XRD and EIS. The results indicate that, when the content of SO_2 is lower, changing pH value has no effect on the corrosion of the steel. When the content of SO_2 is higher, the corrosion rate of Q235B steel influenced by changing pH value shows an extreme phenomenon, that is, when the pH value being a certain value between the "higher" and the "lower" , the corrosion rate of Q235B steel reaches the maximum value. When the SO_2 content is certain, changing pH value almost has no effect on the rust composition. To some extent, the existence of SO_2 inhibits the formation of β-FeOOH. With the increasing of SO_2 content, the relative contents of β-FeOOH and γ-FeOOH are decreasing, and γ-FeOOH maybe reduced back to Fe_3O_4 or transform to α-FeOOH. With the corrosion process prolongs, the rust evolution shows almost the same trend. In addition, when the content of SO_2 in the simulated coastal-industrial atmosphere is lower, the Q235B steel mainly follows Cl^- corrosion mechanism, and the influence of pH value on corrosion behavior of the steel is not obvious. When the content of SO_2 is higher, the Q235B steel also follows Cl^- corrosion mechanism in the early stage; with prolonging the dry/wet cyclic corrosion test number, H_2SO_4 regeneration mechanism accelerates corrosion of the steel as the effect of SO_2 on corrosion increasing significantly.

KEY WORDS Q235B steel, dry/wet cyclic test, coastal-industrial atmosphere, atmospheric corrosion, rust layer

Atmospheric corrosion of steel is very common, and its main environmental factors include relative humidity, temperature, and corrosive pollutants, etc.[1,2]. Under conditions of relatively constant temperature and environmental humidity, Cl^- and SO_2 are the two most common and most important corrosive components[3]. The corrosion behavior of steel in marine atmospheres (containing Cl^-) and industrial atmospheres (containing SO_2) has long received attention[4-7]. However, in many coastal cities and regions worldwide (for example, the entire southeastern coastal economic zone of China), the atmospheric environment has been polluted by industrial development and has gradually evolved into an industrial-coastal atmosphere containing both Cl^- and SO_2[8-10]. In earlier work by this research group[11,12], the influence of SO_2 concentration in simulated industrial-coastal atmospheres on the corrosion behavior of steel was studied, and it was found that the influence of SO_2 on steel corrosion behavior exhibits a concentration extremum. However, differences in the degree of industrial pollution not only cause differences in SO_2 concentration in industrial-coastal atmospheric environments, but also lead to changes in environmental pH. Studies[13-16] have shown that when the pH of an aqueous solution is greater than 4.0, the cathodic reaction in the steel corrosion process is dominated by the reduction of O_2; when the pH is less than 4.0, the cathodic reaction in the steel corrosion process also includes the reduction of H^+. Misawa et al.[17] believed that the initial product of steel corrosion is $Fe(OH)_2$, which is oxidized to α-FeOOH under strongly alkaline conditions and to Fe_3O_4 under weakly alkaline conditions. Benarie and Lipfert[18] showed that the higher the pH value (less than 7) of the atmospheric corrosion thin liquid film, the lower the corrosion rate of the metal. Results of simulated atmospheric corrosion experiments carried out by Nishikata et al.[19] showed that, when the thickness of the thin liquid film is less than 200 μm, the influence of pH on the steel corrosion rate is not significant; when the thickness of the thin liquid film is greater than 200 μm, the steel corrosion rate increases with increasing pH. Graedel and Frankenthal[20], through field exposure experiments, found that the pH value in the atmospheric corrosion thin liquid film directly affects the formation and dissolution of corrosion products and is extremely important to the corrosion behavior of steel. These studies on the initial behavior of steel corrosion show that pH changes caused by changes in corrosive environmental components may also lead to changes in steel corrosion behavior, directly affecting the safe service behavior of steel structural facilities.

Because the on-site exposure environment is complex and variable, and it is difficult to control the effects of specific environmental factors, studies on the influence of pH changes in industrial-coastal atmospheres on the long-term corrosion evolution behavior of steel have not yet been reported.

In this work, a laboratory dry/wet alternate simulated atmospheric corrosion acceleration test (CCT)[21-24], combined with electrochemical measurements and rust-layer phase-composition analysis methods, was used to study the influence of pH changes in a simulated industrial-coastal atmospheric environment on the corrosion behavior of Q235B steel, and the mechanism of the pH effect

was discussed.

1 Experimental methods

The experimental material was Q235B grade low-carbon steel, with chemical composition (mass fraction, %) as follows: C 0.210, Si 0.210, Mn 0.580, S 0.036, P 0.017, Cu 0.020, and balance Fe. The samples were machined by wire cutting into two specifications, 30 mm × 30 mm × 5 mm and 10 mm × 10 mm × 5 mm, respectively for dry/wet alternate corrosion experiments and electrochemical measurements. After cleaning and pre-grinding procedures, the samples were sealed with epoxy resin. The exposed areas of the two types of samples were 30 mm × 30 mm and 10 mm × 10 mm, respectively. They were then ground with waterproof abrasive paper to 600 grit, rinsed with alcohol, dried with cold air, and placed in a desiccator for later use.

The electrolyte solution concentrations used to simulate the industrial-coastal atmosphere are shown in Table 1. The solutions were prepared using analytical-grade reagents and deionized water, and the solution pH was adjusted to the specified value using a pHB-4 acidity meter and 10% H_2SO_4 (mass fraction).

The CCT procedure was as follows[11,23,24]: (1) the initial mass of the sample was weighed with a Sartorius BP 220 electronic microbalance (accuracy 0.1 mg); (2) the electrolyte solution was dropped onto the sample surface at a volume of 40 μL/cm^2 and spread uniformly, and then the sample was placed in a PR-2KP constant-temperature and constant-humidity test chamber, with chamber environmental conditions of 30 °C and 60% relative humidity; (3) after 12 h, the sample was removed and weighed again, and the deposited salts were washed off with distilled water; (4) steps (2) and (3) were repeated.

Electrochemical impedance spectroscopy (EIS) testing was performed using a Princeton Applied

Table 1 The electrolytes for simulating the coastal–industrial atmosphere with different SO_2 contents and pH value

Atmosphere	Na_2SO_3 / (mol · L^{-1})	NaCl / (mol · L^{-1})	pH value
No.1	0.001	0.050	3.5
No.2	0.001	0.050	4.5
No.3	0.001	0.050	6.0
No.4	0.010	0.050	3.5
No.5	0.010	0.050	4.5
No.6	0.010	0.050	6.0
No.7	0.150	0.050	3.5
No.8	0.150	0.050	4.5
No.9	0.150	0.050	6.0

Note: the electrolytes are prepared by adding different amount of Na_2SO_3 into NaCl solutions

The electrochemical tests were carried out using a Research M273A test system and a standard three-electrode system. The working electrode was a low-carbon steel specimen with rust after alternating dry/wet corrosion; the auxiliary electrode was a Pt sheet; and the reference electrode consisted of a saturated calomel electrode (SCE) and a Luggin capillary. The electrochemical test solution was the electrolyte solution used in the simulated corrosion experiments. The frequency range for the EIS tests was 10 mHz–100 kHz, and the amplitude of the applied perturbation AC potential during testing was 10 mV. A Rigaku-D/max 2000 X-ray diffractometer (XRD) and synchrotron-radiation XRD (Shanghai Synchrotron Radiation Facility SSRF, BL14B1 beamline) were used to analyze the phase composition of the rust layer.

2 Experimental Results and Analysis

2.1 Corrosion kinetics

Figure 1 shows the corrosion mass-gain curves of Q235B steel in the simulated industrial–coastal atmospheric environment. It can be seen that, under the nine different simulated conditions, the corrosion mass gain of Q235B steel increased with increasing corrosion time, indicating that the corrosion process proceeded continuously. Figures 1a and b show that when the Na_2SO_3 concentration in the solution used to simulate the industrial–coastal atmosphere was 0.001 and 0.010 mol/L, changes in pH value (pH 3.5–6.0) had no obvious effect on the corrosion mass-gain curves of Q235B steel. Figure 1c shows that when the Na_2SO_3 concentration in the simulated solution increased to 0.150 mol/L, changes in pH value had little effect on the corrosion mass-gain curves of Q235B steel before 20 cyc, and the mass-gain curves nearly overlapped. After 20 cyc, the corrosion mass gain of Q235B steel was greatest in the simulated solution with pH 4.5, followed by that in the simulated solution with pH 3.5, and was smallest in the simulated solution with pH 6.0; moreover, this phenomenon became increasingly pronounced as the corrosion time increased. These results indicate that when the SO_2 concentration in the industrial–coastal atmosphere is relatively low, changes in pH value have no obvious effect on the corrosion mass-gain curves of Q235B steel. When the SO_2 concentration is relatively high, the corrosion mass-gain curve of Q235B steel first increases and then decreases as pH decreases; that is, when the pH value is at a certain point between "relatively high" and "relatively low," the corrosion mass gain of Q235B steel reaches a maximum.

Fig. 1 Corrosion mass gain (ΔW) of Q235B steel in simulated coastal–industrial atmospheres with 0.001 mol/L (a), 0.010 mol/L (b) and 0.150 mol/L (c) Na_2SO_3 solution.

Usually, the kinetics of corrosion mass gain of steel in the atmospheric environ-

ment conforms to the exponential function law[1]:

$$\Delta W = AN^n \tag{1}$$

where N is the number of dry/wet alternating corrosion cycles; ΔW is the cumulative corrosion mass gain per unit area of the specimen when the number of dry/wet alternating cycles is N; A is the corrosion mass gain per unit area of the specimen per unit time, reflecting the magnitude of the corrosion rate during the first dry/wet alternating corrosion cycle; and n is the exponential index, usually a constant. According to Eq. (1), the instantaneous atmospheric corrosion rate of steel can be expressed as:

$$\mathrm{d}\Delta W/\mathrm{d}N = AnN^{n-1} \tag{2}$$

Therefore, taking logarithms on both sides of Eqs. (1) and (2), respectively, gives:

$$\lg \Delta W = \lg A + n \lg N \tag{3}$$

$$\lg(\mathrm{d}\Delta W/\mathrm{d}N) = \lg A + \lg n + (n-1) \lg N \tag{4}$$

From Eq. (4), it can be seen that when $n < 1$, the corrosion rate decreases with increasing N; when $n > 1$, the corrosion rate increases with increasing N; and when $n = 1$, the corrosion rate is constant. Therefore, a smaller n indicates a lower corrosion tendency.

Figure 2 shows the results for corrosion mass gain of Q235B steel in a simulated industrial-coastal atmospheric environment plotted on logarithmic coordinates. It can be seen from Figs. 2a and 2b that, when the concentration of Na_2SO_3 in the solution used to simulate the industrial-coastal atmosphere was 0.001 and 0.010 mol/L, the $\lg \Delta W$-$\lg N$ curves at the three pH values all appeared as straight lines, indicating that changes in pH value (pH 3.5–6.0) had no obvious effect on the corrosion mass gain of Q235B steel. From Fig. 2c, it can be seen that, when the Na_2SO_3 concentration in the simulated solution increased to 0.150 mol/L, the $\lg \Delta W$-$\lg N$ curves at the three pH values no longer appeared simply as straight lines, but consisted of four line segments; the N values at the inflection points were 7, 14, and 25 in sequence, and the change in pH value had no obvious influence on the inflection points. This indicates that the corrosion process of Q235B steel in an industrial-coastal atmosphere with a high SO_2 concentration is relatively complex. Before 7 cyc, the change in pH value had no obvious effect on the corrosion mass gain of Q235B steel, and the three mass-gain curves almost overlapped. At 7–14 cyc, the effect of pH value on the

[1]References [25,26] as cited in the original text.

Fig. 2

Figure 1: Fig. 2

corrosion mass gain of Q235B steel was still not obvious, but compared with the mass-gain results during the first 7 cyc, the change in corrosion mass gain with time in this stage exhibited a slowing tendency. At 14–25 cyc, the change in corrosion mass gain with time again showed an accelerating tendency. After 25 cyc, the change in corrosion mass gain with time once again exhibited a slowing tendency. From the appearance, all three corrosion mass-gain curves showed a "flying swallow" -shaped inflection.

Table 2 lists the fitting equations and correlation coefficients (R^2) obtained by fitting the mass-gain curves shown in Fig. 2 using Eq. (3) for Q235B steel under each simulated environment. It can be seen that, when the Na_2SO_3 concentration in the solution used for the simulated environment was 0.001 mol/L, the n values of Q235B steel under the three pH conditions (3.5, 4.5, and 6.0) were all close to but slightly less than 1, indicating that under these conditions the corrosion rate of Q235B steel was almost constant, only slowly decreasing with increasing corrosion period. However, when the Na_2SO_3 concentration in the simulated solution increased to 0.010 mol/L, the n values of Q235B steel under the three pH conditions were all close to but slightly greater than 1, indicating that under these conditions the corrosion rate of Q235B steel increased slightly with increasing corrosion period. This indicates that, in an industrial–coastal atmosphere with a relatively low SO_2 content, the effect of pH value variation on the corrosion kinetics of Q235B steel is not obvious. When the Na_2SO_3 concentration in the simulated solution increased to 0.150 mol/L, during the first and second stages of corrosion, the n values of the three corrosion mass-gain curves at different pH values were all less than 1; in the third stage they were all greater than 1; but after entering the fourth stage, $n = 0.887$ at pH 6.0, $n = 0.994$ at pH 3.5, and $n = 1.007$ at pH 4.5. This indicates that at high

Fig. 2 Bilogarithmic plots of the corrosion mass gain of Q235B steel in simulated coastal-industrial atmospheres with 0.001 mol/L (a), 0.010 mol/L (b) and 0.150 mol/L (c) Na_2SO_3 solution

Table 2 Fitting results of corrosion mass gain of Q235B steel in the nine simulated coastal–industrial atmospheres in Table 1 (y is $\lg \Delta W$, x is $\lg N$, $\lg A$ is the constant and n is the slope in Eq. (3), R^2 is the fitting correlation coefficient)

Atmosphere	1st stage	2nd stage	3rd stage	4th stage
No.1	$y = -0.108 + 0.991x R^2 = 0.998$	-	-	-

Atmosphere	1st stage	2nd stage	3rd stage	4th stage
No.2	$y = -0.069 + 0.958xR^2 = 0.998$	-	-	-
No.3	$y = -0.122 + 0.996xR^2 = 0.999$	-	-	-
No.4	$y = -0.094 + 1.039xR^2 = 0.999$	-	-	-
No.5	$y = -0.044 + 1.006xR^2 = 0.999$	-	-	-
No.6	$y = -0.072 + 1.031xR^2 = 0.999$	-	-	-
No.7	$y = 0.057 + 0.772xR^2 = 0.977$	$y = 0.232 + 0.566xR^2 = 0.992$	$y = -0.725 + 1.401xR^2 = 0.996$	$y = -0.176 + 0.994xR^2 = 0.999$
No.8	$y = 0.062 + 0.849xR^2 = 0.997$	$y = 0.256 + 0.605xR^2 = 0.992$	$y = -0.664 + 1.405xR^2 = 0.996$	$y = -0.096 + 1.007xR^2 = 0.995$
No.9	$y = 0.047 + 0.795xR^2 = 0.981$	$y = 0.199 + 0.614xR^2 = 0.964$	$y = -0.705 + 1.398xR^2 = 0.995$	$y = -0.014 + 0.877xR^2 = 0.998$

In an industrial-coastal atmosphere containing SO_2, at relatively high pH values the rust-layer products formed during the long-term corrosion of low-carbon steel exert a certain inhibiting effect on subsequent atmospheric corrosion; however, when the pH value is lower than a certain critical value, the rust-layer products have almost no inhibitory effect on later atmospheric corrosion. In a high-SO_2 industrial-coastal atmospheric environment, the influence of pH variation on the corrosion kinetics of Q235B steel becomes increasingly pronounced as the corrosion time is prolonged.

Figure 3 shows the curves of instantaneous corrosion rate versus the number of dry/wet alternations, calculated by Eq. (4) from the intercepts and slopes in the fitting equations listed in Table 2. Figure 3a indicates that, when the Na_2SO_3 concentration in the solution used to simulate the industrial-coastal atmosphere is 0.001 mol/L, the corrosion rate of Q235B steel decreases very slowly with increasing corrosion cycles, and pH has no significant effect on the change in corrosion rate. Figure 3b shows that, when the Na_2SO_3 concentration in the simulated solution is 0.010 mol/L, the corrosion rate of Q235B steel increases extremely slowly with prolongation of the corrosion cycle, and changes in pH likewise have no obvious influence on the corrosion rate. Figure 3c shows that,

Fig. 3

Figure 2: Fig. 3

when the Na_2SO_3 concentration in the simulated solution is further increased to 0.150 mol/L, in the 1st and 2nd stages the three corrosion-rate curves at different pH values decrease rapidly according to a decreasing function. In the 3rd stage, the three corrosion-rate curves increase rapidly according to an increasing function. The abrupt changes in corrosion rate in these three stages correspond to the "swallowtail" -type turning points on the corrosion mass-gain curves shown in Fig. 2c. When corrosion proceeds to the 4th stage, Q235B steel at the three different pH values corrodes at rates lower than those in the 3rd stage. At pH 6.0, the corrosion rate decreases with time, while at pH 3.5 and 4.5 the corrosion rate is essentially time-independent. In addition, when the pH decreases from 6.0 to 4.5, the corrosion rate of Q235B steel increases; when the pH decreases from 4.5 to 3.5, the corrosion rate decreases. That is, when the pH lies at a certain value between "relatively high" and "relatively low," the corrosion of Q235B steel reaches a maximum.

The above results show that, when the SO_2 concentration in an industrial-coastal atmospheric environment is relatively low, changes in pH have no obvious effect on the corrosion kinetics of Q235B steel. When the SO_2 concentration is relatively high, changes in pH have a comparatively pronounced influence on the corrosion kinetics of Q235B steel; moreover, a decrease in pH does not necessarily increase the corrosion rate of Q235B steel, and may instead reduce it.

2.2 Phase composition of the rust layer

Figure 4 shows the XRD patterns of the corrosion products formed on Q235B steel under simulated industrial-coastal atmospheric conditions after different numbers of dry/wet alternating corrosion cycles. When the number of dry/wet alternations is 10 cyc, and when the simulated solution contains ···

Fig. 3 Curves of $\lg r$ vs $\lg N$ of Q235B steel in simulated coastal-industrial atmospheres with 0.001 mol/L (a), 0.010 mol/L (b) and 0.150 mol/L (c) Na_2SO_3 solution (r—corrosion rate)

When the Na_2SO_3 concentration was 0.001 mol/L, the phase composition of the corrosion products formed on Q235B steel under the three pH conditions (3.5, 4.5, and 6.0) was α-FeOOH, γ-FeOOH, Fe_3O_4, and a small amount of β-FeOOH (Fig. 4a1). When the Na_2SO_3 concentration in the simulated solution was 0.010 mol/L, the phase composition of the corrosion products formed under the three pH conditions was α-FeOOH, β-FeOOH, and Fe_3O_4, and no characteristic peak of β-FeOOH was detected (Fig. 4b1). When the Na_2SO_3 concentration in the simulated solution was increased to 0.150 mol/L, only α-FeOOH and a small amount of Fe_3O_4 were detected in the corrosion products formed under the

three pH conditions, and neither β-FeOOH nor γ-FeOOH was detected (Fig. 4c1). These results indicate that, at the initial stage of corrosion, changing the Na_2SO_3 concentration in the simulated solution has a significant effect on the phase composition of the rust layer; however, when the Na_2SO_3 concentration in the simulated solution is kept constant, variation of pH (3.5–6.0) has no effect on the phase composition of the corrosion products. When the number of dry/wet alternate corrosion cycles was 120 cyc, and the Na_2SO_3 concentration in the simulated solution was 0.001 mol/L, the phase composition of the corrosion products on Q235B steel under the three pH conditions was α-FeOOH, γ-FeOOH, and Fe_3O_4, and β-FeOOH was not detected (Fig. 4a2). Compared with 10 cyc (Fig. 4a1), the relative intensity of the diffraction peak of γ-FeOOH at 120 cyc was lower, indicating that, with increasing corrosion time, the contents of the β-FeOOH phase and the γ-FeOOH phase decreased relatively. When the Na_2SO_3 concentration in the simulated solution was 0.010 mol/L, the corrosion products were still mainly composed of α-FeOOH, γ-FeOOH, and Fe_3O_4 (Fig. 4b2). Compared with 10 cyc (Fig. 4b1), the peak intensity of γ-FeOOH at 120 cyc decreased relatively, whereas the peak intensity of α-FeOOH increased relatively, indicating that with prolonged corrosion time, γ-FeOOH may have been reduced to Fe_3O_4 or transformed into the α-FeOOH phase [13]. When the Na_2SO_3 concentration in the simulated solution was 0.150 mol/L, the corrosion products were still mainly composed of α-FeOOH and a small amount of Fe_3O_4 (Fig. 4c2); at 120 cyc, the diffraction intensities of the phases showed no obvious difference and were the same as those at 10 cyc (Fig. 4c1). Therefore, at the same Na_2SO_3 concentration, changing the pH has no obvious effect on the phase composition of the corrosion products of low-carbon steel; however, under the same pH condition, changing the Na_2SO_3 concentration affects the phase composition of the corrosion products of low-carbon steel.

Figure 5 shows the in situ XRD patterns of the corrosion products of Q235B steel after 120 cyc of dry/wet alternate corrosion in simulated solutions with different pH values and different Na_2SO_3 concentrations. Figures 5a and 5b show that, when the Na_2SO_3 concentration in the simulated solution was 0.001 and 0.010 mol/L, the corrosion products were composed of α-FeOOH, γ-FeOOH, Fe_3O_4, and β-FeOOH. This indicates that when the Na_2SO_3 concentration in the simulated solution was relatively low, β-FeOOH was always present in the corrosion products. The reason why β-FeOOH was not detected in the conventional XRD patterns shown in Fig. 4 may be that its content was relatively low or its grain size was small. When the Na_2SO_3 concentration in the simulated solution was 0.150 mol/L, the detected phases were consistent with the results shown in Fig. 4; the corrosion products were mainly composed of α-FeOOH and a very small amount of Fe_3O_4. In addition, under the three simulated conditions, the effect of pH variation on the phase composition of the rust layer was not obvious, which is also consistent with the results shown in Fig. 4.

The above results show that, in the solution used to simulate an industrial-coastal atmosphere, when the Na_2SO_3 concentration is fixed, variation in pH has no effect on the phase composition of the corrosion products of Q235B steel.

Figure 4: XRD spectra of the powdered rust on Q235B steel in the simulated coastal–industrial atmospheres after different corrosion cycles. The symbol legend indicates: α-FeOOH; β-FeOOH; γ-FeOOH; Fe_3O_4. Each panel plots Intensity / a.u. versus $2\theta/(^\circ)$, with curves labeled pH = 6.0, pH = 4.5, and pH = 3.5. Panels are labeled (a1), (a2), (b1), (b2), (c1), and (c2).

Figure 3: Figure 4: XRD spectra of the powdered rust on Q235B steel in the simulated coastal–industrial atmospheres after different corrosion cycles. The symbol legend indicates: α-FeOOH; β-FeOOH; γ-FeOOH; Fe_3O_4. Each panel plots Intensity / a.u. versus $2\theta/(^\circ)$, with curves labeled pH = 6.0, pH = 4.5, and pH = 3.5. Panels are labeled (a1), (a2), (b1), (b2), (c1), and (c2).

2.3 EIS

Figure 6 shows the Bode plots of the rusted Q235B steel electrode in the simulated solution after dry/wet cyclic corrosion in 0.150 mol/L Na_2SO_3 simulated solution. It is generally believed that the impedance modulus in the low-frequency region of a Bode plot reflects the charge-transfer resistance, while the impedance modulus in the high-frequency region reflects the resistance of the rust layer. Figure 6 shows that, in simulated industrial-coastal atmospheric environments with different pH values, the low-

Fig. 4 XRD spectra of the powdered rust on Q235B steel in the simulated coastal–industrial atmospheres after different corrosion cycles

(a1) 0.001 mol/L Na_2SO_3, 10 cyc (a2) 0.001 mol/L Na_2SO_3, 120 cyc

(b1) 0.010 mol/L Na_2SO_3, 10 cyc (b2) 0.010 mol/L Na_2SO_3, 120 cyc

(c1) 0.150 mol/L Na_2SO_3, 10 cyc (c2) 0.150 mol/L Na_2SO_3, 120 cyc

The impedance modulus values in the low-frequency region (0.01 Hz) and the high-frequency region (10^4 Hz) both increase with increasing dry/wet alternating cycles, and tend to become stable after 30 cyc. This indicates that, as the corrosion time is prolonged, the interfacial structure between the rust layer and the steel substrate gradually becomes stable. From the phase-angle–frequency relationship shown in Fig. 6, it can also be seen that at 1 cyc, a phase peak appears in the frequency range of 1–10 Hz (Fig. 6a2, b2, and c2). After 10 cyc, the phase peak rapidly shifts to the left, which may be related to the continuous formation of corrosion products. In addition, owing to the influence of the high-frequency phase shift caused by the internal resistance of the reference electrode, the high-frequency phase angle is not 0°[27,28].

Figure 7 is a schematic diagram of the equivalent circuit used for fitting the EIS shown in Fig. 6. In it, R_r represents the sum of the solution resistance and the rust-layer resistance (where the solution resistance is approximately constant, so the change in R_r directly reflects the change in rust-layer resistance); R_{ct} represents the charge-transfer resistance; the constant-phase-angle elements Q_f and Q_{dl} represent the high-frequency phase-shift capacitance and the double-layer

Figure 5

Figure 4: Figure 5

Figure 6

Figure 5: Figure 6

capacitance, respectively; and Z_{w} is the diffusion impedance. The relationship between Z_{w} and angular frequency ω is shown in Eq. (5):

$$Z_{\mathrm{w}} = (j\omega)^{-0.5} Y_0^{-1} \tag{5}$$

where Y_0 is a constant and j is the imaginary unit. A larger Y_0 indicates a smaller diffusion resistance of the medium. For a rust-covered electrode, the larger Y_0 is, the more the rust layer affects diffusion.

Fig. 5 Synchrotron radiation XRD spectra of the powdered rust on Q235B steel after 120 cyc in simulated coastal-industrial atmospheres

(a) 0.001 mol/L Na_2SO_3 (b) 0.010 mol/L Na_2SO_3 (c) 0.150 mol/L Na_2SO_3

Fig. 6 Bode plots of the EIS results for the rusted Q235B steel samples as a function of the CCT number in the simulated coastal-industrial atmospheres with different pH of 0.150 mol/L Na_2SO_3 solution

(a1) pH = 3.5, impedance-frequency (a2) pH = 3.5, phase angle-frequency

(b1) pH = 4.5, impedance-frequency (b2) pH = 4.5, phase angle-frequency

(c1) pH = 6.0, impedance-frequency (c2) pH = 6.0, phase angle-frequency

Fig. 7 Equivalent circuit for EIS of the rusted Q235B steel samples in the simulated coastal-industrial atmospheres with 0.150 mol/L Na_2SO_3 simulating solution (Q_f—constant phase element (CPE) parameter for the phase shift; R_r—sum of the rust resistance and the solution resistance; Q_{dl}—CPE parameter of the double layer; R_{ct}—charge transfer resistance; Z_w—diffusion impedance)

The weaker the barrier capability against mass transfer, the poorer the compactness of the rust layer.

Figures 8a-c show, respectively, the curves of solution resistance plus rust-layer resistance R_r, diffusion admittance Y_0, and charge-transfer resistance R_{ct} obtained by fitting the EIS results as functions of the number of dry/wet cycles. The statistical error in the fitting process was on the order of 10^{-4}. In simulated industrial-coastal atmospheric environments with three different pH values, Fig. 8a shows that, when the number of dry/wet cycles increased to 30 cyc, R_r increased to approximately 80 $\Omega \cdot \mathrm{cm}^2$, and thereafter fluctuated around this value. This indicates that, with increasing corrosion time and growth of the rust layer,

the rust-layer resistance gradually increased; however, the fluctuations in R_r may be related to random cracking and healing during rust-layer growth. Figure 8b shows that Y_0 decreased rapidly with the prolongation of the dry/wet cycling and then tended to stabilize. This indicates that after a stable rust layer formed, the diffusion and migration of corrosive media in the rust layer also became relatively stable. However, when the pH of the simulated solution was 4.5, Y_0 was slightly larger than those at pH 3.5 and 6.0, indicating that at pH 4.5 the rust layer on the Q235B steel surface was relatively loose and that ionic media migrated more readily through its pores. Figure 8c shows that, before 30 cyc, R_{ct} increased with the number of dry/wet cycles and subsequently decreased. The value of R_{ct} in the simulated environment with pH 4.5 was lower than those at pH 3.5 and 6.0, indicating that the electrochemical corrosion rate of Q235B steel after long-term rusting in the simulated environment with pH 4.5 was greater than those in the simulated environments with pH 3.5 and 6.0. Therefore, the results shown in Fig. 8c are consistent with the corrosion weight-gain curves shown in Figs. 1c and 2c and the corrosion-rate results shown in Fig. 3c; that is, when the SO_2 concentration in the simulated industrial–coastal atmosphere is relatively high, the effect of the initial pH change on the corrosion rate of steel is not obvious. With increasing corrosion time, the corrosion rate of steel first increases and then decreases as the pH decreases. When the pH is directly maintained at a "relatively high" or "relatively low" value, the corrosion of Q235B steel reaches a maximum.

2.4 Discussion of the corrosion mechanism

The anodic process in atmospheric corrosion of steel is the dissolution of Fe, while the cathodic process is relatively complex and is mainly determined by the environmental conditions and the properties of the corrosion products on the steel surface. When the atmosphere contains only Cl^- pollutants, atmospheric corrosion of steel mainly follows the anodic dissolution mechanism of Cl^- [23]. When the atmosphere contains only SO_2, it mainly follows the cyclic regeneration mechanism of $SO_4{}^{2-}$ [29,30]. The cathodic process at the initial stage of corrosion is mainly controlled by oxygen-limited diffusion. In the simulated industrial–coastal atmospheric environment, with a constant Cl^- concentration and a changing SO_2 concentration, it was found that when the SO_2 concentration was relatively low, the influence of pH change on the corrosion behavior of Q235B steel throughout the entire corrosion process was not obvious. This indicates that corrosion of Q235B steel mainly follows the Cl^- cycling mechanism, is not controlled by the cyclic regeneration mechanism of $SO_4{}^{2-}$, and that the cathodic process is unrelated to H^+ reduction. When the SO_2 concentration was relatively high, the influence of pH change on the initial corrosion of Q235B steel was not obvious,

Fig. 8 Evolution of the parameters of R_r (a), Y_0 (b) and R_{ct} (c) obtained from the EIS data for Q235B steel samples in the simulated atmospheres with 0.150 mol/L Na_2SO_3 solution as a function of the cyclic number

As the corrosion time is prolonged, the influence of pH becomes progressively

more significant, indicating that in the initial stage of corrosion Q235B steel mainly follows the cycling mechanism of Cl^-, whereas in the later stage of corrosion it mainly follows the cyclic regeneration mechanism of SO_4^{2-}. The cyclic regeneration mechanism of SO_4^{2-} and the mechanism by which pH affects it are as follows [29, 30]. SO_2 dissolves in water and is oxidized to H_2SO_4:

$$2SO_2 + 2H_2O + O_2 = 2H_2SO_4 \tag{6}$$

H_2SO_4 causes Fe to dissolve:

$$4H_2SO_4 + 2O_2 + 4Fe = 4FeSO_4 + 4H_2O \tag{7}$$

$FeSO_4$ hydrolyzes to form hydroxide compounds and free H_2SO_4:

$$4FeSO_4 + O_2 + 6H_2O = 4FeOOH + 4H_2SO_4 \tag{8}$$

It can be seen that, when the pH is lowered to a certain extent, the equilibrium of Eq. (7) shifts to the right, promoting corrosion of the steel. However, when the pH is very low, the increased acidity causes the equilibrium of Eq. (8) to shift to the left, slowing the corrosion rate of the steel. Therefore, when the pH lies at a certain value between "relatively high"and "relatively low,"the corrosion rate of the steel reaches a maximum. In addition, the presence of Cl^- in the atmospheric environment helps the formation of the β-FeOOH phase in the rust layer, whereas the presence of SO_2 suppresses, to some extent, the existence of β-FeOOH. As the SO_2 concentration in the environment increases, the relative contents of β-FeOOH and γ-FeOOH in the rust layer decrease, possibly because γ-FeOOH undergoes reduction to Fe_3O_4 or a phase transformation to α-FeOOH. With prolonged corrosion time, the evolution of the phase composition of the rust layer exhibits similar regularity.

3 Conclusions

(1) When the SO_2 concentration in the simulated industrial–coastal atmosphere is relatively low, the change in pH has no obvious effect on the corrosion rate of Q235B steel. In a high-concentration SO_2 environment, when the pH decreases from 6.0 to 4.5, the corrosion rate of the steel increases; when the pH is further reduced to 3.5, the corrosion rate decreases. That is, when the pH is at a certain value between "relatively high" and "relatively low," the corrosion of Q235B steel reaches a maximum.

(2) When the SO_2 concentration in the simulated industrial–coastal atmosphere is relatively low, the corrosion products are mainly composed of α-FeOOH, γ-FeOOH, Fe_3O_4, and β-FeOOH. When the SO_2 concentration is relatively high, the corrosion products are mainly composed of α-FeOOH and Fe_3O_4. When the SO_2 concentration in the simulated environment is

constant, changes in pH have no obvious effect on the composition of the rust layer.

(3) When the SO_2 concentration in the simulated industrial-coastal atmosphere is relatively low, the corrosion of Q235 steel mainly follows the cycling mechanism of Cl^-, and changing the pH has no obvious effect on the corrosion behavior of the steel. When the SO_2 concentration is relatively high, the initial corrosion of Q235 steel mainly follows the cycling mechanism of Cl^-. With prolonged corrosion time, the influence of SO_2 on corrosion becomes gradually more significant, and the corrosion of the steel is accelerated through the cyclic regeneration of H_2SO_4.

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