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Electrochemical Corrosion Behavior of Q235B Carbon Steel in 10% NaCl and H2S Solutions with Different pH

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Abstract: The electrochemical corrosion behavior of Q235B carbon steel in 10% NaCl and H2S solutions with different pH was studied by means of electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves. The results show that when the pH is less than 3, the corrosion is mainly controlled by the acidic dissolution process of the anode, and the electrochemical impedance spectrum not only has a capacitive arc in the high frequency region, but also exists an inductive arc in the low frequency region; when the pH is in the range of 3.05 to 6.01, the radius of the capacitive arc increases as the pH increases, and Rr also increases, reaching a maximum at a pH of 5.06, which is related to the deposition and coverage of the black sulfide generated on the surface of the working electrode. Rt and Qdl also increase with the increase of pH; when the pH is higher than 7, the surface of the electrode forms oxide film and sulfide, and the potentiodynamic polarization curve gradually shows passivation characteristics with increasing pH. As large as 9.06, three stages of activation, passivation, and over-passivation can be clearly seen in the potentiodynamic polarization curve. Obvious Warburg impedance characteristics can also be seen in the electrochemical impedance spectrum.

1. Introduction

The oil tanks generally contain substances that are highly corrosive, such as sulfides. Therefore, in the course of use, the tanks will inevitably undergo a variety of different corrosion conditions, resulting in leakage of crude oil in the tanks and other conditions, endangering the safety of personnel property. Hydrogen sulphide is also one of the main factors causing corrosion of oil storage tanks. Therefore, this article takes Q235B, a typical material for oil storage tanks, as the study object, and passes the EIS test and potentiodynamic polarization curve test method for 10% NaCl and H2S solution with different pH environment was performed to examine the electrochemical corrosion mechanism, the characteristics of the corrosion product film, and the change of corrosion rate with pH value.

2. Experimental methods

2.1. Experimental materials and corrosive media

Experimental materials use Q235B carbon steel, the composition of which is shown in Table 1:

| element | C  | Cr  | Mn  | Mo  | Ni  | S   | Si  | P   | Ti   | Fe   |
|---------|----|-----|-----|-----|-----|-----|-----|-----|------|------|
| W, %    | 0.2| 1.4 | 0.045| 0.35| 0.045|      |      |      |       |      |

Table 1. Chemical composition of Q235B carbon steel (mass fraction w, %).
The Q235B carbon steel was cut into circular iron specimens with a working area of 1cm². The back of the specimen was welded to the copper wire and then encapsulated in a Teflon tube using an epoxy resin as a working electrode for electrochemical experiments. Before the experiment, the working electrode should be polished and polished through 120#, 240#, 360#, 600#, and 800# sandpaper to ensure that it can form conductive loops during the experiment. Then it was washed repeatedly with anhydrous ethanol, dried, and placed in a desiccator for use. Corrosion medium is 10% NaCl and H2S solution with different pH. Experimental temperature is 23±1°C.

2.2. EIS and potentiodynamic polarization curve test
The EIS and potentiodynamic polarization curves were tested using the Gamry 600 electrochemical workstation. The three-electrode system was used. The Q235B was used as the working electrode, the saturated calomel electrode (SCE) was the reference electrode, the graphite electrode was the auxiliary electrode. A saturated KCl salt bridge was used for the connection between the working electrode and the reference electrode. The test is conducted under the open circuit potential (OCP) ±0.25V of Q235B carbon steel. The amplitude of the sine wave of the EIS excitation signal is 5mV. The sweep range of frequency is 0.01~1×10⁶Hz. Use the Gamry 600's own software to carry out the numerical fitting of the test. Select the appropriate equivalent circuit when fitting and analyze the structure and parameters of each component. The potentiodynamic polarization curve test scan speed is 0.5mV/s, the scanning range is relative to the open circuit potential (vs OCP), and the working area is 1cm². The same software was used to fit the Tafel fitting and the corresponding fitting parameters were obtained synchronously.

3. The experimental results
3.1. The analysis of EIS
The results of EIS test of hydrogen sulfide solutions at different pH from 1.07~9.06 are shown by the Nyquist and Bode plot, respectively. In the measured frequency range, the Nyquist plot of Figure 1 shows that the impedance of the system not only has a capacitance reactance arc in the high frequency region but also an inductive arc in the low frequency region when the pH is 1.07 and the pH value is 2. The phase angle Bode plot in Figure 2 shows that in addition to a phase angle in the high frequency region, there is also a reverse phase angle in the low frequency region, which corresponds to the inductive arc in the low frequency region of the Nyquist diagram in Figure 1. This is due to the fact that the exposed surface of the working electrode Q235B carbon steel reacts directly with the acidic solution and dissolves. The capacitive-arc in the high-frequency region represents the gradual balance between charge and discharge between the double-layers formed between the surface of the working electrode and the solution. The inductive arc in the low frequency region is generated by the process of adsorbing H⁺ on the surface of the working electrode and the desorption process of H2S and HS⁻ absorbed on the surface of the working electrode. Figure 3(a) is a fitting circuit for the EIS with pH values of 1.07 and 2 corresponding to the presence of inductive arcs. The electrochemical corrosion parameters obtained by the software fitting are shown in Table 2.

In the fitted equivalent circuit, Rs is the solution resistance, Rθ is the charge transfer resistance, and Rr is the corrosion product membrane resistance. Considering that the working electrode may cause corrosion reaction in the simulation liquid to generate corrosion products, the electrode surface is rough, and there is a certain dispersion effect between the electric double layers. Therefore, the constant phase angle element Q is used instead of the pure capacitance C. \[ Q = Y_0^{-1}/(jω)^n \]
where \( Y_0 \) is the admittance constant, \( n \) is the dispersion index, and the value range is 0≤n≤1. Qr is the working electrode. The surface corrosion product film capacitance, Qdl is the electric double layer capacitance between the working electrode and the solution, L is the equivalent inductance, and W is the Warburg impedance.
Fig. 1. The Nyquist plot of Q235B in pH of 1.07~6.01 simulation fluid.

The Nyquist plot shows a single capacitive-resistance arc in the frequency range. The corresponding phase angle Bode plot also shows only a time constant, but a new phase angle appears in the low-frequency region, and the low frequency region in the Nyquist plot. Corresponding to the increase of the corrosion product film, the equivalent circuit shown in Fig. 3(b) is used. The electrochemical corrosion parameters obtained by software fitting are shown in Table 2. As the pH value increases, the radius of the capacitive arc increases, and Rr also increases, reaching a maximum at a pH of 5.06, which is related to the deposition and coverage of sulfide on the surface of the working electrode. Rt and Qd1 also increase with increasing pH. This is due to the discontinuity of the corrosion products formed on the surface of the working electrode and the high density of crystal defects. Ion transport channels still exist on the surface of the electrode, making the reactants in the product. The resistance to electromigration is small, and the charge transfer reaction is not suppressed by the covering of the sulfide on the electrode surface. The ndl is 0.8741 at pH 3.05, which is close to the ideal capacitance. At the rest of the pH, ndl is 1 indicating that the electrode becomes purely capacitive.

| pH   | equivalent circuit | Rs/ohm | R//ohm | Rs/ohm | L/H   | Qa/S*S*a | ndl |
|------|--------------------|--------|--------|--------|-------|-----------|-----|
| 1.07 | a                  | 1.02   | 117    | 19.56  | 54.3  | 1.191E-03 | 0.794 |
| 2.00 | a                  | 0.9946 | 51.66  | 451    | 660.8 | 7.956E-04 | 0.8115 |

When the pH value is between 3.05 and 6.01, the surface of the working electrode, as shown in the middle electrode of Figure 6, shows a clear black corrosion product film. The Nyquist plot shows a single capacitive-resistance arc in the frequency range. The corresponding phase angle Bode plot also shows only a time constant, but a new phase angle appears in the low-frequency region, and the low frequency region in the Nyquist plot. Corresponding to the increase of the corrosion product film, the equivalent circuit shown in Fig. 3(b) is used. The electrochemical corrosion parameters obtained by software fitting are shown in Table 2. As the pH value increases, the radius of the capacitive arc increases, and Rr also increases, reaching a maximum at a pH of 5.06, which is related to the deposition and coverage of sulfide on the surface of the working electrode. Rt and Qd1 also increase with increasing pH. This is due to the discontinuity of the corrosion products formed on the surface of the working electrode and the high density of crystal defects. Ion transport channels still exist on the surface of the electrode, making the reactants in the product. The resistance to electromigration is small, and the charge transfer reaction is not suppressed by the covering of the sulfide on the electrode surface. The ndl is 0.8741 at pH 3.05, which is close to the ideal capacitance. At the rest of the pH, ndl is 1 indicating that the electrode becomes purely capacitive.

| pH   | equivalent circuit | Rs/ohm | R//ohm | Rs/ohm | Qa/S*S*a | ndl |
|------|--------------------|--------|--------|--------|-----------|-----|
| 1.07 | a                  | 1.02   | 117    | 19.56  | 54.3      | 1.191E-03 | 0.794 |
| 2.00 | a                  | 0.9946 | 51.66  | 451    | 660.8     | 7.956E-04 | 0.8115 |

Table 3. EIS fitting parameters for the simulated solution of Q235B at pH 3.05~6.01.

| pH   | equivalent circuit | Rs/ohm | R//ohm | Rs/ohm | Qa/S*S*a | Qr/S*S*a | ndl |
|------|--------------------|--------|--------|--------|-----------|-----------|-----|
| 3.05 | a                  | 1.02   | 117    | 19.56  | 54.3      | 1.191E-03 | 0.794 |
| 4.00 | a                  | 0.9946 | 51.66  | 451    | 660.8     | 7.956E-04 | 0.8115 |

When the pH value is between 3.05 and 6.01, the surface of the working electrode, as shown in the middle electrode of Figure 6, shows a clear black corrosion product film. The Nyquist plot shows a single capacitive-resistance arc in the frequency range. The corresponding phase angle Bode plot also shows only a time constant, but a new phase angle appears in the low-frequency region, and the low frequency region in the Nyquist plot. Corresponding to the increase of the corrosion product film, the equivalent circuit shown in Fig. 3(b) is used. The electrochemical corrosion parameters obtained by software fitting are shown in Table 2. As the pH value increases, the radius of the capacitive arc increases, and Rr also increases, reaching a maximum at a pH of 5.06, which is related to the deposition and coverage of sulfide on the surface of the working electrode. Rt and Qd1 also increase with increasing pH. This is due to the discontinuity of the corrosion products formed on the surface of the working electrode and the high density of crystal defects. Ion transport channels still exist on the surface of the electrode, making the reactants in the product. The resistance to electromigration is small, and the charge transfer reaction is not suppressed by the covering of the sulfide on the electrode surface. The ndl is 0.8741 at pH 3.05, which is close to the ideal capacitance. At the rest of the pH, ndl is 1 indicating that the electrode becomes purely capacitive.
The Nyquist plot at pH 7.14 and 8.00 is similar to the Nyquist plot at pH 3.05 to 6.01. Therefore, the equivalent circuit (b) is also used for the fitting. The fitting parameters are shown in Table 2. When pH>7, the corrosion of the surface of the working electrode is shown on the right side of Figure 6, the surface of the metal is light yellow, and black punctiform sulfides are formed on the edge. When the pH increases to 9.06, the Nyquist plot embodies the obvious Warburg impedance characteristics. The equivalent circuit consists of the membrane impedance and the interfacial electrical bilayer impedance, as shown in Figure 3(c). The fitting parameters are shown in Table 4.

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### Table 4. EIS fitting parameters for Q235B at pH 9.06.

| pH  | equivalent circuit | $R_s$/ohm | $R_r$/ohm | $R_0$/ohm | $Q_{dl}$/S*s^a | $Q_0$/S*s^a | $n_0$ | $W$ | $Q_r$/S*s^(1/2) | $n_r$ |
|-----|-------------------|-----------|-----------|-----------|---------------|-------------|-------|-----|----------------|-------|
| 9.06| c                 | 1.335     | 1.228     | 293.2     | 4.108         | 7.22E-2     | 0.806 | 9.54E-3 | 1.70E-3         | 0.974 |

### 3.2. The analysis of Potentiodynamic polarization curve

Fig. 7 shows the results of determination of potentiodynamic polarization curves with pH of 1.07~6.01. The fitting parameters of Table 2 are obtained after Tafel fitting by software, where $E_{corr}$ is the corrosion potential relative to the reference electrode, $i_{corr}$ is the corrosion current, $\beta_a$ is the slope of the anodic polarization curve and $\beta_b$ is the slope of the cathodic polarization curve. It can be seen from Figure 7 that when the pH is 1.07, the anodic process is controlled by the active dissolution of iron, the
cathodic process is the depolarization process of \( \text{H}^+ \), and the polarization curve of the cathode region is -101.3, which is in the acidic medium. The theoretical value of \( \text{H}^+ \) discharge agrees with that of the electrode in the acid corrosion stage. From Figure 8 it can be seen intuitively that when the pH increases from 1.07 to 3.05, both the corrosion potential and the corrosion current show a significant decrease, indicating that the electrode reaction process has undergone a major change, probably with the rise of the pH, the activity of the iron dissolves less. When the pH was increased from 3.05 to 6.01, the corrosion potential and corrosion current continued to decrease, but the amplitude of the decrease was significantly reduced. This is because during the anodic polarization, a large amount of \( \text{Fe}^{2+} \) was dissolved on the surface of the working electrode. Sulfide ions in the solution generate a large amount of sulfides attached to the surface of the electrode, so that dissolution of the anodized iron is inhibited. The corrosion current can characterize the corrosion rate, so the corrosion current is consistent with the change trend of the corrosion rate.

![Fig.7. Potentiodynamic Polarization Curve of Q235B at pH 1.07–6.01.](image)

![Fig.8. Potentiodynamic Polarization Curve of Q235B at pH 7.14–9.06.](image)

When the pH is 7.13, the corrosion current increases greatly, which shows that when the pH increases to 7.13, the corrosion rate of the electrode is greatly improved, because the HS⁻ in the solution participates in the cathode polarization. When the pH continues to increase to 8 and 9.06, the corrosion current decreases again and the slope of the anode also increases significantly, showing a passivation characteristic, especially when the pH is 9.06, the potentiodynamic polarization curve in Fig 8. There are obvious three stages of activation, passivation and passivation. The corrosion current at this time also reaches the minimum value of 9.15\( \mu \text{A} \cdot \text{cm}^{-2} \).

![Fig.9. Corrosion current as a function of pH.](image)

| pH   | \( E_{\text{corr}} \)/mV vs. Ref | \( i_{\text{corr}} \)/\( \mu \text{A} \cdot \text{cm}^{-2} \) | \( \beta_a \)/mV/dec⁻¹ | \( \beta_c \)/mV/dec⁻¹ |
|------|----------------------------------|---------------------------------|------------------------|------------------------|
| 1.07 |                                  |                                 |                        |                        |
| 2.00 |                                  |                                 |                        |                        |
| 3.05 |                                  |                                 |                        |                        |
| 4.18 |                                  |                                 |                        |                        |
| 5.06 |                                  |                                 |                        |                        |
| 6.01 |                                  |                                 |                        |                        |
| 7.14 |                                  |                                 |                        |                        |
| 8.00 |                                  |                                 |                        |                        |
| 9.06 |                                  |                                 |                        |                        |

Table 5. Polarization Curve Fitting Parameters of Q235B at pH of 1.07–9.06 Simulated Liquids
4. Conclusions

1) When pH<7.13, the corrosion rate of Q235B carbon steel in 10% NaCl and H₂S solutions with different pH values gradually decreases with the increase of pH;

2) The corrosion rate at pH < 3.05 is reduced to a more severe extent. The corrosion is mainly controlled by the active dissolution process of the anode, and no sulfide is generated. For 3.05<pH<7.13, the corrosion rate decline process is relatively gentle. The surface of the working electrode is obviously covered with a layer of black uniform and dense sulfide corrosion product film. This process is mainly controlled by discontinuous deposition of sulfide on the electrode surface, but it is not enough to protect the working electrode;

3) In the alkaline solution with pH>7.13, the working electrode showed obvious passivation characteristics due to the oxide film formed on the surface and the sulphide produced at the edge, and the corrosion rate increased first and then decreased.

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