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Joint effect of temperature, stress states and sulfur ions on the CO_2 corrosion behavior of N80 tubing steel

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The joint influence of solution temperature, stress states and sulfur ions on the CO_2 corrosion behavior of N80 tubing steel, were investigated by using electrochemical impedance spectroscopy (EIS). The results showed that the addition of sulfur ions into the solution and with the introducing of stress into carbon steel can decrease the protective effect of the corrosion scale on the substrate at low temperature; and the protective effect enhances at high temperatures. The corrosion scale formed on N80 steel in stratum water containing sulfur ions are mainly consisted of $FeCO_3$ and FeS.

Keywords: Stress states; CO_2 corrosion; Electrochemical impedance spectroscopy (EIS); Stratum water

1. INTRODUCTION

It is well known that the CO_2 corrosion of carbon steel is a key problem in gas □ oil industry. Recently, the CO_2 corrosion becomes even more serious alongwith increasing the CO_2 and water in oil field as result of exploration in middle or later period and using the technique of enhanced oil recovery (EOR). Several mechanisms have been provided to interpret the mechanism of the CO_2 corrosion of carbon steel [1-3].

During these corrosion processes, the carbon steel surface can be covered by a corrosion scale ($FeCO_3$), which could slow down the corrosion rate and could protect the substrate from further corrosion [4,5]. The tubing steel may be not only suffered from CO_2 corrosion, but also suffered from different stress states underground, moreover, the stratum water may contain some aggressive anions, i.e., sulfur ions and chloride ions. Additionally, temperature plays an important role in the CO_2 corrosion behavior of carbon steel. The CO_2 corrosion may become complex considering the joint effect of temperature, sulfur ions and stress states, while, there is no paper focused on this problem. In this paper, the joint influence of solution temperature, stress states and sulfur ions on the CO_2

corrosion behavior of N80 tubing steel, were investigated by using electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL PART

2.1 Sample preparation

The sample was prepared from API N80 steel, which was composed of 0.04 %C; 0.2%Si; 1.5%Mn; 0.011%P; 0.003%S;0.02%Mo and Fe, balance. The sample was manufactured to a size of Φ10mm×5mm, one of the face exposed to air to act as the working face, which was polished with emery paper of successively decreasing grain size down to about 20μm, and washed by absolute alcohol. Before the test begins, the pure N_2 was poured forcedly into the solution and bubbled for 4h, and then the CO_2 gas was put into for2h. Then the EIS experiments were measured at different temperatures. The electrolyte was simulated stratum water conation 0.05M S^{2-}, and the electrolyte composition was listed in table 1.

Table 1 Concentration of various ions of stratum water from oilfield

Ions	Cl^-	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Ca^{2+}	Na^+	Mg^{2+}	S^{2-}
Concentration (g/L)	19	0.12	0.6	1.14	0.39	11.99	1.05	1.6

2.2 EIS measurement

A conventional three-electrodes system was used, the counter electrode was a Pt wire, and all potentials were measured against a saturated calomel electrode (SCE). The EIS experiments were carried out at EG&G Model 273A potentioststs/galvanostat with M5210 lock-in amplifier, and the experimental data was analyzed by ZsimpWin software. The sweeping frequency is from 100kHz to 10mHz with a potential increment of 10mV/S.

3. RESULTS AND DISCUSSION

3.1 EIS measured at 30 °C

3.1.1 The anodic spectra

Fig.1 shows the anodic impedance of N80 steel in stratum water containing sulfur ions at 30°C. It can be seen that two time-constants appears in the spectra, i.e., the capacitance arc at high frequency and a Warburg impedance at low frequency. The semicircle of the capacitance arc decreases under stress states condition, and the diffusion character becomes apparent. It indicates that the protective effect of corrosion scale on the substrate decreases and the diffusion process enhances with the introducing of stress. An equivalent electron circuit showed in Fig.1 d is used to fit the impedance spectra, in which, R_s is the solution resistance, Q_1 is the double-layer capacitance, R_1 is the transfer resistance, Q_2 and R_2 are the corrosion scale capacitance and resistance, and W is the diffusion admittance. The fitted result is showed in table 1, it shows that the transfer resistance R_1, the scale resistance R_2 and the diffusion admittance W decrease rapidly when carbon steel contains stress, this can be concluded that the compactness of the corrosion scale decreases, the ions can easily transfer through the corrosion scale, and the further corrosion may be occurred.

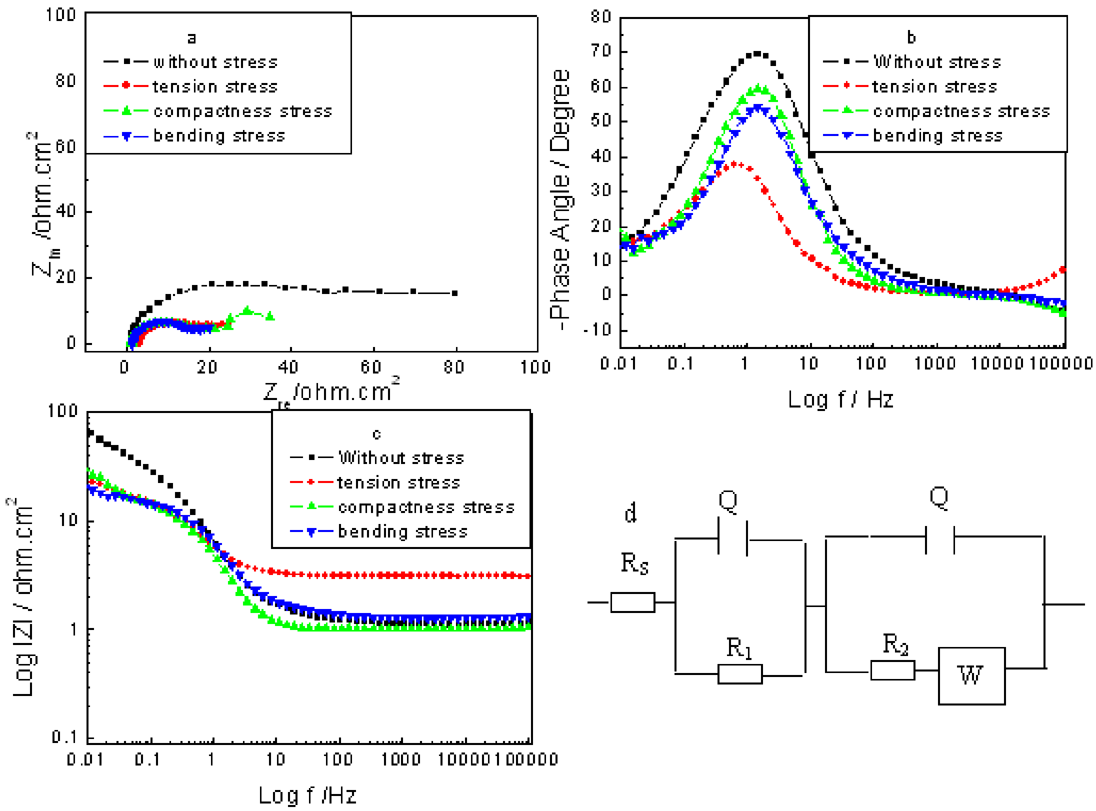

Figure 1. Impedance spectra of the anodic process measured at 30 °C, Nyquist plots (a), corresponding Bode phase angle (b), Bode impedance magnitude (c) plots and equivalent electron circuit (d)

Table 2. Equivalent electronic circuit fitting for the anodic process

Element	Without stress	Tension stress	Compactness stress	Bending stress
$R_S/\Omega\bullet cm^2$	1.119	1.003	0.9808	0.7535
$Q_1/F\bullet cm^{-2}$	0.06721	0.07419	0.08423	0.04269
n	0.7527	0.9949	0.9146	0.9026
$R_1/\Omega\bullet cm^2$	61.98	3.078	2.614	0.5684
$Q_2/F\bullet cm^{-2}$	0.05128	0.04995	0.03654	0.03777
n	1	0.8349	0.9466	0.8671
$R_2/\Omega\bullet cm^2$	145.3	15.33	14.56	14.36
$W/\Omega^{-1}\bullet S^{-0.5}$	0.8852	0.5785	0.3139	0.6247

At stress conditions, Fe ions may disengage from the normal positions in the lattice, the microstructure aberrance increases, and then Fe ions easily dissolve from the substrate to form a corrosion scale $FeCO_3$. Therefore, the occurrence tendency of corrosion increases, and a corrosion scale may be also easily formed on the substrate. Sulfur ions is an aggressive anion which has low atom radius, it cab be react with Fe^{2+} ions to form FeS or FeS_2. Because of the coexistence of FeS and $FeCO_3$ on the substrate, the corrosion scale $FeCO_3$ become inhomogeneous, the diffusion process enhances.

3.1.2 The cathodic spectra

For the dioxide corrosion of carbon steel, the cathodic step controls the total corrosion rate, therefore, it is necessary to investigate the joint effect of temperature and sulfur ions on the mechanism of the cathodic process. The impedance spectra measured at –100mV vs. self-corrosion potential was showed in Fig.2. It shows that the impedance spectra has one time-constant, i.e., a capacitance arc, and the semicircle decreases at stress conditions. An equivalent electron circuit showed in Fig.2d is used to fit the spectra, in this circuit, R_s is the solution resistance, Q_1 is the double-layer capacitance, R_t the transfer resistance, Q_1 and R_2 the corrosion scale capacitance and resistance. The fitted result is showed in table 3, it can be obviously seen that R_1 and R_2 decrease at stress conditions, indicating the increment of the cathodic corrosion rate. As noted above, the cathodic step is the key step of the total corrosion process, higher corrosion rate of the cathodic process higher corrosion rate of dioxide corrosion is, the higher cathodic corrosion rate may be related to the decreased compactness of the corrosion scale for the existence of sulfur ions and stress.

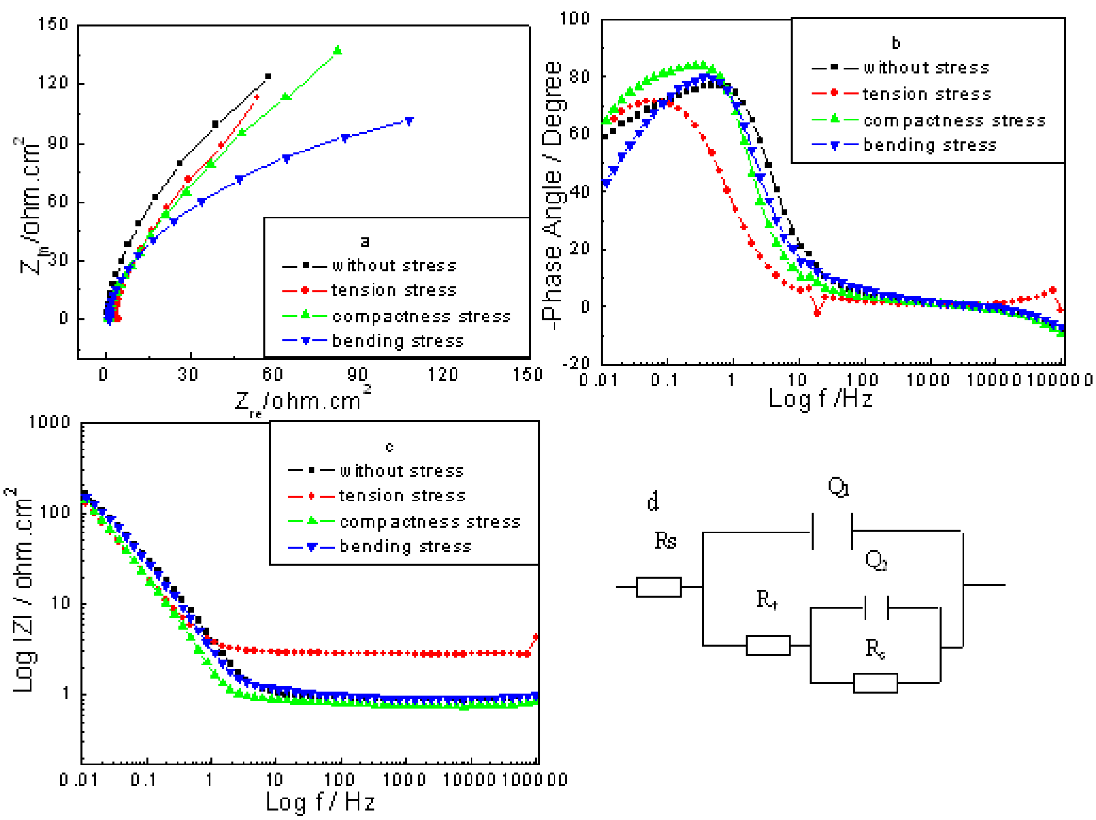

Figure 2. Impedance spectra of the cathodic process measured at 30 °C, Nyquist plots (a), corresponding Bode phase angle (b), Bode impedance magnitude (c) plots and equivalent electron circuit (d)

Table 3. Equivalent electronic circuit fitting for the cathodic process

Element	Without stress	Tension stress	Compactness stress	Bending stress
$R_S/\Omega\bullet cm^2$	0.9264	2.9	0.7867	0.9809
$Q_1/F\bullet cm^{-2}$	0.03959	0.07662	0.01687	0.05052
n	0.9983	0.9318	1	0.9808
$R_1/\Omega\bullet cm^2$	225.5	62.54	92.24	144.6
$Q_2/F\bullet cm^{-2}$	0.02655	0.06013	0.06663	0.1365
n	0.7295	1	1	1
$R_2/\Omega\bullet cm^2$	608.6	177.2	285.5	65.74

3.2 EIS measured at 60 °C

3.2.1 The anodic spectra

In order to investigate the influence of temperature on the impedance spectra, Fig.3 shows the anodic spectra measured at 60 °C. Similarly, the spectra is also consisted of two time-constants, i.e., the capacitance arc at high frequency and the Warburg impedance at low frequency. However, the semicircle in Nyquist plot enlarge and the diffusion character become more obvious with the introduction of stress into the substrate.

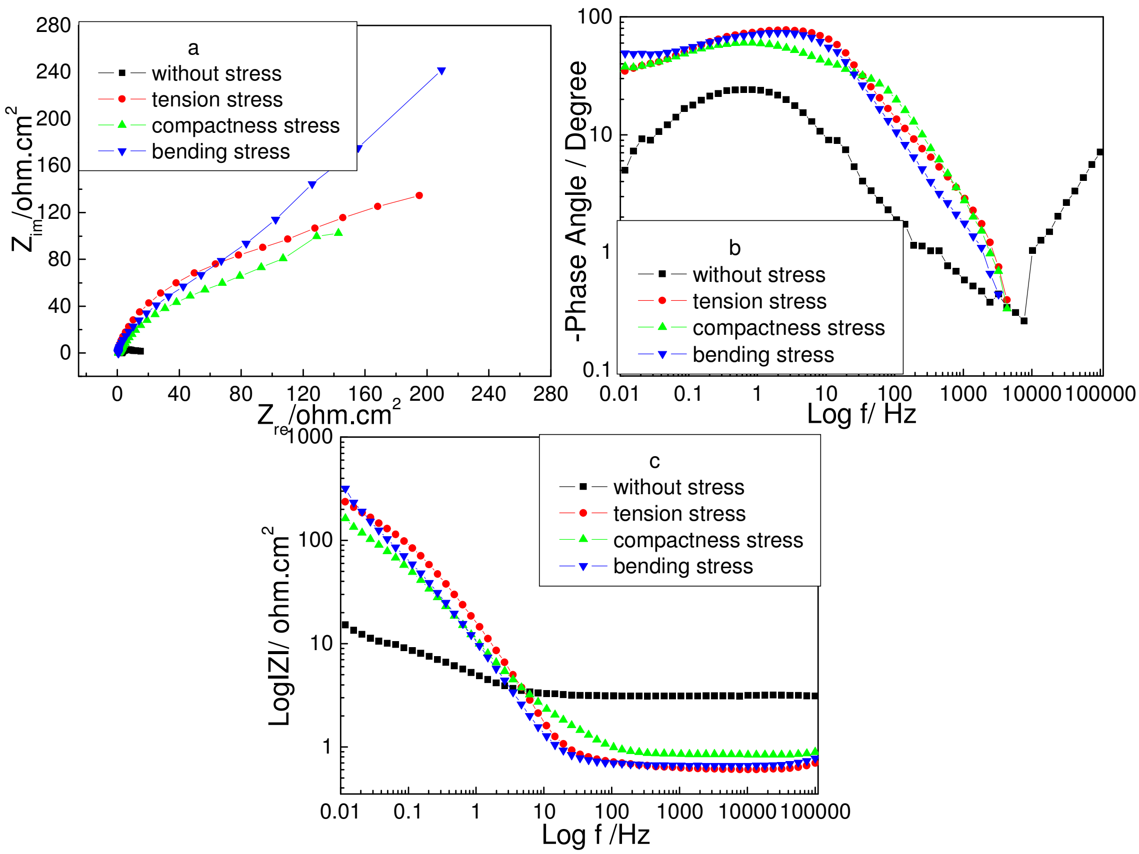

Figure 3. Impedance spectra of the anodic process measured at 30 °C, Nyquist plots (a), corresponding Bode phase angle (b) and Bode impedance magnitude (c) plots

Table 4. Equivalent electronic circuit fitting for the anodic process

Element	Without stress	Tension stress	Compactness stress	Bending stress
$R_S/\Omega\cdot cm^2$	3.1	0.6341	0.8452	0.6752
$Q_1/F\cdot cm^{-2}$	0.0811	0.01725	0.01233	0.0472
n	0.7821	0.9996	1	1
$R_1/\Omega\cdot cm^2$	6.273	10.09	47.41	348.6
$Q_2/F\cdot cm^{-2}$	0.1155	0.01053	0.02174	0.02352
n	1	0.9708	0.8022	0.9411
$R_2/\Omega\cdot cm^2$	4.413	99.79	123.9	46.28
$W/\Omega^{-1}\cdot S^{-0.5}$	0.06442	0.0207	0.03795	0.03495

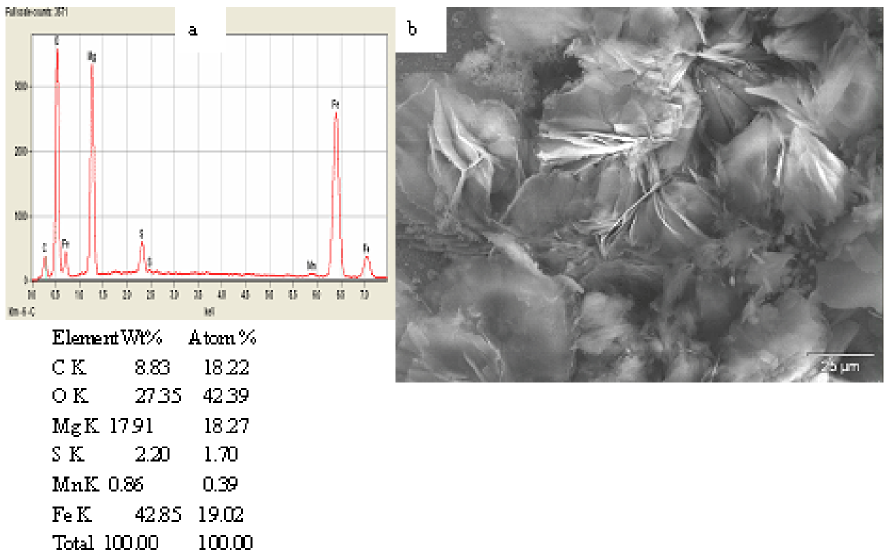

Figure 4. The SEM image and the EDS result of the corrosion scale formed at 60 ^{o}C, a) EDS result; b) SEM image

According to the experimental results in part 3.1.1, the same fitted equivalent electron circuit is used in Fig.1d, the fitted result is showed in table4, it can be found that the transfer resistance R_1, corrosion scale resistance R_2 and diffusion admittance W increase under stress conditions, this indicates that the protective effect of corrosion scale on the substrate increase under stress conditions. The increased protective effect may be explained as followings: firstly, carbon steel easily erodes under stress condition in stratum water for its inhomogeneous microstructure, that is Fe^{2+} ions easily dissolves from the substrate; secondly, sulfur ions has low band price, with the addition of sulfur ions into the stratum water it may react with Fe^{2+} ions to form a corrosion scale FeS, moreover, Fe^{2+} ions may react with CO_3^{2-} or HCO_3^- ions to form $FeCO_3$. Under the joint effect of CO_3^{2-} and S^{2-}, a mixture corrosion scale with a composition of FeS and $FeCO_3$ may be formed on the substrate surface. This conclusion can be verified by the SEM image and the EDS measurement result of corrosion scale, as showed in Fig.4, it can be seen that the corrosion product appears a slice shape, and its major composition are $FeCO_3$ and FeS. Connecting with the impedance spectra result, it can be concluded that the addition of sulfur ions may increase the protective effect of the corrosion scale on carbon steel in stratum water under stress condition, and the increment of protective effect may be related to the compactness of FeS scale.

3.2.2 The cathodic spectra

Comparison to the anodic measurement results, a similar conclusion can be obtained from the cathodic measurement results. Fig.5 is the impedance spectra, it shows that one time-constant appears in the spectra, that is only one capacitance arc, the semicircle radius enlarges with the introduction of stress. The fitted result is listed in table 5. Based on the fitted result, it can be seen that the transfer resistance and scale resistance increase, it indicates that the cathodic corrosion rate may be decreased. For the cathodic process of carbon steel in stratum water, the main mechanism can be illustrated as following [6,7]:

$$2H^{+} + 2e \rightarrow H_2 \qquad (1)$$

$$2H_2CO_3 + 2e \rightarrow 2HCO_3^- \qquad (2)$$

$$2HCO_3^- + 2e \rightarrow 2CO_3^{2-} + H_2 \qquad (3)$$

$$2H_2O + 2e \rightarrow 2OH^- + H_2 \qquad (4)$$

According to Nesic and Ogundele [6,7], the current of H_2O deoxidization was far lower than those of H^+ and H_2CO_3 deoxidization in CO_2 acid environment, while the currents of H^+ and H_2CO_3 deoxidization was close, and the H^+ deoxidization reaction has the diffusion character, the H^+ and H_2CO_3 deoxidization appear activation characters. Based on the former discussions and the experimental results, it can be obtained that the dominate cathodic reaction for N80 carbon steel are reactions (1) and (2).

Table 5 Equivalent electronic circuit fitting for the cathodic process

Element	Without stress	Tension stress	Compactness stress	Bending stress
$R_S/\Omega\bullet cm^2$	0.9264	2.9	0.7867	0.9809
$Q_1/F\bullet cm^{-2}$	0.03959	0.07662	0.01687	0.05052
n	0.9983	0.9318	1	0.9808
$R_1/\Omega\bullet cm^2$	9.224	225.5	62.54	144.6
$Q_2/F\bullet cm^{-2}$	0.02655	0.06013	0.06663	0.1365
n	0.7295	1	1	1
$R_2/\Omega\bullet cm^2$	28.55	177.2	60.86	65.74

When sulfur ions is added into the solution, the followed reactions may be occurred:

$$S^{2-} + H^{+} \rightarrow HS^{-} \qquad (5)$$

$$HS^{-} + H^{+} \rightarrow H_2S \qquad (6)$$

Because of low band price of S^{2-}, Eqs. (5) and (6) easily occur. Considering this effect, it can be obtained that the reactions of Eqs (1) and (2) are inhibited. As Eqs. (1) and (2) are the controlled steps of dioxide corrosion on carbon steel, it can be concluded that the dioxide corrosion rate may be decreased with the addition of S^{2-} and the introduction of stress.

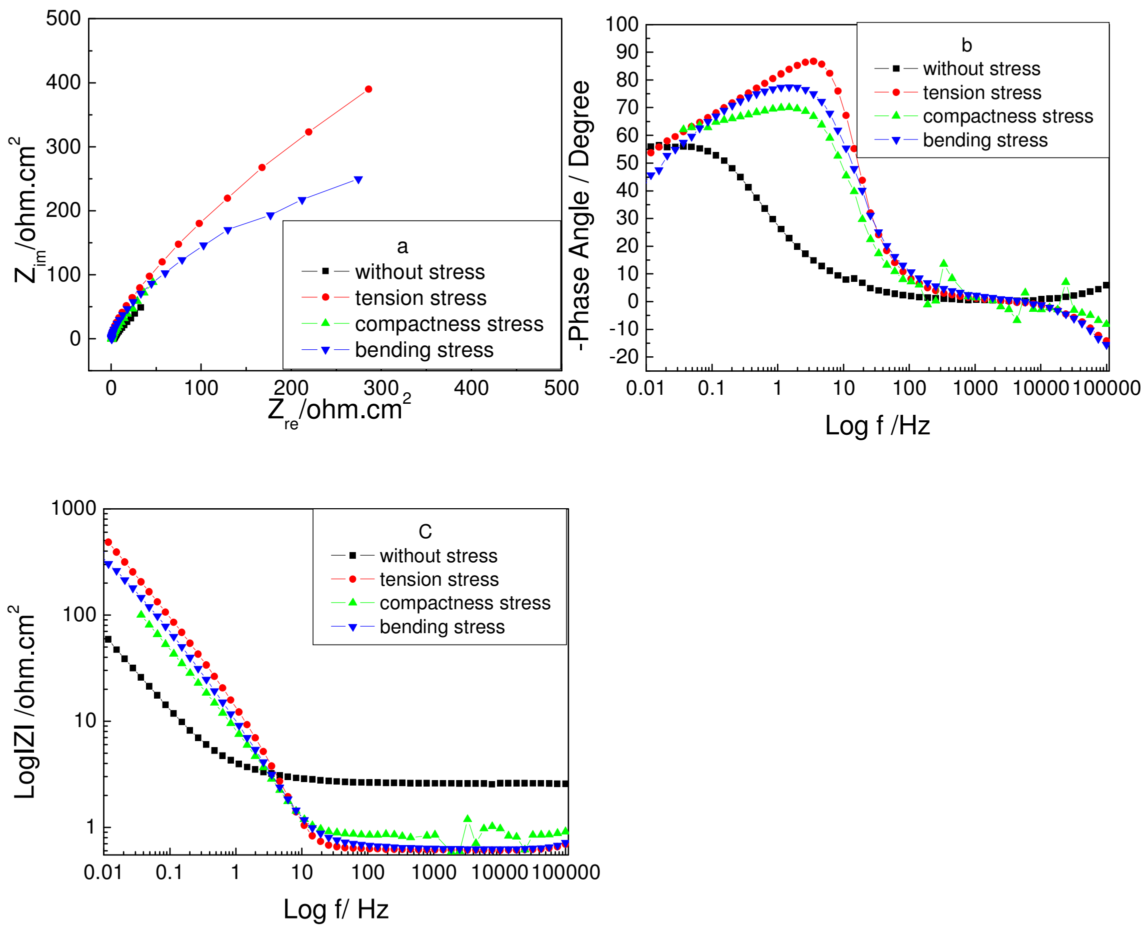

Figure 5. Impedance spectra of the cathodic process measured at 30 °C, Nyquist plots (a), corresponding Bode phase angle (b) and Bode impedance magnitude (c) plots

3.3 EIS measured at 90 °C

3.3.1 The anodic process

Fig.6 shows the impedance spectra of the anodic process measured at 90 °C. It can be seen that the Warburg impedance character becomes more obvious, the semicircle radius enlarges and the Warburg impedance increases with the introduction of stress. The same equivalent circuit used to fit the impedance spectra is showed in Fig.1d, and the fitted result is listed in table 6. The fitted result shows that the transfer resistance R_1, scale resistance R_2 and the diffusion admittance W decrease under stress conditions. It is an indicator of the increment of protective effect of corrosion scale on the substrate with the introduction of stress. The reasons of the increment of the protective effect have been discussed in part 3.2.1. The increasing protective effect can be illustrated by the polarization resistance of the anodic process, according to the equivalent electron circuit and the fitted result, it can obtain the polarization resistance for carbon steel without stress or tension stress, compactness stress and bending stress, are 11.899Ω•cm^2, 431.76Ω•cm^2, 284.78Ω•cm^{2}and 542.55Ω•cm^2, respectively. Obviously, the polarization resistance R_p increases with the introduction of stress, this indicating the increased protective of corrosion scale on the substrate.

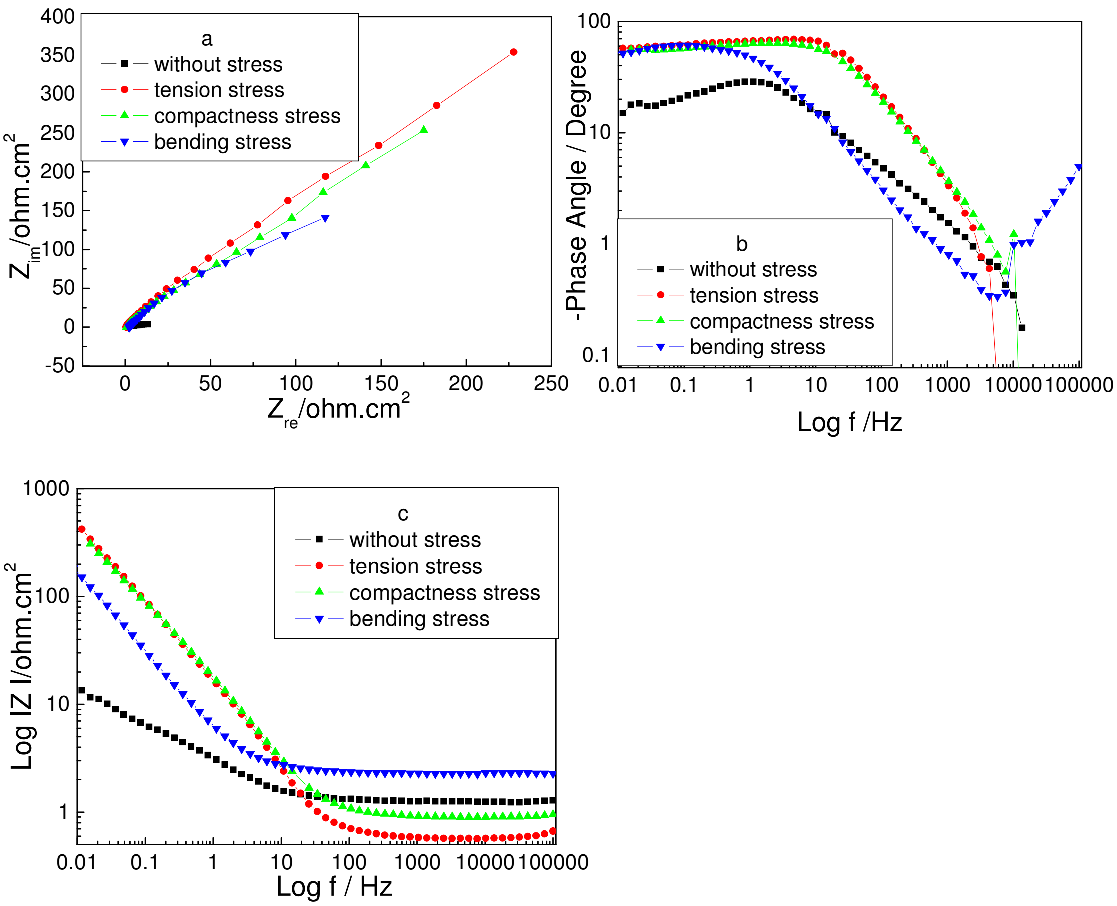

Figure 6. Impedance spectra of the anodic process measured at 30 °C, Nyquist plots (a), corresponding Bode phase angle (b) and Bode impedance magnitude (c) plots

Table 6. Equivalent electronic circuit fitting for the anodic process

Element	Without stress	Tension stress	Compactness stress	Bending stress
$R_S/\Omega\bullet cm^2$	1.253	0.5952	0.9129	1.365
$Q_1/F\bullet cm^{-2}$	0.01094	0.03185	0.08673	0.06954
n	0.672	1	1	0.8888
$R_1/\Omega\bullet cm^2$	6.364	339.2	231.2	93.15
$Q_2/F\bullet cm^{-2}$	0.01342	0.01266	0.0117	0.004545
n	1	0.8979	0.8407	0.7805
$R_2/\Omega\bullet cm^2$	5.535	92.56	53.58	449.5
$W/\Omega^{-1}\bullet S^{-0.5}$	0.02761	0.006306	0.01405	0.004797

3.3.2 The cathodic process

The cathodic impedance spectra measured at 90 °C is showed in Fig.7, the shape of Nyquist plot is similar to these measured at 30 °C and 60 °C, and they are all consisting of one capacitance arc. The same equivalent circuit showed in Fig.2d is used to fit the impedance spectra, and the fitted result is showed in table 7. The result shows that the transfer resistance R_1 and scale resistance R_2 increase under stress conditions, it can be concluded that the cathodic corrosion rate may be decrease under stress conditions. Based on the fitted result and the equivalent electron circuit, the polarization resistance for carbon steel without stress or tension stress, compactness stress and bending stress, are calculated, and the results are 55.801Ω•cm^2, 1115.2Ω•cm^2, 90.22Ω•cm^2 and 263.58Ω•cm^2, respectively. Apparently, the polarization resistance R_P increase with stress for carbon steel, indicating the cathodic corrosion rate may decrease.

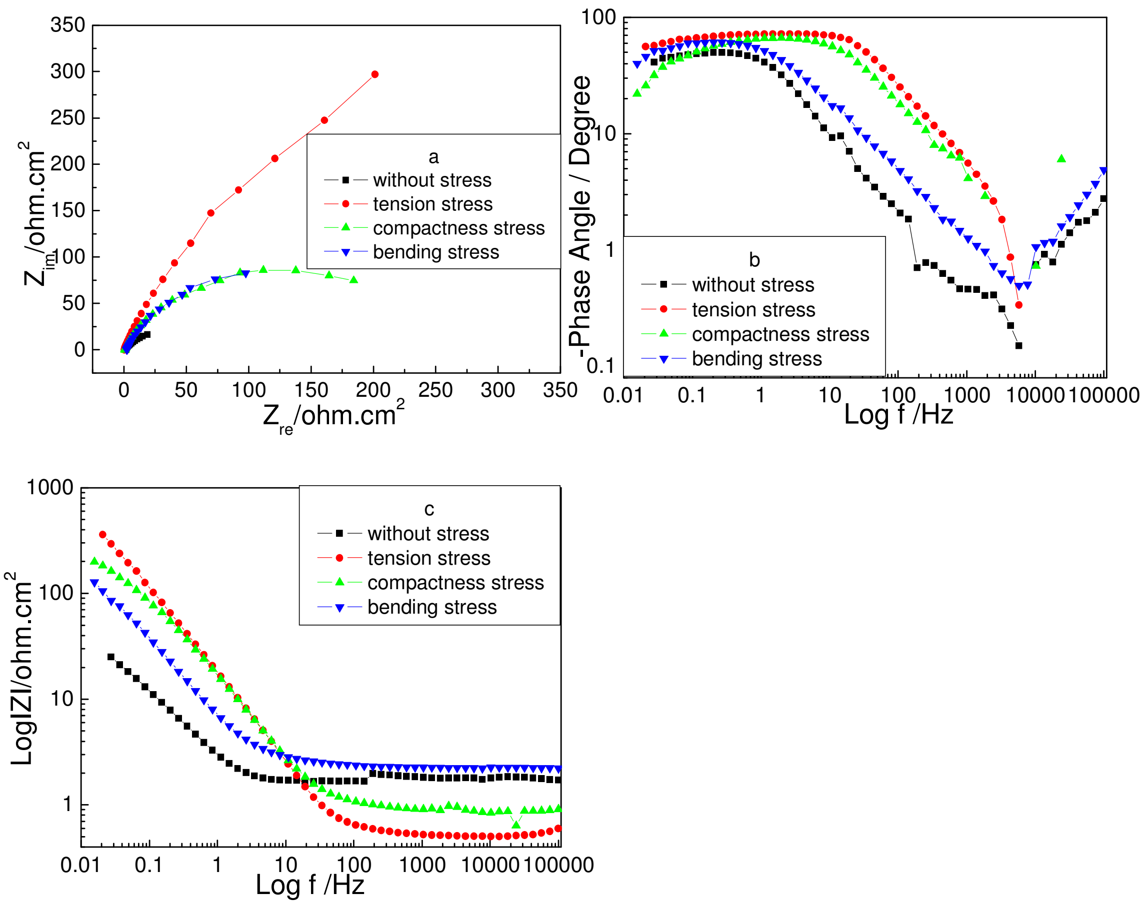

Figure 7. Impedance spectra of the cathodic process measured at 30 °C, Nyquist plots (a), corresponding Bode phase angle (b) and Bode impedance magnitude (c) plots

Table 7. Equivalent electronic circuit fitting for the cathodic process

Element	Without stress	Tension stress	Compactness stress	Bending stress
$R_S/\Omega\bullet cm^2$	1.769	0.5304	0.8948	2.249
$Q_1/F\bullet cm^{-2}$	0.06841	0.008529	0.01253	0.03019
n	1	0.9277	0.8635	0.759
$R_1/\Omega\bullet cm^2$	6.731	43.2	15.54	24.68
$Q_2/F\bullet cm^{-2}$	0.001057	0.005255	0.003334	0.007103
n	0.698	0.6838	1	0.9687
$R_2/\Omega\bullet cm^2$	49.07	1072	74.68	238.9

4. CONCLUSIONS

Temperature, stress states and sulfur ions can significantly affect the mechanism of dioxide corrosion, at low temperature, the transfer resistance, the scale resistance and the diffusion admittance decrease for the anodic and cathodic processes. However, at high temperature, the transfer resistance, the scale resistance and the diffusion admittance increase for the anodic and the cathodic process. EDS result shows that the corrosion scale formed on N80 carbon steel in stratum water containing 0.05M sulfur ions, are composed of $FeCO_3$ and FeS.

References

1. M. B. Kermani, A. Morshed. Corrosion 59 (2003) 659.
2. K. Videm, J. Kvarekval. Corrosion 51(1995) 260.
3. T. Hong, Y. H. Sun, W. P. Jepson. Corros. Sci. 44 (2002) 101.
4. D. A. Lopez, W. H. Schreiner, S. R. de Sanchez, S. N. Simison. Appl. Surf. Sci. 207 (2003) 69.
5. S. L.Wu, A. D.Cui. F. He, Z. Q. Bai, S. L. Zhu, X. J. Yang. Materials Letters, 58(2004)1076.
6. G. I. Ogundele, W. E. White. Corrosion 42 (1986) 71.
7. S. Nesic, J. Postlethwaite, S. Olsen. Corrosion 52 (1996)280.