

Article

Corrosion Behavior of J55 and N80 Carbon Steels in Simulated Formation Water under Different CO₂ Partial Pressures

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Abstract: The purpose of this paper is to reveal the corrosion behavior of J55 and N80 carbon steels in formation water under oil wells at different partial pressures, explore the formation process of corrosion product films under supercritical CO₂ conditions, and analyze the reasons why the microstructure of carbon steel affects the corrosion behavior. The results show that the corrosion rate gradually increases with the increase in CO₂ partial pressure. When the pressure exceeds 10 MPa, the corrosion rate of J55 increases slightly, and that of N80 decreases slightly. Under different partial pressures, the surface composition of the corrosion product film of J55 steel is FeCO₃, and that of N80 steel is FeCO₃ with a small amount of Fe₃C. The analysis shows that the corrosion product films of two kinds of carbon steels can be divided into three layers under the condition of supercritical CO₂. There are holes in the middle layer, which are formed first, and then the inner layer and the outer layer are formed at the same time. It is believed that the difference in the morphology and distribution of Fe₃C is the reason why the corrosion rate of J55 steel is lower than that of N80 steel. Fe₃C in J55 steel is lamellar, which can anchor FeCO₃, promote the formation of corrosion product films, and improve the compactness of corrosion product films. However, the Fe₃C in N80 is granular and dispersed in the ferrite matrix, which makes it easy to fall off the surface, form pits, and destroy the integrity of the corrosion product film.

Keywords: carbon capture utilization and shortage; supercritical CO₂ condition; corrosion product film; microstructure



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1. Introduction

The global climate change problem has aroused widespread concern in the international community, and it has gradually become an international consensus to reduce CO₂ emissions to meet the climate challenge [1]. Carbon capture utilization and shortage (CCUS) is considered one of the effective means to reduce CO₂ emissions and slow down global climate change [2,3]. CCUS refers to the industrial process in which carbon dioxide is separated from industrial production or the atmosphere and then directly used or injected into the strata or the seabed to achieve CO₂ emission reduction. With the development of science and technology, CCUS has become one of the essential technologies for achieving the goal of carbon neutrality in the world [2,3]. The process of injecting CO₂ into existing oil fields is a well-known "CO₂ enhanced oil recovery" (CO₂-EOR) technique, which is the utilization method in CCUS [4]. Although CO₂-EOR can improve oil recovery and reduce CO₂, it also results in CO₂-corrosion of oil country tubular goods due to the injection of high-pressure CO₂ [5]. Furthermore, in order to improve the oil recovery, the pressure of CO₂ (p_{CO_2}) injected is increased and even exceeds the supercritical pressure [6,7], which aggravates the CO₂ corrosion [5]. The CO₂-EOR technique plays an important role in ensuring economic and stable petroleum products. Therefore, it is necessary to solve the corrosion problem of tubing under the condition of CO₂ oil displacement.

J55 and N80 carbon steels are widely used in oil production. The CO₂ corrosion of these steels in oil wells has received extensive attention. The structure of the CO₂-corrosion

product film on the steel surface is an important factor affecting the CO₂ corrosion of carbon steel. Many scholars have studied the structure and formation process of CO₂-corrosion product films through immersion experiments and morphology observations. Zhang found that ($p_{\text{CO}_2} = 1$ MPa, temperature = 90 °C, simulated formation water) the composition of N80 carbon steel-corrosion product film was FeCO₃, and the corrosion product film was composed of inner and outer layers. Due to the different formation mechanisms, the outer layer was formed by the precipitation of FeCO₃ on the surface of the inner layer, so its binding force was weak. The inner layer was formed by the reaction of HCO₃[−] with the metal matrix in situ, and its binding force is relatively large [8]. Wei found that ($p_{\text{CO}_2} = 1, 9.5$ MPa, temperature = 80 °C, 3.5% NaCl solution) the corrosion product film composition of X65 pipeline steel was FeCO₃. The corrosion product film was composed of inner and outer layers. Under the condition of supercritical CO₂ (temperature > 31.1 °C, $p_{\text{CO}_2} > 7.38$ MPa), an amorphous FeCO₃ layer is preferentially formed on the surface of carbon steel, which is gradually transformed into a dense inner FeCO₃ layer, and the outer layer is finally formed [9]. Chen found that ($p_{\text{CO}_2} = 1$ MPa, temperature = 78 °C, simulated formation water) the corrosion product film of N80 steel had a three-layer structure and believed that the three layers were formed at the same time. The middle layer and the outer layer were formed by FeCO₃ deposition, and delamination occurred during the deposition process. The corrosion product film of the inner layer was mainly formed by the direct reaction of CO₃^{2−} and HCO₃[−] ions with the steel matrix at the interface, so the binding force was strong [10]. Li also believed that ($p_{\text{CO}_2} = 1$ MPa, temperature = 60 °C, simulated formation water) the corrosion product film of X65 pipeline steel had a three-layer structure: the surface layer and inner layer were dense, and the middle layer was porous. The middle layer was formed first, and the inner and outer layers were formed simultaneously [11]. Through the study of X65 pipeline steel ($p_{\text{CO}_2} = 1, 9.5$ MPa, temperature = 50, 80 °C, simulated formation water), Zhang found that under the conditions of low pressure and supercritical CO₂, the outer layer and middle layer of corrosion product film had holes, while the inner layer was dense [12]. Although researchers have not reached a consensus on the structure and formation process of corrosion product films for carbon steel, they all found that the inner layer was dense and had the best corrosion resistance.

On the other hand, the formation process of the corrosion product film of carbon steel under different CO₂ partial pressures was explored with electrochemical technology. Wang studied the influence of CO₂ partial pressure on the Nyquist impedance spectrum ($p_{\text{CO}_2} = 0.3\text{--}2$ MPa, temperature = 60 °C, 1% NaCl solution), and found that CO₂ partial pressure obviously changed the “size” of the semicircle but had little effect on the shape of the impedance spectrum. This means that with the increase in CO₂ partial pressure, the corrosion rate changed, but the corrosion mechanism did not change, because the “size” of the semicircle corresponds to the corrosion rate and the resistance of the corrosion product film, while the shape of the impedance spectrum determines the corrosion mechanism [13]. Zhang ($p_{\text{CO}_2} = 5, 8$ MPa, temperature = 60 °C, simulated formation water) used electrochemical impedance spectroscopy (EIS) to study the formation process of corrosion product films for N80 carbon steel in simulated formation water [14]. Under the conditions of 5 MPa and 8 MPa (supercritical CO₂ condition), the corrosion mechanism did not change, but with the increase in partial pressure, the resistance and corrosion resistance of the corrosion product film increased. Wei found that ($p_{\text{CO}_2} = 1, 9.5$ MPa, temperature = 60 °C, carbon steel, 1% NaCl solution) under the conditions of low CO₂ partial pressure and supercritical CO₂, the impedance spectrum of Nyquist showed a capacitive arc. With the increase in immersion time, the radius of the capacitive arc became larger, and the charge transfer rate decreased [15]. These researchers used electrochemical technology to study the formation process of corrosion product films on carbon steel under the conditions of low CO₂ partial pressure and supercritical CO₂. They found that the Nyquist impedance spectrum showed a capacitive arc, and that the shape of the impedance spectrum did not change with time, but the radius of the capacitive arc gradually expanded. This shows that the increase in CO₂

partial pressure does not change the corrosion mechanism but enhances the compactness of the corrosion product film.

Moreover, the mechanical properties of the corrosion product film also have an important impact on the corrosion behavior. Studies [16–19] showed that the mechanical characteristics of corrosion product scales, especially Young's modulus, strongly affect the CO₂ corrosion process of steels. They found that the corrosion rate decreased as the Young's modulus of FeCO₃ increased.

Most researchers have studied the corrosion behavior of carbon steel under one or two partial pressures of CO₂. Due to the complexity of oil well production conditions, the partial pressure of CO₂ changes continuously from low pressure to supercritical, and these research results can no longer provide better theoretical guidance for oil well safety production. Therefore, the corrosion behavior of J55 and N80 carbon steels in a wider range of CO₂ partial pressures (0.1, 3, 5, 7, 10, and 15 MPa) was studied in this paper, and the change law of corrosion rate and corrosion morphology under different CO₂ partial pressures were revealed. These works may provide a theoretical basis for preventing CO₂ corrosion in oil wells with complex working conditions. At the same time, under the condition of supercritical CO₂, the structure and formation process of the corrosion product film of carbon steel are still unclear and need further exploration. Hence, the structure and formation process of the corrosion product film of carbon steel under supercritical CO₂ conditions were explored in this paper to enrich people's understanding of this.

In addition, researchers have extensively discussed the effect of microstructure on corrosion behavior under low CO₂ partial pressures [20–22]. However, there are few studies under supercritical CO₂ conditions, and more research and attention are needed. Thus, in this paper, two kinds of commonly used tubing (J55 and N80 steels) with different microstructures were selected, and the corrosion behavior of these steels under supercritical CO₂ conditions was analyzed to reveal the reasons why the microstructure affects the corrosion behavior.

2. Experimental Section

2.1. Materials

The materials used in the experiment are J55 and N80 carbon steels, whose chemical compositions are shown in Table 1 (ARL4460 direct reading spectrometer). As shown in Figure 1, the microstructure of J55 is a mixture of lamellar ferrite and lamellar pearlite, while the microstructure of N80 steel is tempered sorbite. The sizes of samples for immersion test, X-ray diffraction test, and scanning electron microscopy observation are 50 mm × 10 mm × 3 mm, 10 mm × 10 mm × 3 mm, and 10 mm × 10 mm × 3 mm, respectively.

Table 1. Chemical compositions of the experimental steels (wt, %).

Materials	C	Si	Mn	P	S	Mo	Cr	Ni	Cu
J55	0.40	0.26	1.53	0.012	0.012	0.0024	0.015	0.008	0.012
N80	0.31	0.29	1.64	0.010	0.0034	0.013	0.044	0.021	0.037



Figure 1. Microstructures of J55 and N80 steels: P (pearlite); F (ferrite).

2.2. Immersion Test

The experimental conditions at different CO₂ partial pressures are shown in Table 2. In order to simulate the working conditions under oil wells, the parameters were set to the following: 80 °C, 168 h, 0.3 m/s. Additionally, the chemical compositions of the simulated formation water are shown in Table 3. Immersion tests were carried out in a 10-L dynamic autoclave produced by Cortest (JB/T 7901-1999). Before the experiment, the samples were polished step by step with 1000# metallographic sandpaper, and then cleaned with acetone and deionized water. After dehydrating with ethanol, the samples were dried with hot air, and then weighed and measured for geometric dimensions. The simulated formation water was injected into the autoclave and the samples were immersed in water, and then the water was deoxygenated with nitrogen for 8 h. After that, the system was heated to the preset temperature, and then CO₂ was injected into the solution to ensure that the CO₂ partial pressure reached a predetermined value. Finally, the total pressure reached 20 MPa by injecting N₂. The immersion time tests were carried out to study the formation process of the corrosion product film and the effect of microstructure on the corrosion behavior of the steels under supercritical CO₂ conditions. The test parameters are shown in Table 4.

Table 2. Experimental conditions under different CO₂ pressures.

No.	CO ₂ Partial Pressure, MPa	Corrosion Rate of J55, mm/y	Corrosion Rate of N80, mm/y
1	0.1	0.096	0.081
2	3	1.524	1.095
3	5	1.788	2.184
4	7	2.482	2.679
5	10	4.570	6.549
6	15	5.599	5.279

Table 3. Chemical compositions of simulated formation water (mg/L).

Cl [−]	SO ₄ ^{2−}	HCO ₃ [−]	Ca ²⁺	Ba ²⁺	Na ⁺
15,610.05	113.59	114.67	305.41	1109.32	9479.99

Table 4. Experimental conditions at different immersion times.

No.	Immersion Times, h	Corrosion Rate of J55, mm/y	Corrosion Rate of N80, mm/y
7	20	17.485	21.425
8	66	7.949	9.451
9	114	4.239	5.178
10	168	4.002	4.946

After immersion tests, the samples were washed with deionized water, dehydrated with ethanol, and dried with cold air. One sample was used to observe the morphology and analyze the phase of the corrosion products. The corrosion products of the other three samples were removed by some kind of solution (appropriate amount of deionized water, 500 mL of hydrochloric acid (density is 1.19 mg/mL), and 3.5 g of hexamethylene tetramine were prepared into a 1000-mL solution) according to the ASTM G1-03 standard. The three samples were washed, then dehydrated, dried, and weighed to observe the weight loss. The corrosion rate was calculated with the equation (ASTM G31-27 standard):

$$CR = \frac{8.76 \times 10^4 \Delta m}{S \rho t} \quad (1)$$

where *CR* is the corrosion rate, mm/y; Δm is the weight loss, g; *S* is the surface area of a sample, cm²; ρ is the density of the steel, g/cm³; *t* is the immersion time, h. The average corrosion rate is the mean value of the corrosion rates of three samples.

2.3. Characterization of the Corrosion Product

The microstructure of J55 and N80 steels, the surface, and cross-section morphologies of the corrosion product were observed with a Tescan Vega II scanning electron microscopy (SEM) (an acceleration voltage of 20 Kv, a working distance of 15 mm). The chemical compositions and phases of the corrosion product were analyzed with X-ray diffraction (XRD) with a Cu K α X-ray source operated at 40 kV and 150 mA.

3. Results

3.1. Corrosion Behavior of J55 and N80 under Different CO₂ Partial Pressures

As shown in Figure 2, as CO₂ partial pressure rises, the corrosion rates of J55 and N80 increase in general. It should be noted that the corrosion rate of the N80 steel reaches the maximum at 10 MPa and then decreases slightly. The corrosion rate under supercritical CO₂ conditions is higher than that under low CO₂ partial pressures.

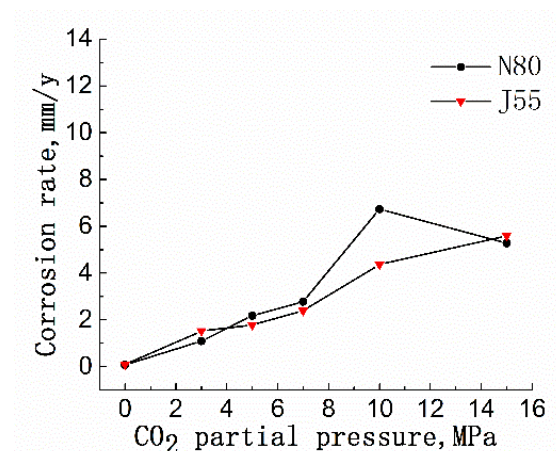


Figure 2. Corrosion rates of J55 and N80 steels under different CO₂ pressures.

Figure 3 shows the different states of CO₂. When the temperature exceeds 31.1 °C, the CO₂ partial pressure exceeds 7.38 MPa, and CO₂ is in a supercritical state [23–26]. In this paper, No.5 and No.6 immersion tests are all in the supercritical state. Under these conditions, the solubility of CO₂ is much higher than that under low CO₂ pressures [27]. The higher the solubility, the higher the concentration of the hydrogen ions, leading to a large increase in the dissolution rate of the metal. Hence, the corrosion rate under supercritical CO₂ conditions is higher than that under low CO₂ partial pressures. The reason why the corrosion rate of the N80 steel decreases slightly when the CO₂ partial pressure exceeds 10 MPa may be related to the formation of a dense corrosion product film.

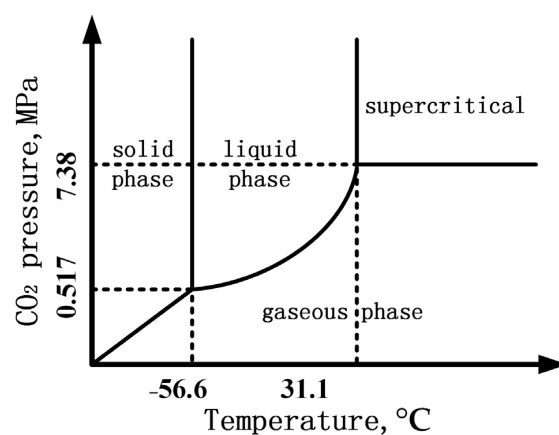


Figure 3. States of CO₂.

Figure 4 shows the phases of corrosion products of J55 and N80 steels at various CO₂ partial pressures. Only FeCO₃ was detected on the surface of the J55 steel, while FeCO₃ and Fe₃C were detected on the surface of the N80 steel. The difference in the phase between J55 and N80 steels may be due to the different shapes and distributions of carbides in steels.

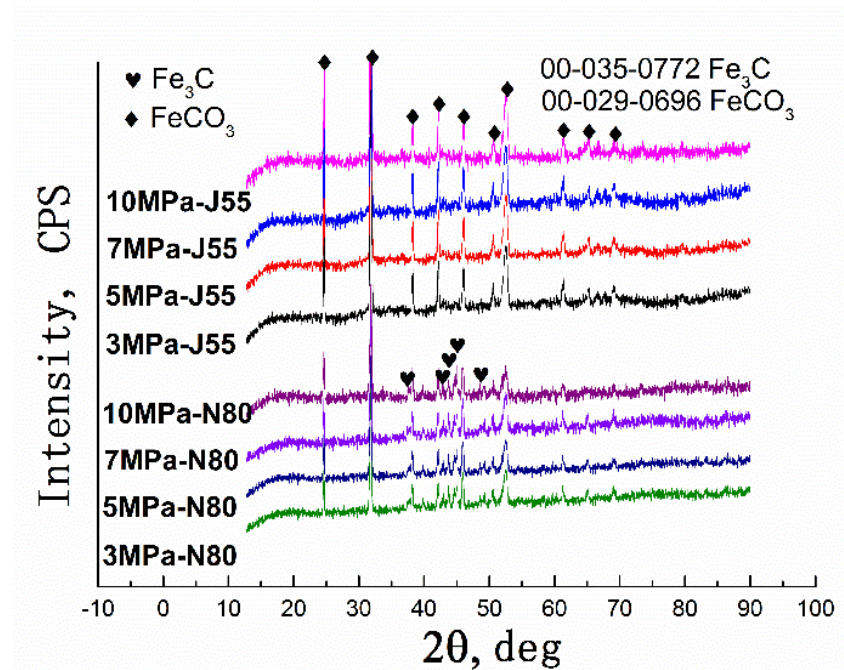


Figure 4. XRD spectra of corrosion product films under different CO₂ pressures.

As shown in Figure 1, after normalizing, the microstructure of the J55 steel is composed of ferrite (F) and pearlite (P). In Figure 1, ferrite is black, and pearlite is gray. The fine structure of pearlite consists of lamellar ferrite and lamellar Fe₃C [20–22]. Through XRD analysis (Figure 4), the main component of the corrosion product films on the surface of the J55 steel is FeCO₃. During the formation of the corrosion product film, the residual Fe₃C was not easy to fall off and was completely covered by FeCO₃, so it was not detected. As shown in Figure 1, after quenching and high-temperature tempering, the microstructure of the N80 steel is tempered sorbite [20–22], that is, a ferrite matrix (gray or white) and dispersed Fe₃C particles (black dot). Under different CO₂ partial pressures, the main components of the N80 steel corrosion product films are FeCO₃ and Fe₃C (Figure 4). In the corrosion process, the ferrite matrix was preferentially dissolved, and the granular Fe₃C was easy to fall off and mix into the FeCO₃ corrosion product film. Fe₃C was not completely covered by FeCO₃, so it was detected. At 7 MPa, the surface of corrosion products of the N80 steel contained approximately 78% FeCO₃ and 22% Fe₃C (mass fraction). At 10 MPa, it contained 76% FeCO₃ and 24% Fe₃C (mass fraction).

Figures 5 and 6 show the surface and cross-section morphologies of the J55 steel at various CO₂ partial pressures. When the partial pressure of CO₂ was 0.1 MPa and 3 MPa, the thickness of the corrosion films was less than 10 µm (Figure 6), no crystalline corrosion products were observed on the surface of the samples, and the flaky corrosion products peeled off and shallow corrosion pits were formed (Figure 5). At 5, 7, 10, and 15 MPa, the thickness was approximately 100, 110, 140, and 140 µm, respectively. At 5 MPa, the surface of the sample was covered by amorphous and crystalline corrosion products, and after exceeding 5 MPa, the corrosion products were crystalline particles. As shown in Figure 6, as the CO₂ partial pressure rose, the thickness of the corrosion product film increased.

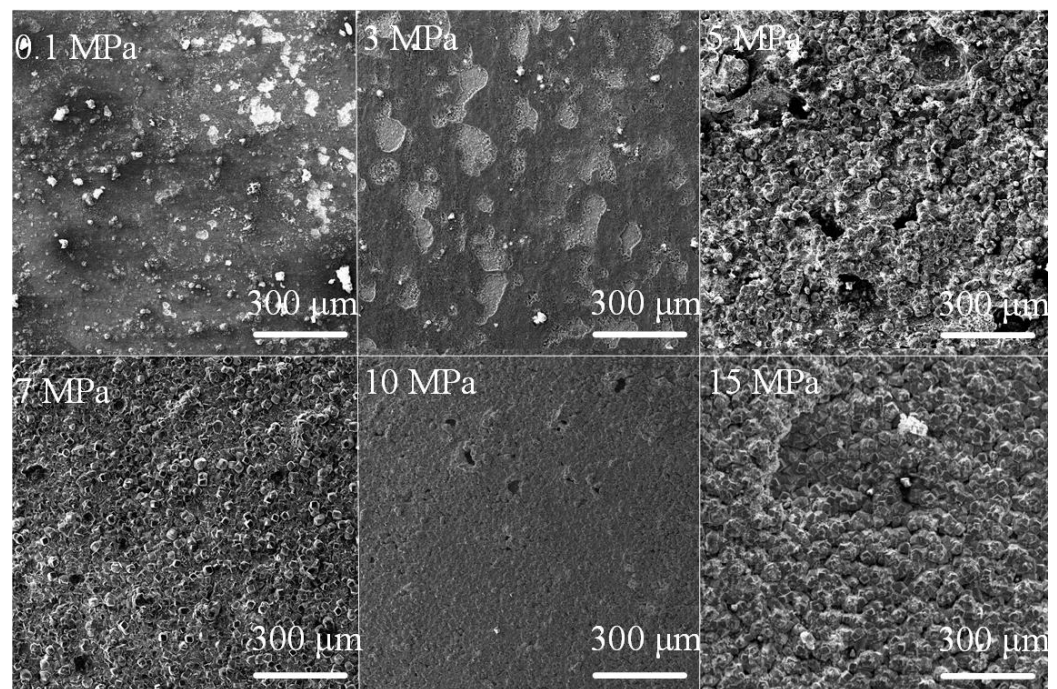


Figure 5. Surface morphologies of J55 steel at various CO₂ partial pressures (200 $\times$).

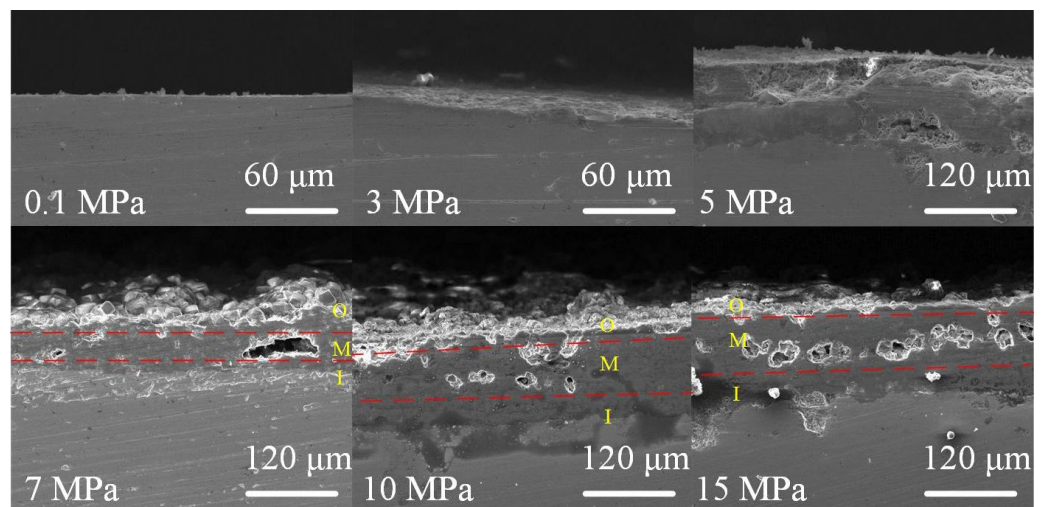


Figure 6. Cross-section morphologies of J55 steel at various CO₂ partial pressures: 0.1, 3 MPa, 1000 $\times$; 5, 7, 10, 15 MPa, 500 $\times$; O (the outer layer); M (the middle layer); I (the inner layer).

When the pressure was low (0.1, 3 MPa), no crystalline corrosion product particles were found (Figure 7) on the surface of the N80 samples and the thickness was less than 10 μm (Figure 8). When the pressure exceeded 3 MPa, the thickness increased, obviously, and all thicknesses were greater than 120 μm (Figure 8). When the pressure was 5 MPa, the surface of the sample was covered by amorphous corrosion products and crystalline corrosion products. At 7 MPa and 15 MPa, the surface of the sample was covered by crystalline corrosion product particles, and the corrosion product film was dense. On the contrary, at 10 MPa, the corrosion product film was porous, and consisted of granular and sludge-like corrosion products. At 10 MPa, it was observed from the cross-section picture that holes appeared at the interface between the corrosion product film and the metal matrix. The porous corrosion product film led to the maximum corrosion rate of 10 MPa.

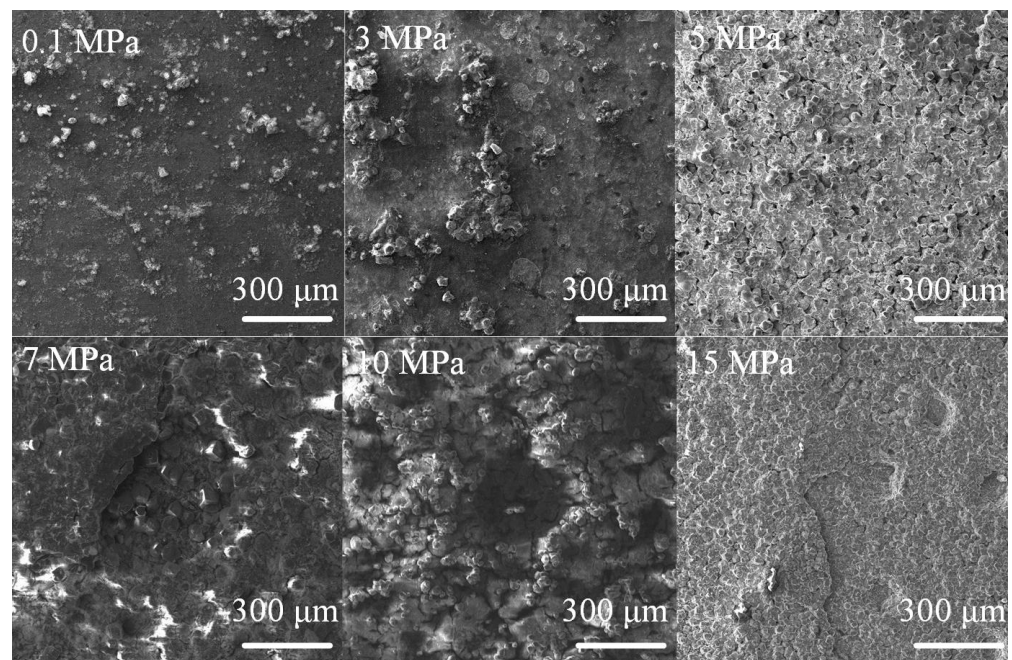


Figure 7. Surface morphologies of N80 steel at various CO₂ partial pressures (200×).

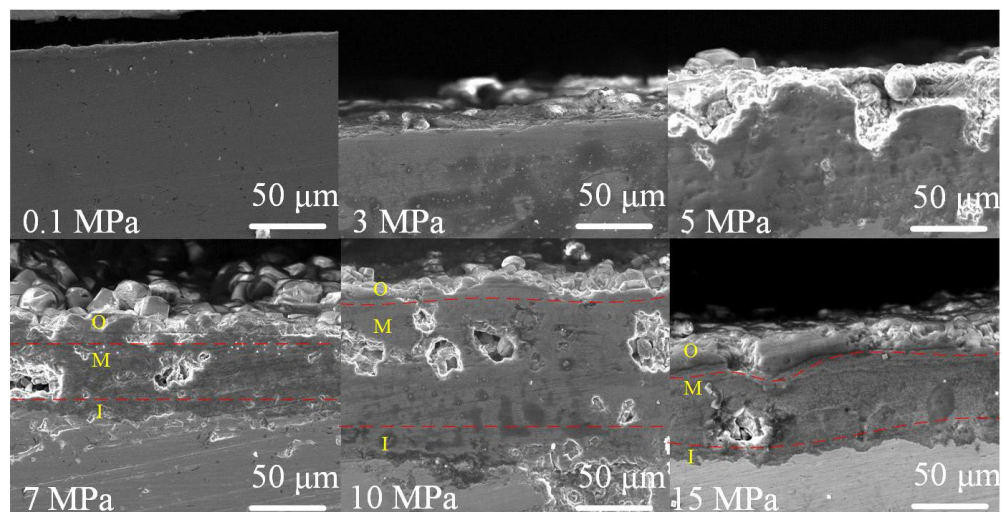


Figure 8. Cross-section morphologies of N80 steel at various CO₂ partial pressures (1000×): O (the outer layer); M (the middle layer); I (the inner layer).

As shown in Figures 6 and 8, when the pressure exceeded 5 MPa, the corrosion product films consisted of three layers: the outer layer, the porous middle layer, and the dense inner layer.

3.2. Corrosion Behavior of J55 and N80 Steels at Different Immersion Times under Supercritical CO₂ Conditions

In order to study the formation process of corrosion product films under supercritical CO₂ conditions, immersion tests were carried out (shown in Table 4, temperature = 60 °C, velocity = 0 m/s). The immersion time of the samples in simulated formation water was 20 h, 66 h, 114 h, and 168 h, respectively. As shown in Figure 9, the average corrosion rates of the J55 and N80 steels decrease rapidly as immersion times increase from 20 h to 66 h. After 66 h, the corrosion rates decrease slowly, and after 114 h, the average corrosion rates tend to be stable. The changing trend of the corrosion rate was similar to the experimental

results of Zhang [28,29] and Wei [30]. In addition, the corrosion rate of the N80 steel was higher than that of J55 steel at different immersion times.

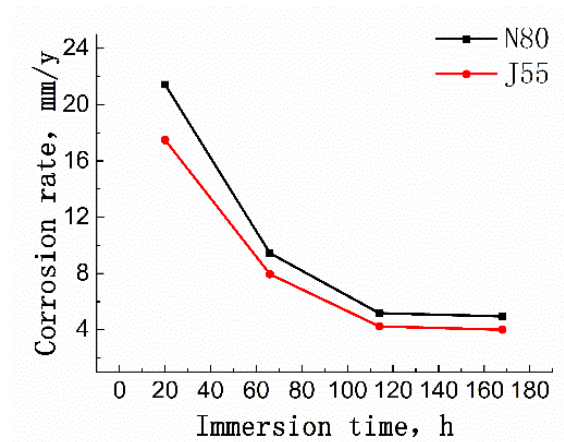


Figure 9. Corrosion rates of J55 and N80 steels at different immersion times.

As shown in Figures 10 and 11, with the increase in immersion time, the film thickness of corrosion products of the J55 and N80 steels continued to increase. Before 66 h, the thickness was less than 10 μm . When the immersion time exceeded 66 h, the thickness increased rapidly. At 114 h, the thickness of all samples exceeded 100 μm . After 114 h, the thickness did not change noticeably. Zhang [12,28] and Wei [29] discovered the same phenomenon. It can be seen that the period from 20 h to 66 h is a period of rapid decline in corrosion rate, and the thickness of the corrosion product film is small and increases slowly. From 66 h to 114 h, the corrosion rate decreased slowly, and the thickness of the corrosion product film increased rapidly. After 114 h, the corrosion rate was stable, and the thickness of the corrosion product film did not change noticeably.

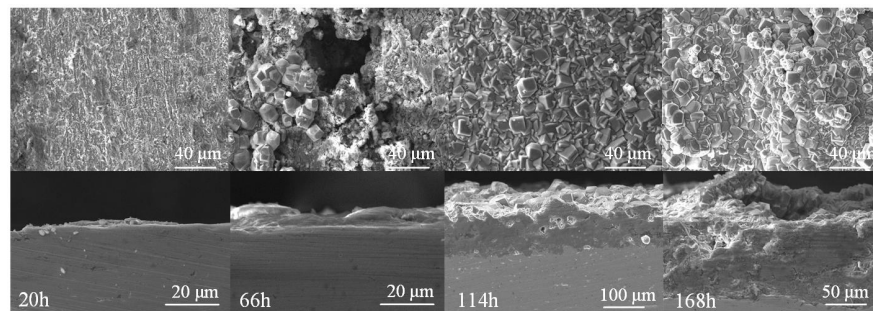


Figure 10. Surface and cross-section morphologies of J55 steel at different immersion times: surface morphologies, 1000 $\times$; cross-section morphologies 20 h and 66 h, 3000 $\times$; cross-section morphologies 114 h, 500 $\times$ and 168 h, 1000 $\times$.

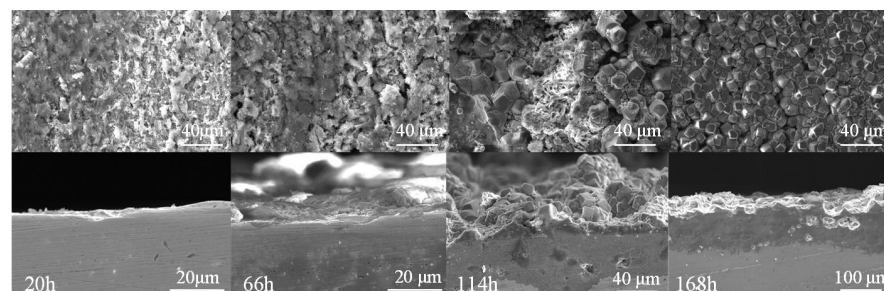


Figure 11. Surface and cross-section morphologies of N80 steel at different immersion times: surface morphologies, 1000 $\times$; cross-section morphologies 20 h and 66 h, 3000 $\times$; cross-section morphologies 114 h, 1000 $\times$; cross-section morphologies 168 h, 500 $\times$.

4. Discussion

4.1. Influence of CO₂ Partial Pressure on the Corrosion Behavior of J55 and N80 Steels

Zhang [14] and Wei [15] used EIS to study the corrosion behavior of carbon steel under supercritical CO₂ and low CO₂ partial pressure. They found that under both conditions, after 7 h, the impedance spectrum showed a capacitive reactance arc, and the radius of the capacitive reactance arc increased with time, which showed that the protectiveness of the corrosion product film increased with time. In addition, when the immersion time was the same, the impedance of the corrosion product film under supercritical CO₂ was greater than that under high CO₂ partial pressure and low CO₂ partial pressure. This indicated that the protective property of the corrosion product film increased with the increase in CO₂ partial pressure. The corrosion rate of carbon steel is the result of the joint action of the protection of the corrosion product film and the corrosiveness of the solution in which carbon steel is located. When the protection of the corrosion product film dominates, the corrosion rate decreases, while when the corrosiveness of the solution dominates, the corrosion rate increases. As shown in Figure 2, with the increase in CO₂ partial pressure, the corrosion rate of J55 steel continues to increase, which indicates that the corrosivity of the solution is dominant. The corrosion rate of the N80 steel continued to increase, reaching a maximum of 10 MPa, and then decreased. This shows that the corrosivity of the solution is dominant when it is lower than 10 MPa, and the protection of the corrosion product film is dominant when it is higher than 10 MPa.

According to research [30,31], the deposition process of FeCO₃ includes nucleation and growth. It is generally believed that the nucleation and growth of particles are related to the relative supersaturation (RS) of FeCO₃. The nucleation rate of particles is exponentially related to the relative supersaturation, and the growth rate of particles is linearly related to the relative supersaturation. Therefore, the deposition of FeCO₃ is controlled by growth at low supersaturation and is controlled by nucleation at high supersaturation. The supersaturation and relative supersaturation of FeCO₃ are expressed by Formulas 2 and 3:

$$S = \frac{[\text{Fe}^{2+}] \times [\text{CO}_3^{2-}]}{K_{sp}} \quad (2)$$

$$RS = S - 1 \quad (3)$$

where S is the supersaturation of FeCO₃; $[\text{Fe}^{2+}]$ is the equilibrium concentration of iron ion, mol/L; $[\text{CO}_3^{2-}]$ is the equilibrium concentration of carbonate ion, mol/L; K_{sp} is the solubility product of FeCO₃. When the temperature and the composition of the solution are constant, K_{sp} is constant; RS is the relative supersaturation.

At low CO₂ partial pressures, the relative supersaturation of FeCO₃ was low, the growth of FeCO₃ dominated, and the growth of FeCO₃ was inhibited [30,31]. Therefore, FeCO₃ particles were coarse, and the corrosion product films were porous. Conversely, under supercritical CO₂ conditions, the relative supersaturation was high and the growth of FeCO₃ dominated. Therefore, FeCO₃ particles were fine, and the corrosion product films were dense. As shown in Figures 12 and 13, the size of FeCO₃ particles in supercritical states is smaller than that in low CO₂ partial pressures.

Small holes were observed in the middle layer of the corrosion product films of the J55 steel (Figure 6). This was because FeCO₃ grew along the lamellar Fe₃C and then FeCO₃ sheets squeezed against each other, increasing the stress, leading to the fracture of FeCO₃ sheets [32]. It can be observed from Figure 12 that there are cracks (10 MPa, 15 MPa) on the surface of the corrosion product film of the J55 steel, which may have originated from the middle layer of the corrosion product film. Similarly, there were small holes in the middle layer and the surface of corrosion product films for the N80 steel at 7, 10, and 10 MPa (Figures 8 and 13). This was due to the falling off of Fe₃C particles.

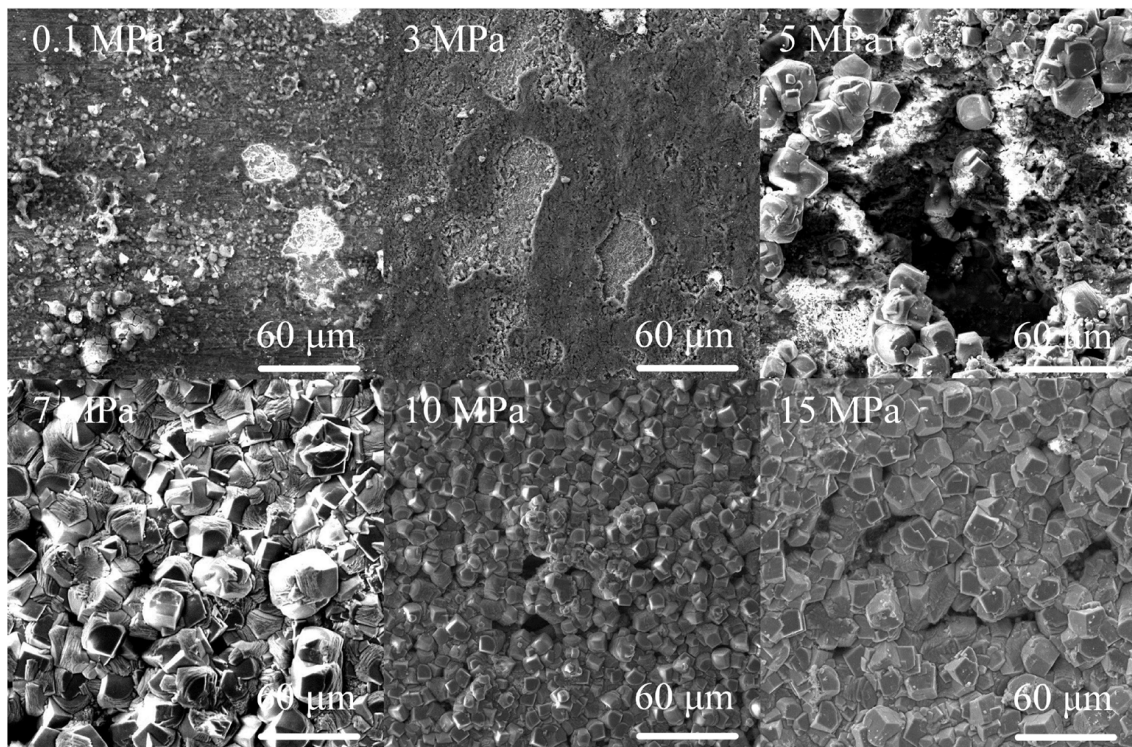


Figure 12. Surface morphologies of J55 steel at various CO_2 partial pressures ($1000\times$).

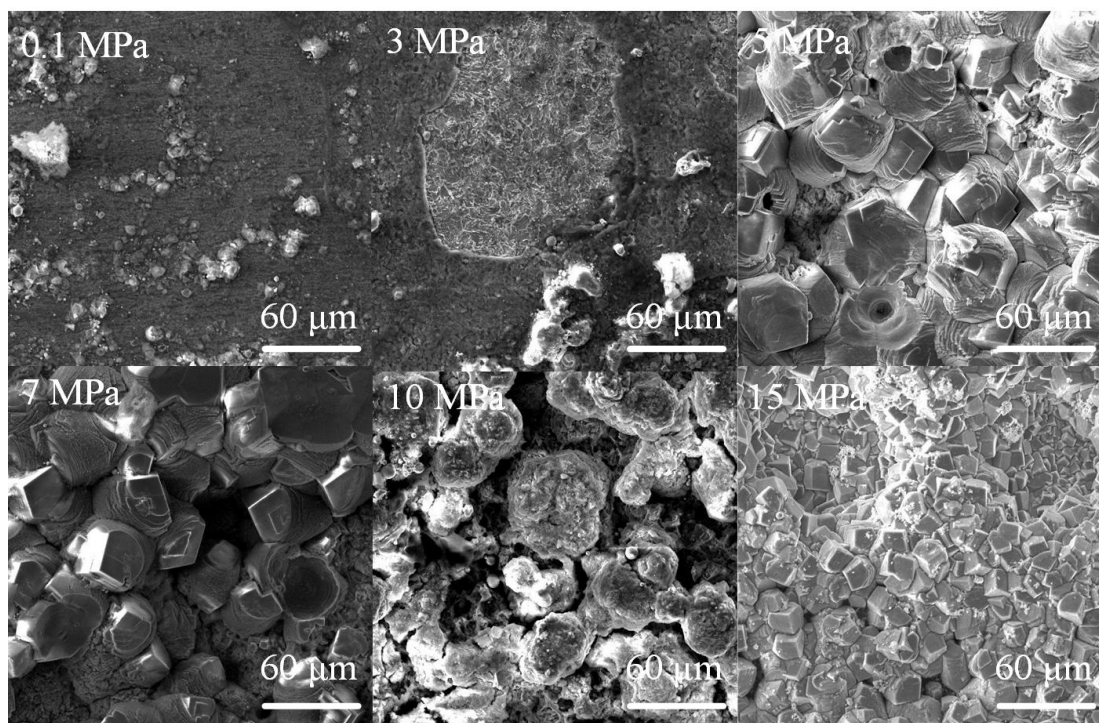


Figure 13. Surface morphologies of N80 steel at various CO_2 partial pressures ($1000\times$).

4.2. Formation Process of the Corrosion Product Film under Supercritical CO_2 Conditions

As shown in Figures 14 and 15, at 20 h, Fe and a small amount of Fe_3C were detected on the surface of the corrosion products. This indicated that there was no FeCO_3 on the steel surface, or the content was too low to be detected. At 66 h, Fe, Fe_3C , and FeCO_3 were detected on the surface of the corrosion products. This indicated that FeCO_3 was deposited on the surface of the steel. The FeCO_3 did not completely cover the surface of the steel, so

the diffraction peak of Fe was found. At 114 h and 168 h, the surface of the J55 steel was completely covered by FeCO_3 , while the surface of the corrosion product film of the N80 steel was a mixture of Fe_3C and FeCO_3 . Since Fe_3C in the N80 steel is granular, it is easy for it to fall off from the metal matrix in the process of Fe dissolution, mix with the precipitated FeCO_3 , and cover the steel surface. On the contrary, Fe_3C in the J55 steel is lamellar, which means it is not easy for it to fall off, and it is beneficial to fix the deposited FeCO_3 so that the corrosion product film of FeCO_3 can form quickly and cover the surface of the J55 steel.

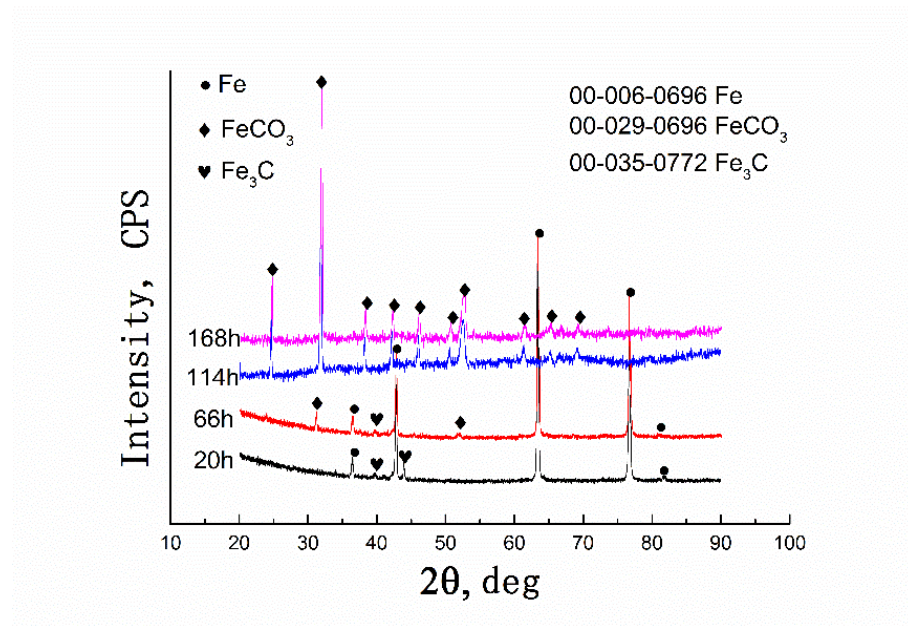


Figure 14. XRD spectra of corrosion product films of J55 steel at different immersion times.

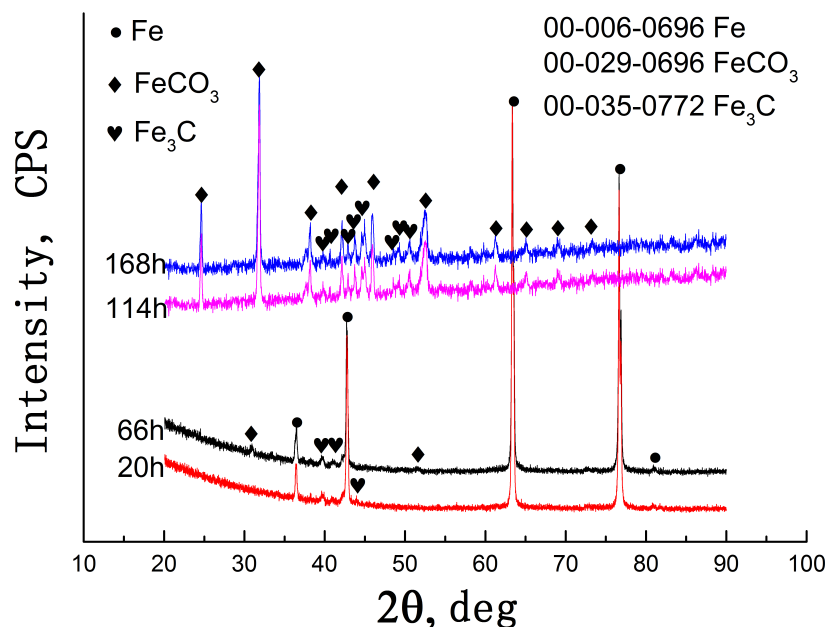


Figure 15. XRD spectra of corrosion product films of N80 steel at different immersion times.

Researchers have studied the film structure and formation process of the corrosion products of carbon steel [8–12]. The research focuses on the structure of corrosion product films and the formation mechanisms of each layer. Table 5 lists the specific contents of the study.

Table 5. References of corrosion product film.

Reference	Steel	Temperature, °C	CO ₂ Pressure, MPa	Solution	Structure	Mechanism
[8]	N80	90	1	simulated formation water	inner and outer layers	outer layer was formed first
[9]	X65	80	1, 9.5	3.5% NaCl solution	inner and outer layers	inner layer was formed first
[10]	N80	78	1	simulated formation water	three-layer structure	formed at the same time
[11]	X65	60	1	simulated formation water	three-layer structure	middle layer was formed first
[12]	X65	50, 80	1, 9.5	simulated formation water	three-layer structure	/

According to Figures 6 and 8 (7, 10, and 15 MPa), the corrosion product film is divided into three layers: the middle layer is porous, the inner layer, and the outer layer are dense. Figures 16 and 17 show the delamination morphology of the J55 and N80 steels at 15 MPa. As shown in Figures 16 and 17, the middle layer of the J55 steel is composed of crystalline particles and amorphous corrosion products, and its structure is loose. Both the inner layer and the outer layer are composed of crystalline particles, which are dense. On the other hand, all three layers of the N80 steel are composed of crystalline particles, and holes and cracks are distributed in the middle layer. This is consistent with the morphology of Figures 6 and 8.

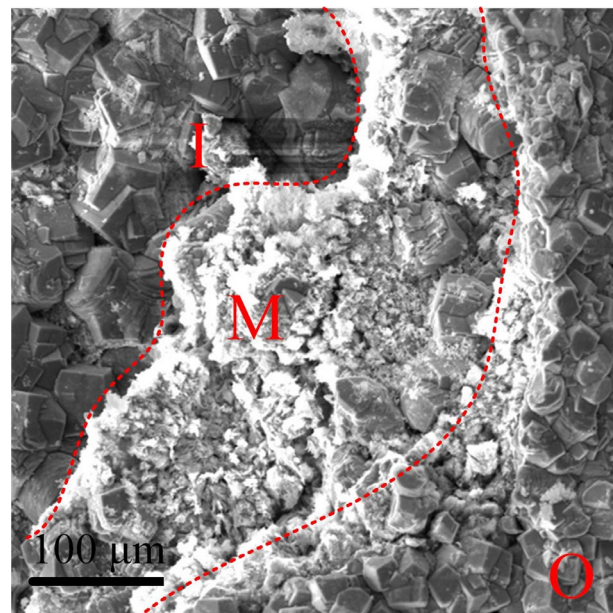


Figure 16. Structure of corrosion product film of J55 steel at 15 MPa (500×): O (the outer layer); M (the middle layer); I (the inner layer).

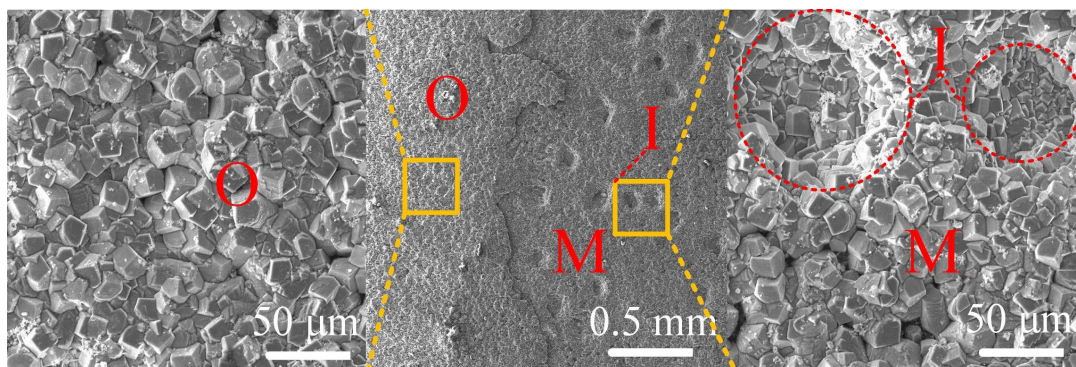


Figure 17. Structure of corrosion product film of N80 steel at 15 MPa (1000×; 100×; 1000×): O (the outer layer); M (the middle layer); I (the inner layer).

A mechanism is proposed to explain the formation process of the corrosion product film for the J55 and N80 steels under supercritical CO₂ conditions. The formation process of the corrosion product film is as follows: (1) Rapid corrosion stage. From 0 h to 20 h, ferrite in the matrix dissolves quickly, leaving Fe₃C, and FeCO₃ is hardly deposited on the matrix, which is covered with Fe₃C residues [33]. Since no protective corrosion product film is formed, the corrosion rate is high. Zhang [14] found a similar phenomenon using EIS research. Under the conditions of supercritical CO₂, before 7 h, the impedance spectrum was composed of an inductive reactance arc and a capacitive reactance arc. Inductive arcing is related to metal dissolution on carbon steel surfaces, and capacitive arcing is related to the formation of corrosion product films. This indicates that the initial stage of corrosion is accompanied by the dissolution of metal, and no protective corrosion product film is formed at this time. (2) Initial formation of FeCO₃-corrosion product film. From 20 h to 66 h, with the continuous dissolution of ferrite, the concentration of Fe²⁺ near the surface of the substrate increases. When $S > 1$, FeCO₃ will preferentially nucleate and grow on Fe₃C. At this stage, the surface of the corrosion product film consists of residual Fe₃C, FeCO₃, and Fe (Figures 14 and 15), and the corrosion rate drops rapidly. Under supercritical CO₂ conditions, Zhang and Wei [14,15] found that in the middle and late corrosion periods, the impedance spectrum consisted of a capacitive arc, and the radius of the capacitive arc increased with time. This shows that the corrosion resistance of the corrosion product film increases with the increase in immersion time. The increase in the thickness and compactness of the corrosion product film is consistent with this conclusion (Figures 10 and 11). (3) The total formation of the FeCO₃-corrosion product film. From 66 h to 114 h, with the deposition of FeCO₃, the compactness of the corrosion product film is improved, and the surface of the steel is completely covered by the corrosion product film, which inhibits the diffusion of Fe²⁺ from the substrate to the outer surface of the corrosion product film. However, anions can still pass through the FeCO₃ corrosion product film. (4) The formation of outer and inner layers. When the immersion time exceeds 114 h, anions pass through the corrosion product film and react with the matrix to form FeCO₃, then FeCO₃ is directly attached to the matrix. Under this condition, the compactness of the FeCO₃ film is higher than that of the FeCO₃ film formed in the previous stage [34]. Meanwhile, a small amount of Fe²⁺ ions diffuse to the surface of the corrosion product film and react with CO₃^{2−} to generate FeCO₃. With the formation of the dense inner layer, the ion exchange is inhibited, the corrosion rate decreases, and tends to be stable.

4.3. Influence of Microstructure on the Corrosion Behavior of Steels under Supercritical CO₂ Conditions

In this paper, the corrosion resistance of J55 steel is higher than that of N80 steel, which is mainly due to the difference in fine structure. The microstructure of the J55 steel is ferrite and pearlite. The fine structure of pearlite consists of lamellar ferrite and lamellar Fe₃C (Figure 18a). The microstructure of N80 is tempered sorbate (granular Fe₃C is distributed on the matrix ferrite (Figure 19a). The difference between the two microstructures lies in the morphology of Fe₃C.

The corrosion mechanism of the J55 steel is shown in Figure 18. In the CO₂ corrosion process, ferrite preferentially dissolves, leaving the lamellar Fe₃C (Figure 18b); with the increase in Fe²⁺ concentration between Fe₃C flakes, FeCO₃ preferentially nucleates on Fe₃C flakes when $S > 1$. As lamellar Fe₃C is beneficial for fixing FeCO₃ [35], FeCO₃ gradually fills the gaps between Fe₃C flakes; with the continuous deposition of FeCO₃, FeCO₃ grows rapidly along the gaps of Fe₃C flakes, forming a corrosion product film to cover the surface of steel (Figure 18d); due to the directional growth of FeCO₃ along the Fe₃C flakes, FeCO₃ sheets squeeze against each other, increasing the stress, which eventually leads to the fracture of FeCO₃ sheets (Figure 12) [10,32]. This is the reason for the formation of the small holes in the middle layer and the cracks on the surface of the corrosion product films. Anions can easily pass through the holes generated by cracking (Figure 18e) and direct contact with the metal matrix, resulting in FeCO₃ directly attaching to the metal matrix,

forming a dense inner corrosion product film (Figure 18f) [34]. At the same time, Fe^{2+} will also diffuse to the surface of the corrosion product film through holes, generating FeCO_3 , which will be deposited in the middle layer to form an outer layer. With the formation of the dense inner layer, the corrosion rate decreases and tends to be stable. In the formation process of the corrosion product film, the porous middle layer is first formed, and then the inner layer and the outer layer are formed simultaneously. The inner and outer layers are dense, while the middle layer is porous.

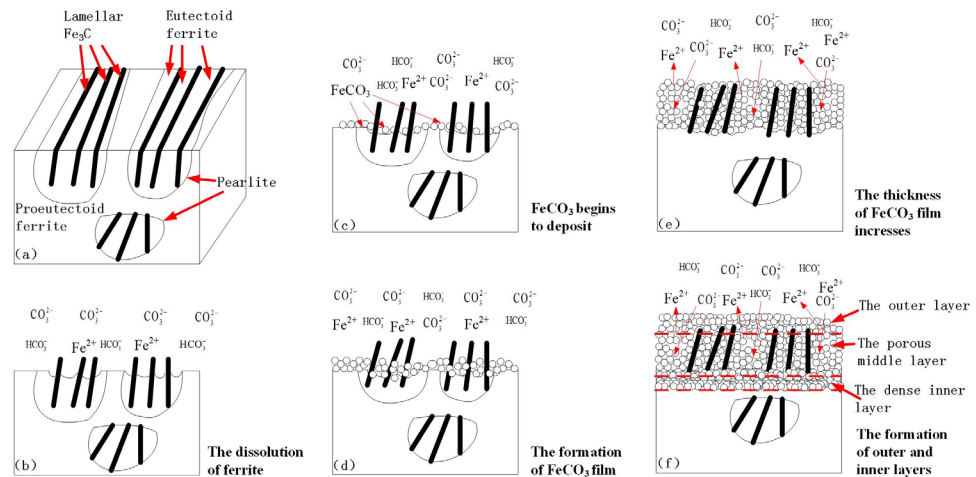


Figure 18. Schematic diagram of the corrosion mechanism of J55 steel. (a) is the Schematic diagram of microstructure; (b) is the dissolution of ferrite; (c) is the beginning of FeCO_3 deposit; (d) is the formation of FeCO_3 film; (e) is the increase of the thickness of FeCO_3 film; (f) is the formation of outer and inner layers.

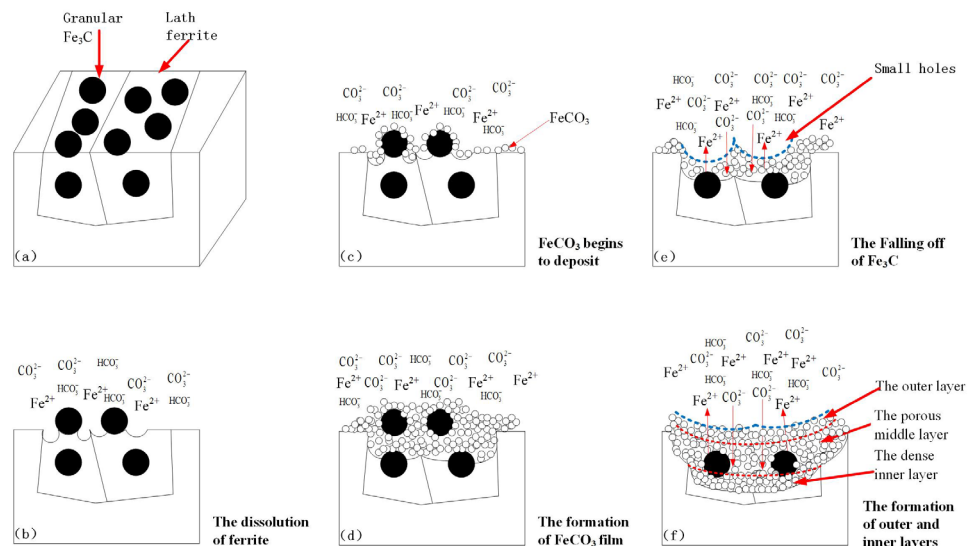


Figure 19. Schematic diagram of the corrosion mechanism of N80 steel. (a) is the Schematic diagram of microstructure; (b) is the dissolution of ferrite; (c) is the beginning of FeCO_3 deposit; (d) is the formation of FeCO_3 film; (e) is the falling off of Fe_3C ; (f) is the formation of outer and inner layers.

The corrosion mechanism of the N80 steel is shown in Figure 19. Ferrite preferentially dissolves (Figure 19b), and the residual granular Fe_3C is distributed on the matrix; the specific surface area of granular Fe_3C is larger than that of lamellar Fe_3C , so when the volume content of Fe_3C is the same, the surface area of granular Fe_3C is larger. A larger cathode surface area leads to a larger corrosion rate. The increase in the concentration of Fe^{2+} promotes the deposition of FeCO_3 . Fe^{2+} easily nucleates and grows in Fe_3C (Figure 19c). With the deposition of FeCO_3 , FeCO_3 gradually covers Fe_3C and the metal matrix (Figure 19d).

Granular Fe_3C easily falls off from the metal matrix [34], resulting in the formation of holes (Figure 19e). Due to the porous corrosion structure near the holes, the diffusion of anions to the metal matrix and the outward diffusion of Fe^{2+} were not inhibited. The anions contact the metal matrix to form FeCO_3 , which is directly attached to the metal matrix and forms a dense inner layer. On the other hand, Fe^{2+} diffuses outward to form FeCO_3 and FeCO_3 deposits in the middle layer, forming an outer layer with FeCO_3 and Fe_3C . Since the granular Fe_3C is easy to fall off, it will also lead to the formation of holes in the outer layer (Figures 13, 19f and 20). In the formation process of the corrosion product films, the middle layer is formed first, and then the inner layer and the outer layer are formed simultaneously. The inner layer is dense, while the middle layer is porous. In other words, because of the different shapes and distributions of Fe_3C , the outer and inner layers are dense for the J55 steel while the inner layer is dense for the N80 steel. This may be the reason why the corrosion resistance of the J55 steel is better than that of the N80 steel.

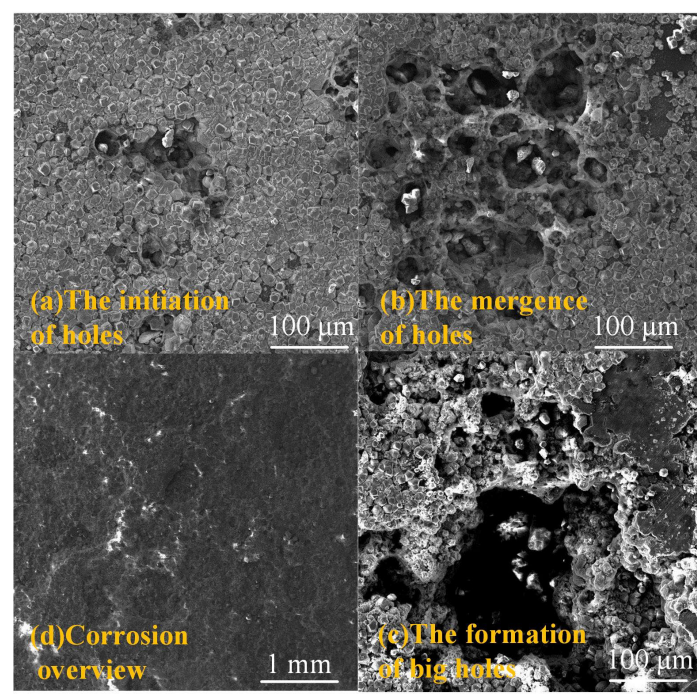


Figure 20. The formation process of big holes in N80 steel (7 MPa): (a–c) (500 $\times$); (d) (50 $\times$). (a) is the initiation of holes; (b) is the mergence of holes; (c) is the formation of big holes; (d) is the corrosion overview.

Cr, Mo, and Ni elements can improve the corrosion resistance of steel, but the content of these elements in this paper is very low, so the influence on corrosion resistance can be neglected. The carbon content of the J55 steel is higher than that of the N80 steel, so the Fe_3C content of the J55 steel is higher than that of the N80 steel, which reduces the corrosion resistance of the J55 steel and improves the corrosion resistance of the N80 steel. On the other hand, because the Fe_3C in the J55 steel is flaky, it can anchor Fe_3C and promote the formation of dense corrosion product films, while the Fe_3C in the N80 steel is granular, which is easy to fall off and form pits, which improves the corrosion resistance of the J55 steel and reduces the corrosion resistance of the N80 steel. From the experimental results, the corrosion rate of the J55 steel is generally lower than that of N80 steel, which indicates that the morphology of Fe_3C plays a dominant role in corrosion resistance.

5. Conclusions

By studying the corrosion behaviors of J55 and N80 steels in simulated formation water of oil wells under different partial pressures, we have reached the following conclusions:

(1) With the rise in CO₂ partial pressure, the corrosion rate of J55 and N80 steels increases continuously. At 10 MPa, the corrosion rate of N80 steel reaches its maximum value and then decreases.

(2) From 0.1 to 3 MPa, no crystalline particles were observed on the surface of J55 and N80 samples; at 5 MPa, the surface of the sample is covered with muddy corrosion products and crystalline particles; over 5 MPa, the surface of most samples is completely covered with crystalline particles, except for the N80 sample at 10 MPa.

(3) Under different partial pressures, the surface of the corrosion product of J55 steel consists of FeCO₃, and the surface of the corrosion product for N80 steel consists of FeCO₃ and a small amount of Fe₃C.

(4) In the formation process of the corrosion product film, the middle layer is formed first, and then the inner layer and the outer layer are formed simultaneously. The outer and inner layers are dense for J55, while only the inner layer is dense for N80 steel.

(5) The continuous lamellar Fe₃C is beneficial to the fixation of FeCO₃ and the formation of a dense corrosion product film, which improves the corrosion resistance of J55 steel. The granular Fe₃C in N80 steel has a larger cathode surface area and is easy to fall off, resulting in damage to the corrosion product film. Therefore, the corrosion resistance of J55 steel is better than that of N80 steel under experimental conditions.

There are some things that can be improved in this paper. Due to the limitations of the equipment, no high-pressure electrochemical tests were carried out. High-pressure electrochemical technology can reflect the formation process of the corrosion product film of carbon steel under supercritical CO₂ corrosion in real-time, and it is an important means for revealing the corrosion mechanism of carbon steel under high CO₂ partial pressure. However, due to the difficulty of manufacturing and maintaining high-pressure electrochemical electrodes, there is little research in this area at present, which requires researchers to conduct in-depth research. In addition, the influence of microstructure on the corrosion behavior of carbon steel can be studied with the help of scanning Kelvin probe force microscopy, which may reveal the relationship between them in more detail and more accurately.

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