Effects of tensile stress on electrochemical characteristics and structural morphology of P110SS steels in carbon dioxide-saturated solution

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Abstract
A high-temperature autoclave was used to grow CO2 corrosion-product films on P110SS steel specimens while the surface of the specimens was continuously subjected to tensile stress in a four-point bending jig; the autoclaving times were 6, 18, 36, and 72 h. A scanning electron microscope was used to observe the surface topography of the corrosion-product films formed on the P110SS steels. An x-ray diffraction was used to analyze the phase compositions of the corrosion products. The electrochemical performance of the films was investigated using electrochemical impedance spectroscopy and potentiodynamic polarization curves. The results showed that tensile stress could hinder the formation of corrosion-product films; the integrity and compactness of the films worsened, but the phase compositions of the films did not change. The applied tensile stress resulted in a smaller grain size of the corrosion-product films, and the grain boundaries increased. In addition, owing to the induced tensile stress, the charge transfer resistances decreased, and the corrosion current densities increased for the P110SS steels with corrosion-product films in a 3.5 wt% NaCl solution saturated with CO2.

1. Introduction

At present, the exploration of oil and gas mainly involves deep and ultra-deep wells. The reserves of these wells are very rich, but the mining conditions are harsh and challenging [1], including high-temperature and high-pressure environments, the presence of highly corrosive gases, and complex formations of strata. These factors can cause serious corrosion damage to pipelines in oil and gas fields [2, 3]. CO2 is the gas most commonly encountered during oil and natural gas exploitation, and it usually accumulates naturally within the strata and the application of the CO2-enhanced oil recovery (EOR) process. When CO2 gas comes into contact with water or wet steam, the reaction products cause corrosion damage to oil and gas pipes and seriously affect the safe operation of gas and oil fields [4, 5].

A large number of researchers [6–8] have concluded that the surfaces of casing steels form FeCO3 corrosion-product films because of the existence of wet CO2 in high-temperature, high-pressure environments. Corrosion-product films have a decisive influence on the corrosion behavior of casing steels, regardless of whether further corrosion reactions occur. The main factors that affect the corrosion rate of casing steels include the structure and compactness of the films and the bonding strength between the films and substrate. However, the formation and behavior of corrosion-product films are heavily influenced by environmental factors, including temperature, CO2 partial pressure, pH value, formation water type, and flow rate [9]. Meanwhile, changes in the surface state also have a certain impact on the morphology and structure of the corrosion-product films formed on casing steels. More importantly, as a result of the complex structure of strata, when casing steels
are deployed underground, they are subjected to tensile stress, extrusion stress, bending stress, torsion stress, and many other combined stresses [10, 11]. High elastic or plastic deformation and residual stress cause significant changes in the surface energy of steel. Therefore, the protective effect of corrosion-product films is greatly reduced in harsh corrosive environments [12, 13].

This study aimed to determine the elastic strain caused by the applied tensile stress on P110SS casing steels using the four-point bending stress loading method. Different stress-loaded samples were put into high-temperature and high-pressure CO₂ environments to form corrosion-product films; the exposure times were 6, 18, 36, and 72 h respectively. Scanning electron microscopy (SEM) and x-ray diffraction (XRD) were used to observe and analyze the surface morphology and phase composition of the corrosion-product films. The
2. Experimental

2.1. Material and environment
P110SS carbon steels cut from oil tube steels via wire-electrode cutting were used as the experimental samples for this study. The chemical composition listed in table 1 was determined using spectroscopic methods. The metallographic structure of the P110SS steel is shown in figure 1, where tempered sorbite and small spherical carbide particles are uniformly dispersed in the ferrite substrate phase. The P110SS steel exhibits excellent resistance to sulfide stress corrosion cracking (SSCC). The test results for the metallographic structures are listed in table 2.

The tensile curve shown in figure 2 was obtained using an electronic tensile-testing machine. The results in table 3 were calculated using the stress-strain relationship, which revealed that the yield strength ($\sigma_s$), tensile strength ($\sigma_b$), and elastic modulus of the P110SS steels were 840, 930, MPa and 210 GPa, respectively.

The specimens were machined to $74 \times 10 \times 2$ mm using a wire-cut electrical discharge machine. They were polished using silicon carbide paper (up to 1000 grit), cleaned successively with distilled water and anhydrous ethanol, and blown dry with $N_2$.

Figure 3 shows the four-point bending jigs that were used to produce constant deformation of the specimens [14]. The specimens and jigs were electrically isolated from each other using glass or polytetrafluoroethylene rods to avoid galvanic corrosion.

The elastic stress at the mid-portion of the specimen (between the contact points of the inner support) in the outer surface of the four-point loaded specimens was calculated using the following relationship:

$$
\sigma = \frac{12Ety}{3H^2 - 4A^2}
$$

where,
- $\sigma$ = maximum tensile stress,
- $E$ = modulus of elasticity,
- $t$ = thickness of specimen,
- $y$ = maximum deflection (between outer supports),
- $H$ = distance between outer supports,
- $A$ = distance between inner and outer supports.

The dimensions are often chosen so that $A = H/4$. 

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Table 3. The test result of tensile mechanical properties of P110SS steel.

| Material        | Yield strength ($\sigma_s$) | Tensile strength ($\sigma_b$) | Elastic modulus ($E$) |
|-----------------|----------------------------|------------------------------|-----------------------|
| P110SS steel    | 840 MPa                    | 930 MPa                      | 210 GPa               |
The corrosion sensitivity of the P110SS steels with corrosion-product films grown under tensile stress can be compared by pre-loading different stress levels using the four-point bending jigs. The loading tensile stress values used in this study are listed in Table 4.

A WHF-25 Hastelloy alloy high-temperature, high-pressure static autoclave was used to prepare the CO$_2$ corrosion-product films. The corrosive medium was an anoxic saturated carbon dioxide solution (2.5 l). The solution was sealed in the autoclave and continuously deoxidized with N$_2$ for 1 h. The corrosion times were 6, 18, 36, and 72 h, and the temperature was fixed at 90 °C. The total pressure was maintained at 5 MPa and the partial pressure of CO$_2$ was maintained at 1 MPa. After the experiment, the specimens were removed from the jigs, and their surfaces were rinsed with de-ionized water and then dried using N$_2$.

Table 4. Loading tensile stress of P110SS steels.

| Stress state | 0% $\sigma_s$ | 20% $\sigma_s$ | 80% $\sigma_s$ |
|--------------|----------------|----------------|----------------|
| $\sigma$ (MPa) | 0 | 168 | 672 |

Figure 4. Schematic of the working electrode.

Figure 5. Surface morphologies of P110SS corroded for 6 h in the autoclave under different tensile stress levels: (a) 0% $\sigma_s$; (b) 20% $\sigma_s$; (c) 80% $\sigma_s$.
2.2. SEM and XRD

The microtopography of the corrosion-product films was observed using a ZEISS EVO MA15 scanning electron microscope and an energy dispersive spectrometer (EDS). The phases of the corrosion-product films were analyzed using a DX-2700B x-ray diffractometer. All of the test areas were selected from within the central 1 cm² of the P110SS steel samples.

2.3. Electrochemical measurements

Electrochemical measurements were performed using an Autolab PGSTAT302N electrochemical workstation. The PGSTAT302N electrochemical system was a conventional three-electrode system. The working electrode, with a working area of 1 cm², is shown in figure 4. The working surface was a corrosion-product film that had been rinsed with distilled water and then dried by blowing N₂. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum plate was used as the counter electrode. Potentiodynamic polarization tests were performed at a constant sweep of 1 mV·s⁻¹ from 300 mV below the open-circuit potential (OCP) to +300 mV above the OCP. EIS measurements were conducted over a frequency range of 100 kHz to 10 mHz using a sine wave signal with an amplitude of 10 mV at the OCP. All electrochemical experiments in this study were conducted in a 3.5 wt% NaCl solution saturated with CO₂, and the test temperature was 25 ± 1 °C. At the beginning of each experiment, the electrochemical system was immersed in the solution for 40 min until the OCP was attained. The corrosion potential (E_corr) corresponds to a steady OCP.

3. Results

3.1. Analysis of SEM images

3.1.1. After 6 h in the autoclave

Figure 5 shows the morphology of the corrosion-product films when P110SS steels were corroded for 6 h in a high-temperature, high-pressure CO₂ atmosphere. It can be seen from the figure that, regardless of the amount of tensile stress, the surface morphology of the corrosion-product films is scaly with many pits and strip bulges on the uneven surface.
In addition, there are many defects in the film, especially with the loaded tensile stress. The number of defects in the corrosion-product films may increase, and the integrity of the corrosion-product films worsens because of the loaded tensile stress. This makes the corrosion-product film less protective to the substrate.

3.1.2. After 18 h in the autoclave

Figure 6 shows the morphology of the corrosion-product films when the specimens were corroded for 18 h in a high-temperature, high-pressure CO2 atmosphere. At this time, the inner film gradually became denser compared with the corrosion for 6 h, and the main structure of the inner films was sponge-like. It can be observed that grain nucleation and production began on the inner films without the applied tensile stress. With the increase in tensile stress, the number of crystal nuclei on the surfaces decreased, and the grain size decreased sharply.

3.1.3. After 36 h in the autoclave

The surface morphologies of the corrosion-product films corroded for 36 h under different tensile stresses are shown in figure 7. It can be seen that the inner films become thicker at this time, and the main structures of both inner and outer layers can be seen. The grains on the outer films are cubic structures stacked randomly against each other.

It can be observed that with the increase in tensile stress, the number and volume of crystal nuclei on the films gradually decreased. Under 80% $\sigma_s$ tensile stress, the integrity and adhesion between the inner and outer films became weak, and defects in the films were extended. The size and shape of different grains vary greatly with large tensile stress; therefore, the outer films have not yet formed very well and can barely cover the inner films fully, and the protective capability of these corrosion-product films is poor.

3.1.4. After 72 h in the autoclave

Figure 8 shows the surface morphologies of the corrosion-product films corroded for 72 h in a high-temperature, high-pressure CO2 environment. It can be seen that the corrosion-product films are composed of rhombohedral grains. These grains formed thick and dense outer films by stacking closely with each other. With an increase in the tensile stress, the size of the grains decreased. In particular, under 80% $\sigma_s$ tensile stress, there
are many tiny grains distributed irregularly on the outer films. These gains overlap and pile up with each other; thus, the outer films are rough and uneven, which can lead to an increase in the number of grain boundaries. Therefore, the corrosive medium easily entered the corrosion-product films through the boundaries. This increases the reaction area on the surface, causing a higher probability of further corrosion.

3.2. Analysis of XRD and EDS Data
Figure 9 shows the XRD patterns of the corrosion-product films formed on the P110SS steels in a CO₂ environment under different tensile stresses. As shown in figure 9(a), the XRD spectra of the P110SS steel corroded for 6 h show obvious Fe peaks. Since (as shown by the SEM images), these corrosion-product films are thin and fragmentary, x-rays can penetrate them, and the diffraction peaks are characteristic of the iron substrate [15]. Figure 9(b) shows the XRD pattern of the corrosion-product films on the P110SS steel corroded for 18 h. With 20% tensile stress and without tensile stress, there was a small amount of FeCO₃ crystals on the steel. Under 80% tensile stress, because the number of FeCO₃ crystals was small, only Fe could be detected, which is consistent with the SEM results. Figures 9(c) and 9(d) show the main components of P110SS steels corroded for 36 h and 72 h under different tensile stresses, indicating that the composition of the gains is FeCO₃, which indicates that tensile stress does not change the phase composition of the corrosion-product films formed on P110SS steels [16]. In addition, the peak intensity of the FeCO₃ crystal diffraction peak decreases with the increase in tensile stress, as shown in figure 9(c), which shows that the tensile stress hinders the formation of the outer corrosion-product film. Additional FeCO₃ crystal diffraction peaks appeared when the steel was corroded for 72 h. At this time, a complete and dense corrosion-product film was formed.

To reconfirm the chemical composition of the corrosion-product films with corrosion for 72 h, EDS energy spectra were used to analyze the elemental content, and the results are listed in figure 10 and table 5. The results show that all the films are composed of only Fe, C, and O, and the amount of each element is almost the same in each case, which illustrates that tensile stress does not change the composition of the corrosion products. No other elements were found, which also proves that the corrosion products completely covered the substrate.
3.3. Analysis of EIS Data

3.3.1. After 6 h in the autoclave

Figure 11 shows the EIS plots of P110SS steels with corrosion-product films formed under different tensile stresses in an autoclave for 6 h; figure 11(a) shows Nyquist plots, and figure 11(b) shows Bode plots. The Nyquist plots comprise a high-frequency capacitive reactance arc, low-frequency capacitive reactance arc, and inductive reactance arc. There may have been two time constants in the reaction system, as inferred from the Bode plots. The high-frequency capacitive reactance arc may be related to the reaction between the initial corrosion product on the metal substrates and the electric double layer in the solution. The low-frequency capacitive arc is related to the dissolution of the area covered by the corrosion-product film on the sample surface. The low-frequency inductive arc is related to the active dissolution of the covered area without corrosion products on the sample surface and the adsorption of intermediate products [17].

ZSimpWin software was used to fit the data of the EIS plots, and the corresponding fitting circuit is shown in figure 12, where $R_s$ is the solution resistance, $Q_{dl}$ is the constant phase angle element, $n$ is the parameter with constant phase angle, $R_t$ represents the charge transfer resistance, $L$ represents the reactance, and $R_L$ is the corresponding reactance resistance.

It can be inferred from the fitted EIS parameters in table 6 that the charge transfer resistance $R_t$ decreases with increasing tensile stress. When the tensile stress increases from 0% $\sigma_s$ to 80% $\sigma_s$, the value of charge transfer resistance $R_t$ decreases from 165.9 $\Omega \cdot \text{cm}^2$ to 116.4 $\Omega \cdot \text{cm}^2$. The decrease in charge transfer resistance shows that the formation of corrosion products becomes easier with an increase in tensile stress. More significantly, the decrease in inductive reactance indicates that active adsorption on the sample surface was reduced. When there was no tensile stress, the surface ion concentration was uniform, and the reaction ions could be adsorbed. However, the defects caused by tensile stress produce a concentration that forms active adsorption sites. The number of defects is limited; thus, the number of active adsorption sites is reduced. This eventually leads to a reduction in inductive reactance.

3.3.2. After 18 h in the autoclave

Figure 13 shows EIS plots of P110SS steels with corrosion-product films formed under different tensile stress in the autoclaves for 18 h; figure 13(a) displays Nyquist plots, and figure 13(b) displays Bode plots. All the Nyquist
plots consist of high-frequency capacitive reactance arcs, low-frequency capacitive reactance arcs, and inductive reactance arcs. It has been well accepted that capacitive reactance arcs are related to the double electric layer of corrosion-product films, while the low-frequency reactance arcs are related to the active reaction of the area which is not covered with corrosion-product films [18]. It can be seen that the radius of the capacitive reactance arcs decreases with increasing tensile stress, and the inductive reactance arcs also tend to shrink. The corresponding equivalent circuit is shown in figure 14.

Table 5. The element content of P110SS corroded for 72 h in the autoclave under different tensile stress levels (wt%).

| Tensile stress | C   | O   | Fe  |
|----------------|-----|-----|-----|
| 0% $\sigma_s$  | 15.76 | 53.81 | 30.43 |
| 20% $\sigma_s$ | 17.57 | 53.17 | 29.26 |
| 80% $\sigma_s$ | 16.58 | 51.18 | 32.24 |

Figure 10. EDS spectra of P110SS corroded for 72 h in the autoclave under different tensile stress levels: (a) 0% $\sigma_s$; (b) 20% $\sigma_s$; (c) 80% $\sigma_s$. 

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Figure 11. EIS plots of P110SS corroded for 6 h in the autoclave under different tensile stress levels: (a) Nyquist plots; (b) Bode plots.

Figure 12. The equivalent circuit diagram of P110SS corroded for 6 h in the autoclave.

Figure 13. EIS plots of P110SS corroded for 18 h in the autoclave under different tensile stress levels: (a) Nyquist plots; (b) Bode plots.

Table 6. EIS parameters of P110SS corroded for 6 h in the autoclave under different tensile stress levels.

| Tensile Stress | $R_s$ (Ω·cm$^2$) | $Q_{dl}$ (Ω$^{-1}$·cm$^{-2}$·S$^{-n}$) | $n$ | $R_i$ (Ω·cm$^2$) | $R_L$ (Ω·cm$^2$) | $L$ (H·cm$^{-2}$) |
|----------------|------------------|-----------------------------------|----|-----------------|-----------------|-----------------|
| 0% $\sigma_s$  | 7.677            | $8.359 \times 10^{-4}$           | 0.8248 | 165.9          | 335.5           |
| 20% $\sigma_s$ | 8.579            | $8.058 \times 10^{-4}$           | 0.8341 | 165.6          | 41.63           | 272.3           |
| 80% $\sigma_s$ | 8.698            | $9.489 \times 10^{-4}$           | 0.7965 | 116.4          | 61.55           | 263.1           |
a corrosion time of 18 h, with an increase in tensile stress, the active adsorption area decreased and the inductive reactance decreased.

3.3.3. After 36 h in the autoclave

The EIS plots of the P110SS steels with corrosion-product films formed under different tensile stresses in an autoclave for 36 h are shown in figure 15. Figures 15(a) and (b) show the Nyquist plots and Bode plots.

Table 7. EIS parameters of P110SS corroded for 18 h in the autoclave under different tensile stress levels.

| Tensile Stress | $R_s$ (Ω·cm$^2$) | $Q_{dl}$ (Ω$^{-1}$·cm$^{-2}$·S$^{-n}$) | $n$ | $R_t$ (Ω·cm$^2$) | $R_L$ (Ω·cm$^2$) | $L$ (H·cm$^{-2}$) |
|----------------|-----------------|---------------------------------|-----|-----------------|-----------------|----------------|
| 0% $\sigma_s$  | 9.473           | $9.056 \times 10^{-4}$           | 0.8453 | 142.9           | 57.18           | 560.3       |
| 20% $\sigma_s$ | 9.017           | $9.658 \times 10^{-4}$           | 0.8400 | 133.8           | 44.35           | 366.4       |
| 80% $\sigma_s$ | 7.734           | $1.619 \times 10^{-4}$           | 0.7699 | 77.1            | 33.82           | 196.5       |
respectively. Capacitive reactance arcs correspond to the electrical double-layer capacitance of reactions caused by a corrosive medium, and inductance arcs are still related to the adsorption of intermediate reagents or the active dissolution of corrosion-product films [19]. The corresponding equivalent circuit is shown in figure 16.

Without tensile stress, the corrosion-product films were relatively complete, and most of the grains could accumulate with one another to form dense films. At this time, the integrity and protective capacity of the films improved. However, the small radii of the inductive reactance arc still appear in the Nyquist plots, which indicates that there are still tiny active dissolution areas between the FeCO₃ crystals. The grain size of the corrosion product decreased slightly, and the structure become loose under applied tensile stress. Therefore, the corrosive medium can pass through these ‘channels,’ causing adsorption and active reactions of the intermediate reactants [20].

Table 8 presents the corresponding EIS fitting parameters. As shown in table 8, the charge transfer resistance $R_t$ gradually decreased with increasing tensile stress. Tensile stress expands the defect corrosion-product films, which increases the reaction area of the corrosive medium; thus, corrosion-product films are easily dissolved by the reaction of the corrosive medium. Some anions with strong penetration can pass through these ‘channels,’ causing adsorption and active reactions of the intermediate reactants [20].

Table 8. EIS parameters of P110SS corroded for 36 h in the autoclave under different tensile stress levels.

| Tensile Stress | $R_s$ (Ω·cm²) | $Q_{dl}$ (Ω⁻¹·cm⁻²·S⁻¹) | $n$ | $R_t$ (Ω·cm²) | $Q_{dl}$ (Ω⁻¹·cm⁻²·S⁻¹) | $n$ | $L$ (H·cm⁻²) |
|----------------|----------------|-------------------------|-----|----------------|-------------------------|-----|----------------|
| 0% $\sigma_s$  | 9.880          | $1.163 \times 10^{-3}$  | 0.7751 | 331.1          | 0.05858              | 0.3272 | 277.2         |
| 20% $\sigma_s$ | 9.635          | $8.685 \times 10^{-4}$  | 0.8011 | 311            | 0.07134              | 0.2876 | 192.8         |
| 80% $\sigma_s$ | 9.074          | $1.106 \times 10^{-3}$  | 0.8492 | 198.8          | 0.1239               | 0.3588 | 182.9         |

Figure 17. EIS plots of P110SS corroded for 72 h in the autoclave under different tensile stress levels: (a) Nyquist plots; (b) Bode plots.

Figure 18. The equivalent circuit diagram of P110SS corroded for 72 h in the autoclave different tensile stress levels.
The defects were expanded by the tensile stress, which significantly reduced the protective effect of the corrosion-product films. Therefore, the charge transfer resistance decreased, and the possibility of further corrosion of the P110SS steel increased.

### Table 9. EIS parameters of P110SS corroded for 72 h in the autoclave under different tensile stress levels.

| Tensile stress | $R_s$ (Ω·cm²) | $Q_{dl}$ (Ω⁻¹·cm⁻²·S⁻¹) | $n$ | $R_t$ (Ω·cm²) | $C_f$ (F·cm⁻²) | $R_f$ (Ω·cm²) |
|----------------|---------------|--------------------------|-----|---------------|---------------|---------------|
| 0%σ_s         | 64.4          | $3.268 \times 10^{-4}$   | 0.5837 | 353.9         | 2.944 $\times 10^{-5}$ | 4259          |
| 20%σ_s        | 81.35         | $6.858 \times 10^{-5}$   | 0.5535 | 410.2         | 8.961 $\times 10^{-7}$ | 1718          |
| 80%σ_s        | 60.98         | $4.695 \times 10^{-5}$   | 0.6833 | 455.6         | 3.403 $\times 10^{-6}$ | 1503          |

Figure 19. Polarization curves of P110SS corroded in the autoclave under different tensile stress levels: (a) 6 h; (b) 18 h; (c) 36 h; (d) 72 h.

decreased to 198.8 Ω·cm². The defects were expanded by the tensile stress, which significantly reduced the protective effect of the corrosion-product films. Therefore, the charge transfer resistance decreased, and the possibility of further corrosion of the P110SS steel increased.

#### 3.3.4. After 72 h in the autoclave

Figure 17 shows the EIS plots of P110SS steels with corrosion-product films formed under different tensile stresses in the autoclave for 72 h. Figure 17(a) shows Nyquist plots, figure 17(b) shows Bode plots, and the equivalent circuit is shown in figure 18.

In contrast to the former corrosion conditions, there was only one arc of capacitive reactance in the Nyquist plots. By comparing the Nyquist and Bode plots, it can be inferred that there are two time constants in the system. One of the time constants corresponds to the high-frequency capacitive reactance arcs; it represents the double capacitance layers generated by the reaction between the outer corrosion-product films and the solution, whereas the low-frequency capacitive reactance arcs represent another time constant. This indicates the reaction of the corrosive medium through the microchannels in the films, thus generating the corresponding double capacitance layer and corresponding transfer resistances [22].

By this time, inductive reactance arcs no longer appear, which indicates that the corrosion-product films were very dense and could completely cover the surface of the P110SS substrates; therefore, active dissolution between the P110SS substrates and the corrosive medium no longer occurred.

Table 9 presents the corresponding EIS fitting parameters. From the data, the charge transfer resistance $R_t$ and film resistance $R_f$ of the P110SS steels gradually decreased with the increase in the applied tensile stress.
When the tensile stress increased from 0% to 20% $\sigma$, the charge transfer resistance $R_t$ decreased from 4254 $\Omega$·cm$^2$ to 1718 $\Omega$·cm$^2$; and when the tensile stress increased to 80% $\sigma$, $R_t$ decreased to 1503 $\Omega$·cm$^2$. Meanwhile, the corresponding film resistance $R_f$ also exhibits a certain amount of decrease.

The SEM diagrams in figure 8 show that small grains appeared with the applied tensile stress, which caused more grain boundaries to appear in the films. Therefore, there are more microchannels for ion transfer to the films, which will increase the reaction area. Even though some of the anions can get through to the corrosion-product films via these micro-channels, further corrosion will occur at the interface of the film and substrates or the substrates of P110SS steels. Therefore, tensile stress can increase the reaction rate of P110SS steels in NaCl solutions and promote further corrosion [23].

### 3.4. Analysis of Polarization behavior

To characterize the corrosion rate of P110SS steels with corrosion-product films corroded at different times in the autoclave, dynamic polarization tests were carried out with typical samples in 3.5 wt% NaCl solution saturated with CO$_2$. The results are shown in figure 19.

Figures 19(a)–(d) represent the experimental times of 6, 18, 36, and 72 h, respectively. The calculation results of the corrosion rate for different times are listed in tables 10–13, where $E_{corr}$ is the self-corrosion potential, $b_a$ and $b_c$ are the anodic and cathodic Tafel slopes, respectively, and $i_{corr}$ represents the corrosion current density.

It can be observed that the trends of the polarization curves in each figure are almost the same. When corroded for 6, 18, or 36 h in the autoclave, some vertical lines appeared on the anode polarization curve, which was similar to the characteristics of concentration polarization. At 6, 18, and 36 h, the corrosion-product films cannot completely cover the surface of P110SS steels, and there is a mass of defects [24]. The corrosive medium can reach the substrate of the P110SS steel, causing active reactions. When the anode overpotential is high, the current density of the anode reaction increases, and active reactions can occur at a faster rate. As a result, many corrosion products or intermediates are generated by these reactions, which are adsorbed on the surface of the P110SS substrates. There are differences between the electrolyte and electrode surface concentrations. This phenomenon is similar to the concentration polarization of steel [25].

| Table 10. Polarization curves parameters of P110SS corroded for 6 h in the autoclave under different tensile stress levels. |
| Tensile Stress | $R_p$ (Ω·cm$^2$) | $b_a$ (mV·decade$^{-1}$) | $b_c$ (mV·decade$^{-1}$) | $i_{corr}$ (μA·cm$^2$) |
|----------------|-----------------|-----------------|-----------------|-----------------|
| 0% $\sigma$     | 256             | 215             | 293             | 210             |
| 20% $\sigma$    | 244             | 204             | 299             | 212             |
| 80% $\sigma$    | 196             | 233             | 314             | 352             |

| Table 11. Polarization curves parameters of P110SS corroded for 18 h in the autoclave under different tensile stress levels. |
| Tensile Stress | $R_p$ (Ω·cm$^2$) | $b_a$ (mV·decade$^{-1}$) | $b_c$ (mV·decade$^{-1}$) | $i_{corr}$ (μA·cm$^2$) |
|----------------|-----------------|-----------------|-----------------|-----------------|
| 0% $\sigma$     | 338             | 243             | 304             | 173             |
| 20% $\sigma$    | 281             | 235             | 248             | 186             |
| 80% $\sigma$    | 267             | 271             | 247             | 210             |

| Table 12. Polarization curves parameters of P110SS corroded for 36 h in the autoclave under different tensile stress levels. |
| Tensile Stress | $R_p$ (Ω·cm$^2$) | $b_a$ (mV·decade$^{-1}$) | $b_c$ (mV·decade$^{-1}$) | $i_{corr}$ (μA·cm$^2$) |
|----------------|-----------------|-----------------|-----------------|-----------------|
| 0% $\sigma$     | 1796            | 95              | 253             | 16.7            |
| 20% $\sigma$    | 1173            | 107             | 250             | 27.8            |
| 80% $\sigma$    | 324             | 119             | 293             | 113.6           |

| Table 13. Polarization curves parameters of P110SS corroded for 72 h in the autoclave under different tensile stress levels. |
| Tensile Stress | $E_{corr}$ (V) | $R_p$ (Ω·cm$^2$) | $b_a$ (mV·decade$^{-1}$) | $b_c$ (mV·decade$^{-1}$) | $i_{corr}$ (μA·cm$^2$) |
|----------------|---------------|-----------------|-----------------|-----------------|-----------------|
| 0% $\sigma$     | −0.626        | 7805            | 117             | 296             | 4.67            |
| 20% $\sigma$    | −0.608        | 6785            | 137             | 350             | 6.30            |
| 80% $\sigma$    | −0.629        | 4624            | 106             | 379             | 7.79            |
However, when corroded for 72 h, the corrosion-product films were very thick and dense, and the films completely covered the surface of the P110SS steel. Under these conditions, the protection of the films is excellent, the corrosive medium cannot penetrate the corrosion-product films, and the main reactions are the dissolution of the outer films. Even at a high anode potential, corrosion products were no longer generated on the surface of the substrates; therefore, the passivation phenomenon disappeared.

As shown in tables 10–13, all absolute values of the cathode reaction Tafel slopes $b_c$ are higher than the values of the anode reaction Tafel slopes $b_a$, which indicates that the corrosion processes of P110SS steels in high-temperature, high-pressure CO2 environments are controlled by the cathode. More importantly, under these four experimental conditions, with an increase in tensile stress, all polarization resistances $R_p$ decreased gradually, while the corrosion current density $i_{corr}$ increased gradually.

Table 10 shows that without tensile stress, the $i_{corr}$ is 210 $\mu$A·cm$^{-2}$, and $i_{corr}$ increased sharply to 352 $\mu$A·cm$^{-2}$ when loaded to 80% $\sigma_s$ tensile stress. It has been found that the protective capability of corrosion-product films with a corrosion time of 6 h is poor, reaction rates are at a high level, and further corrosion easily occurs. Tensile stress can weaken the protective corrosion-product films, increasing the corrosion rate of P110SS steels.

As shown in table 11, when 0% $\sigma_s$ tensile stress was applied and the autoclaving time was 18 h, the corrosion current density $i_{corr}$ was 173 $\mu$A·cm$^{-2}$. However, at 80% $\sigma_s$, the corrosion rate was 210 $\mu$A·cm$^{-2}$, which is 1.21 times higher. After being corroded for 18 h, the structure of the corrosion-product films remained relatively loose, and there were many defects in the films, resulting in a high corrosion rate.

Table 12 shows the polarization curve parameters of the P110SS steels corroded for 36 h in the autoclave under tensile stress. When 0% $\sigma_s$ tensile stress was applied, $i_{corr}$ was 16.7 $\mu$A·cm$^{-2}$, which is relatively small, illustrating that the corrosion-product films have a certain degree of protection. However, when 80% $\sigma_s$ tensile stress was applied, the $i_{corr}$ increased sharply to 113.6 $\mu$A·cm$^{-2}$, which is 6.80 times higher than 16.7 $\mu$A·cm$^{-2}$. As seen from the SEM images in figure 7, a larger tensile stress will cause more defects in the dense corrosion-product films, resulting in a significant increase in the defects in the films and a conspicuous increase in the corrosion current density $i_{corr}$.

When corroded for 72 h, according to the fitting data in table 13, the changes in the polarization resistance $R_p$ and corrosion current density $i_{corr}$ have the same regularity. Without tensile stress, the value of $i_{corr}$ was 4.67 $\mu$A·cm$^{-2}$, and when 20% $\sigma_s$ and 80% $\sigma_s$ tensile stress were applied, $i_{corr}$ rose to 6.30 $\mu$A·cm$^{-2}$ and 7.79 $\mu$A·cm$^{-2}$ respectively. Compared with the other three autoclaving times, the corrosion current densities at this time are significantly lower, and the films have better protection ability, which can prevent further corrosion.

However, tensile stress is still deleterious, and even if corrosion-product films can fully cover the surface of P110SS substrates, tensile stress can still increase the corrosion rate. The tensile stress decreased the grain size and roughness of the surface. As the grain boundaries and microchannels in the films increased, the reaction areas between the corrosive medium and films also increased. In addition, more grain boundaries can cause erosive ions to easily pass through these microchannels to penetrate the films or reach the interface between films and substrates [26]. Consequently, the value of the corrosion current density $i_{corr}$ increased, and further corrosion occurred.
4. Discussion

Based on the results of the SEM and electrochemical experiments, the effects of tensile stress on the growth process of the corrosion-product films were analyzed and summarized. The following physical and chemical models are proposed:

Figure 20 shows the physical and chemical models of the P110SS steel corroded for 6 h in a high-temperature, high-pressure CO2 environment. Regardless of the presence or absence of tensile stress, no obvious differences were found in the surface morphology of the corrosion-product films formed on P110SS steels when corroded for 6 h in an autoclave. It can be seen from the SEM images (figures 5(a)–(c)) that the surface morphologies are all scaly, the surfaces are rough with many defects, and films of this type have no protective effect against further corrosion [8]. However, further corrosion of steel is more likely to occur under applied tensile stress, particularly with high elastic deformation. The defects existing on steels and in films have a significant effect on the surface of P110SS steels, causing stress concentration or changes in chemical energy. Thus, the charge transfer resistances in the system decreased, resulting in a higher electrochemical corrosion rate of the steels. Gao et al [27] proposed the following relationship for the crystal growth rate R:

\[
R = h v \exp \left( \frac{-Q_f}{k_B T} \right) \sigma
\]

where \( h \) is the crystal plane spacing, \( v \) is the molecular vibration frequency, \( Q_f \) is the activation energy, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, and \( \sigma \) is the relative supersaturation.

The corrosion-product films without tensile stress were relatively flat, the crystal plane spacing \( h \) and molecular vibration frequency \( v \) were large, the growth rate \( R \) was relatively high, and the grain boundaries were relatively complete. It can be seen that a few structural defects existed in the film (figure 20(a)). Under a low tensile stress, the number of nucleation points increased. According to the same theory, it can be inferred that the integrity of the formed corrosion-product film deteriorates (figure 20(b)). When the P110SS steel matrix is in the stage of high elastic deformation, the activation energy is large, there are more nucleation and adsorption points on the steel matrix surface, there are more nucleation grains, the crystal plane spacing \( h \) and molecular vibration frequency \( v \) are small, and the crystal growth rate is slow. The resulting inner layer film is thin, and its structural integrity is also very poor; relatively speaking, the surface becomes rougher, and the structure is extremely unstable. Many defects were observed in the films (figure 20(c)). At this time, the corrosion-product films does not provide a strong barrier to the corrosion medium. Corrosive anions can easily enter the corrosion-product film, corrode in the film, and even penetrate the corrosion-product film to reach the metal substrate surface for further oxidation reactions. Therefore, the integrity of the corrosion-product film under tensile stress becomes poor, reverse oxidation occurs, the transfer resistance in the stress system is relatively low, and the self-corrosion current density is relatively large.

The physical and chemical models of the P110SS steel corroded for 18 h in a high-temperature, high-pressure CO2 environment are shown in figure 21. At this time, the inner films gradually formed, but the structure of the inner films was relatively loose and porous, and there were some large defects in the films. The morphology of the inner films was somewhat spongy with poor protection. Without applied tensile stress, the integrity of the inner films is better, and the surface of the films is flat and smooth, which causes the ion concentration to be homogeneous. Nucleation and growth of rhombohedral FeCO3 grains occurred uniformly.

![Figure 21](image-url)
on the relatively flat inner films. Under these circumstances, the hindrance to nucleation was small, and the grains grew very fast, driven by the supersaturation of Fe$^{2+}$ and CO$_3^{2-}$ (figure 21(a)). Under tensile stress, many defects may exist in the films, and the ions in the solution may concentrate at these defects. Therefore, the corrosion medium can migrate into the films through these microchannels [13]. The ion concentration in these areas was comparatively high, and new grains were preferentially nucleated in these defects, leading to a smaller number of crystal nuclei on the surface of the inner films (figure 21(b) and figure 21(c)). Meanwhile, small grains filled the defects in the films. As these early nucleated grains grow, they may also have some internal stress, resulting in further defects in the corrosion-product films, and the protection ability decreases.

Figure 22 shows the physical and chemical models of the P110SS steels corroded for 36 h in a high-temperature, high-pressure CO$_2$ environment under different tensile stress levels. At this time, the thickness of the inner films increased and the structure became relatively compact and integrated. The outer corrosion-product films gradually formed on the inner films; however, the structures of these secondary films were relatively loose and porous. Moreover, the binding force between the inner and outer films was weak [27], and the defects in the films could be expanded by tensile stress.

As shown in figure 22(a), without applied tensile stress, the nucleation of corrosion products occurred homogeneously on the outer films. Reactive ions were gradually deposited between the primary grains, driven by supersaturation, and then the grains nucleated and grew. Meanwhile, the boundaries between the small grains had not yet been completely formed, which created conditions for the formation of larger grains [28]. In addition, because of the action of internal stress as the grains grow, the boundaries can proliferate and entangle with each other to form larger grains. Large grains constituted the outer films, which preliminarily had certain protective abilities.

Figure 22. Physical and chemical models of P110SS steels corroded for 36 h under different tensile stress levels: (a) Without tensile stress; (b) Lower elastic deformation; (c) Higher elastic deformation.

Figure 23. Physical and chemical models of P110SS steels corroded for 72 h under different tensile stress levels: (a) Without tensile stress; (b) Lower elastic deformation; (c) Higher elastic deformation.
When steels were subjected to low elastic deformation, the concentration of ions was caused by defects in the inner films, which led to orientation nucleation of the FeCO₃ grains (figure 22(b)). Therefore, the nucleation and growth of grains were induced more slowly in some areas. At the same time, owing to the poor structure of the corrosion-product films, corrosive media can pass through the films, resulting in reactions at the interface between the films and the steel substrate; and FeCO₃ grains are generated continuously to form integrated inner films preferentially. The growth of the outer films was relatively slow because of oriented growth. However, owing to sufficient supersaturation in the reaction system, the grains on the outer FeCO₃ films can still nucleate and grow on the inner and outer films or among primary grains. As the steels are subjected to high elastic deformation, there will be more defects in the corrosion-product films, and ions such as HCO₃⁻ and CO₃²⁻ can easily penetrate the corrosion-product films. The nucleation and growth process occurred at the interface between the steels and films, mainly increasing the thickness and density of the inner films; the number of FeCO₃ grains on the outer films was small.

As corrosion reactions continue, the physical and chemical models of the P110SS steel corroded for 72 h are shown in figure 23. The corrosion-product films have a good structure without applied tensile stress, and FeCO₃ grains can nucleate and grow continuously on the outer films with lower hindrance. The size of the grains was rather large, and the grains piled up together with a compact structure (figure 23(a)). Therefore, the protective abilities of the films were excellent. When P110SS steels are subjected to low elastic deformation, secondary FeCO₃ grains nucleate between primary grains or at defects of the inner films, so the resistance to nucleation and growth is larger. More importantly, during nucleation, there is a certain internal stress between these two types of grains, which destroys the intercrystalline structure. As a result, the number of grains increased, and the size of the grains decreased, as shown in figure 23(b). When steels are subjected to high elastic deformation, the nucleation and growth of FeCO₃ grains occur preferentially in the defects of the inner films, and the grains grow with mutual competition, causing greater intergranular stress. Therefore, there were more FeCO₃ grains and their sizes were very small, as shown in figure 23(c). This also indicates that there were more grain boundaries and microchannels in the films. However, based on the experimental conditions in this study, the high-temperature, high-pressure saturated CO₂ environment has a high degree of supersaturation, and the nucleation and growth process of the corrosion-product films are only affected by stress. Generally, these corrosion-product films can still protect the metal matrix from further contact with the corrosion medium and provide relatively good protection.

5. Conclusions

The electrochemical and stress corrosion behaviors of P110SS steel in high-temperature, high-pressure CO₂ environments under tensile stress were investigated in this study. The main findings are as follows:

(1) The tensile stress did not change the composition of the CO₂ corrosion-product films on the P110SS steels, and the corrosion products were all FeCO₃. The corrosion-product films had a two-layer structure; the inner films were relatively loose and scaly, and the outer films were composed of rhombohedral FeCO₃ grains stacked together.

(2) Under tensile stress, the electrochemical activity of the P110SS steel increased. Meanwhile, the defects in the P110SS steels expanded, increasing the nucleation adsorption positions. In addition, there is some internal stress between the grains, which blocks the growth of the secondary grains. Therefore, the crystal nuclei were small, and the structure of the corrosion-product films was destroyed.

(3) With the extension of the corrosion time, FeCO₃ grains continuously accumulated on the surface of the corrosion-product films or between the grains. The grains gradually grew and formed an integrated film. Under these conditions, tensile stress causes only a slight reduction in the protective effect of the films.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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