International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Effects of Temperature on Corrosion Behaviour of 2205 Duplex Stainless Steel in Carbon Dioxide-Containing Environments

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Received: 4 Janaury 2020 / Accepted: 5 March 2020 / Published: 10 April 2020

Temperature plays a decisive role in carbon dioxide corrosion and stainless steel passive film stability. The effects of temperature on the corrosion behaviour of 2205 duplex stainless steel in oil and gas field environments containing carbon dioxide were studied in the range of 30–150 °C by electrochemical analysis, scanning electron microscopy and X-ray photoelectron spectroscopy. The results showed that increasing temperatures increased the amount of corrosion products and the pit area on the material surface. At 150 °C, the surface oxide film broke, and the pit density was highest. As the temperature increased, the hydroxide ion content in the passive film increased, whereas the oxide ion content decreased, and chromium(III) oxide was converted into chromium(III) hydroxide, which has poor corrosion resistance. As the temperature increased, the slopes of the Mott-Schottky curves and the donor and acceptor densities increased. The increase in acceptor density resulted in an increased anion concentration in the electrical double layer in the passive film, accelerating the intrusion of anions into the film. The increase in donor density resulted from the oxidation of iron(II) iron(III) owing to the increased temperature, which thereby increased the oxygen vacancy density in the film.

Keywords: 2205 duplex stainless steel; film; carbon dioxide corrosion; high temperature

1. INTRODUCTION

Modern petroleum extraction technologies inject carbon dioxide into the ground to improve the oil recovery rate [1,2.] However, carbon dioxide is highly corrosive when dissolved in water, and its total acidity and corrosiveness are even higher than hydrochloric acid at the same pH value, which can easily lead to local corrosion-induced failures of pipelines and equipment, causing serious economic losses and social harm [3]. There have been many cases of tubing corrosion leakage or stress corrosion cracking failures in high-temperature and high-pressure oil and gas wells around the world [4].

Therefore, corrosion resistance and material stability are very important in these environments. The excellent corrosion resistance and mechanical properties of 2205 duplex stainless steel (DSS), make DSS an ideal choice in the oil, nuclear and marine industries [5-8]. However, few studies have been conducted on the carbon dioxide electrochemical corrosion of DSS in high-temperature and high-pressure environments [9].

Liu et al [10]. studied the stress corrosion cracking behaviour of 2205 DSS in a hydrogen sulfide-carbon dioxide environment. They found that the passive current density increased with decreased solution pH in the presence of carbon dioxide. At a solution pH value of 2.7, hydrogen induced cracking dominated the stress corrosion cracking behaviour, to which the DSS was more sensitive when the solution was saturated with both hydrogen sulfide and carbon dioxide. Yang et al [11]. studied the corrosion rate of 2205 DSS in saturated hydrogen sulfide-carbon dioxide solutions containing different chloride ion concentrations and found that the pit corrosion area increased with increasing concentrations. Zhao et al [12]. studied the corrosion behaviour of 2205 DSS in an oilfield environment by electrochemical and microscopic characterisation methods and found that the material was slightly and uniformly corroded in the water containing carbon dioxide gas and a high chloride ion concentration. They observed pronounced selective corrosion of the ferrite phase of 2205 DSS in a well completion environment, as well as active dissolution of the steel in a fresh acid solution. Sabouri studied the passive film stability of 2205 DSS in water from an oilfield via critical pitting temperature tests and wavelet analysis [13]. The results indicated that the pitting nucleation temperature was 30 °C, and the highest stability of the passive film was obtained between 30 and 40 °C. Compared with austenite, ferrite was more prone to pitting corrosion, owing to the difference in the chemical compositions of the two phases.

Previous studies showed that temperature is one of the most important parameters affecting carbon dioxide corrosion and plays a decisive role in the formation of corrosion product membranes [14,15]. Okoro et al [16]. performed a numerical simulation verified by a field experiment, and the results showed that the corrosion rate of the carbon dioxide-containing oil and gas pipelines increased with increased temperature, with the rate of corrosion almost doubling for every 6 °C increase. Hua et al [17]. found that when the temperature of a carbon dioxide-containing solution increased from 90 to 250 °C, the corrosion scale on the surface of an experimental steel changed from a dense siderite to comingled siderite and iron(II,III) oxide. Lin found that increased temperature accelerated the electrochemical process on the electrode surface and the mass transfer process in the solution, with consequent changes in the corrosion rate [18].

In the work presented here, the influence of temperature on the carbon dioxide-induced corrosion behaviour of 2205 DSS in oil and gas well environments was studied using an electrochemical autoclave. The corrosion products were analyzed by SEM, EDS and XPS. The carbon dioxide corrosion mechanism of 2205 DSS at different temperatures was analysed, and the results provide useful data and theoretical foundations to support for metal corrosion protection in acidic oil and gas field environments.

2. EXPERIMENTAL

2.1 Materials and Solutions

The experimental material was 2205 DSS, and its chemical composition (wt.%) was 0.02 carbon, 0.45 silicon, 1.43 manganese, 0.023 phosphorous, 0.009 sulphur, 22.11 chromium, 5.56 nickel and 3.10 molybdenum. The plate was cut into specimens with dimensions of $10 \times 50 \times 2$ mm for soaking, or 15 mm long \times 3 mm diameter for electrochemical testing. Before the experiments, the samples were polished with wet sandpapers with grits from 80 to 2000 to eliminate scratches. The metallographic samples were polished to a surface roughness of 2.5 µm. All samples were degreased with anhydrous ethanol and acetone after polishing and then washed with deionised water and dried.

The experimental solution was prepared with analytical reagents and deionized water according to data from an oil and gas field in western China. The specific composition was $(g L^{-1}) 0.136$ sodium bicarbonate, 1.672 magnesium chloride, 9.768 calcium chloride, 0.142 sodium sulphate, 36 sodium chloride, and 0.25 potassium chloride. The pH of the solution was adjusted to 6 using 10% glacial acetic acid.

2.2 Immersion Experiment and Surface Analysis

Four samples were tested separately in autoclaves containing the experimental solution at 30, 90, 120, and 150 °C, respectively. Before the experiment, the solution was purged with high-purity nitrogen gas for 1 h, and then carbon dioxide was introduced into the autoclave to bring the total pressure to 2.5 MPa. The samples remained in the solution for 168 h.

After soaking, the samples were removed and the morphologies of the corrosion products were observed by scanning electron microscopy (SEM) (Hitachi SU8010), and the surface compositions were analysed by energy-dispersive X-ray spectroscopy (EDS) (Detector 5030). The corrosion product components were examined by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha) with an Al K α X-ray emission source. The argon ion sputtering intensity was 2 keV, and the sputtering area was 2 × 2 mm². The sputtering speed was 0.1 nm s⁻¹ and the data were fitted using XPSpeak 4.1 software.

2.3 Electrochemical Experiment

The electrochemical experiment was conducted in a high temperature and high pressure electrochemical autoclave, as shown in Fig. 1. The 2205 DSS electrochemical samples served as the working electrodes, and they were spot-welded on a C276 lead cylinder with an outer diameter of 0.5 mm and sealed with a polytetrafluoroethylene tube. A platinum electrode served as the auxiliary electrode, and an external silver chloride electrode served as the reference electrode.



Figure 1. Schematic diagram of the high temperature and high pressure electrochemical autoclave

A CHI660C electrochemical workstation was employed to carry out the electrochemical experiment. The temperature and pressure were set to match those in the immersion experiments. Before the experiment, the working electrode was polarized at -1.0 V relative to a saturated calomel electrode for 3 min to remove the oxide film formed in air, and then the sample was stabilised at the open-circuit potential for 1 h. Electrochemical impedance spectroscopy (EIS) was conducted by applying an AC amplitude of 10 mV in the frequency range from 100 kHz to 10 mHz at the open-circuit potential (OCP). The impedance data were analysed using the ZsimpWin software. The potentiodynamic polarization measurements were acquired over the potential range from -0.7 to 0.5 V relative to the saturated calomel electrode at a scan rate of 0.667 mV s⁻¹. The Mott-Schottky plots were taken over the range from -0.6 to 1.5 V relative to the saturated calomel electrode with an AC amplitude of 10 mV at a fixed frequency of 1000 Hz and with a scan rate of 50 mV per step. All the potentials in this paper are presented relative to the saturated calomel electrode.

3. RESULTS

3.1 Macroscopic Corrosion Morphology

The macroscopic corrosion morphologies of the DSS specimens after immersion in the autoclave for 168 h at various temperatures were shown in Fig.2. Although no macroscopic corrosion occurred, the material became gradually darker with increasing temperatures, and the surfaces lost their original metallic lustre.



Figure 2. Corrosion morphologies of 2205 DSS after immersion in CO₂-containing environments for 168 h, (a) 30 °C, (b) 90 °C, (c) 120 °C and (d) 150 °C.

3.1 SEM and EDS Results

SEM images of the DSS corrosion products after immersion for 168 h were shown in Figure 3, and the elemental contents of the corrosion is listed Table 1, as obtained by EDS. The SEM images show that at 30 °C (Fig. 3(a1)), the surface of the 2205 DSS exhibited almost no corrosion, and from the EDS results, the chromium content on the surface of the substrate was high. From 90 to 150 °C, the surface area covered by corrosion products increased with increasing temperature, and at 90 (Fig. 3(b1)) and 120 °C (Fig. 3(c1)), the sample surfaces were lightly corroded, such that the scratches left by machining were clearly visible. At 150 °C (Fig. 3(d1)), the corrosion of the sample surface was the most severe, and a large area of the surface oxide film was broken. The results in Table 1 show that carbon, nickel, chromium, oxygen and iron were the main constituents of the oxide film. Iron, nickel and chromium generally originate from the metal matrix, and oxygen and carbon generally originate film varied significantly with increasing temperature, indicating that the structure and component of the oxide film significantly changed. Moreover, the chromium content in the oxide film decreased monotonously as the temperature increased, showing the passive film's corrosion resistance loss.

Figure 4 shows SEM images of the DSS after the corrosion products were removed. The images show the pit corrosion morphology. As the temperature increased, the pitted area increased gradually, indicating that the corrosion resistance of the 2205 DSS decreased. The corrosion level was most severe at 150 $^{\circ}$ C, and dense pits appeared on the steel surface, as shown in the blue box in Fig. 4(d).

3.2 XPS Results

To further investigate the temperature-induced changes in the composition of the DSS passive film, the film surface was analysed by XPS. Figure 5 shows the XPS analysis of the $Cr2p_{3/2}$ in the passive films after immersion at various temperatures, and Table 2 presents the film compositions.



Figure 3. SEM and EDS images of 2205 DSS after immersion in CO₂-containing environments for 168 h, (a) 30 °C, (b) 90 °C, (c) 120 °C and (d) 150 °C.

Table	1.	EDS	analysis	of 2	205	DSS	after	immersion	in	CO ₂ -containing	environments	for	168	h	at
	va	rious	temperat	ures	(at.%	ó)									

<i>t</i> (°C)	С	Cr	0	Fe
30	10.17	17.45	3.90	54.09
90	20.53	12.60	6.94	35.17
120	29.57	12.22	1.91	49.79
150	25.45	11.23	3.90	35.21

The figure shows that with immersion at 30–120 °C, chromium appeared in the metallic state (Cr^0 , 574.1 eV) and as chromium(III) oxide (576.6 eV) [19], and the latter content decreased with increasing temperature.



Figure 4. SEM images of 2205 DSS after removing corrosion products, (a) 30 °C, (b) 90 °C, (c) 120 °C and (d) 150 °C.





Figure 5. XPS analysis of the Cr2p3/2 in the passive films of samples immersed in CO₂-containing environments for 168 h, (a) 30 °C, (b) 90 °C, (c) 120 °C and (d) 150 °C.



Figure 6. XPS analysis of the Fe 2p_{3/2} in the passive films of samples immersed in CO₂-containing environments for 168 h, (a) 30 °C, (b) 90 °C, (c) 120 °C and (d) 150 °C.





Figure 7. XPS analysis of C 1s in the passive films of samples immersed in CO₂-containing environments for 168 h, (a) 30 °C, (b) 90 °C, (c) 120 °C and (d) 150 °C.



Figure 8. XPS analysis of Ni 2p3/2 in the passive films of samples immersed in CO₂-containing environments for 168 h , (a) 30 °C, (b) 90 °C, (c) 120 °C and (d) 150 °C.





Figure 9. XPS analysis of O 1s in the passive films of samples immersed in CO₂-containing environments for 168 h, (a) 30 °C, (b) 90 °C, (c) 120 °C and (d) 150 °C.

With immersion at 150 °C, chromium(III) oxide could not be detected in the passive film, but chromium(VI) trioxide (578.1 eV) and chromium(III) hydroxide (577.3 eV) were observed, and the chromium(III) hydroxide content was high [19-21].

Figures 6 and Figures 7 show the fitted high-resolution XPS spectra for Fe $2p_{3/2}$ and C 1s, respectively. At 30–120 °C, the iron in the passive film appeared as iron metal (707.7 eV), ferrous oxide (709.4 eV) and siderite[22,23]. Although the carbonate ion peak in the EDS of the sample immersed at 120 °C, shown in Fig. 3(c2), confirmed the presence of siderite, ferrous oxide was no longer observed at 150 °C, and iron(II,III) oxide (710.9eV) and iron(III) oxide-hydroxide (711.8eV) were observed in the passive film[123, 24]. The C 1s fitting curves for the samples immersed at 30–150 °C had three peaks: carbon (285 eV), carbon monoxide (287 eV) and carbonate ion (289.3 eV) [24]. Table 2 shows that the carbonate ion content increased with temperature, indicating a gradual decrease in the amount of siderite produced.

Composition	30°C	90°C	120°C	150°C
Cr	50.06	52.13	53.04	31.61
Cr_2O_3	50.03	47.86	46.95	-
CrO ₃	-	-	-	31.37
$Cr(OH)_3$	-	-	-	37.00
O ²⁻	48.05	45.24	44.75	43.87
OH-	51.94	54.47	55.24	56.12
Fe	43.85	43.94	44.62	29.08
FeO	38.94	39.39	39.44	-
Fe ₃ O ₄	-	-	-	29.20
FeOOH	-	-	-	31.09
FeCO ₃	17.21	16.67	15.94	10.63
Ni	69.70	67.97	68.90	37.20
NiO	30.30	32.03	31.08	21.29
Ni(OH) ₂	-	-	-	41.51

Table 2. Composition of 2205 DSS passive films immersed in CO₂-containing environments for 168 h at various temperatures (wt.%)

Figure 8 shows the Ni $2p_{3/2}$ XPS spectra of the passive films formed at various temperatures. Nickel appeared in the passive film as nickel metal (852.6 eV) and nickel(II) oxide (859.6 eV) at 30–120 °C[25]. After immersion at 150 °C, nickel was present as nickel metal, nickel(II) oxide (862 eV) and nickel(II) hydroxide (855.4 eV) [25-27]. As shown in Fig. 8 and Table 2, nickel(II) oxide was relatively stable and was not involved in the reactions. Figure 9 shows the O 1s XPS spectra of the passive films. Two peaks appeared in the spectra of the films obtained at 30–150 °C: oxide ion (530.4 eV) and hydroxide ion (532.9 eV) [28,29], indicating that oxygen was present mainly in the form of oxides and hydroxides. As shown in Table 2, as the temperature increased, the hydroxide ion content gradually increased, whereas the oxide ion content decreased.

3.3 Potentiodynamic polarization curves

Figure 10 shows the polarization curves of the DSS samples immersed at various temperatures, and the fitting results are shown in Table 3. The results show that as the temperature rose, the corrosion potential E_{corr} decreased slightly, and the polarization curve shifted significantly to the right, indicating that the corrosion current density I_{corr} increased. The initiating passive current I_{pp} increased with increasing temperature, whereas the passivation zone and the pitting potential E_{tp} decreased significantly. When the temperature was higher than 30 °C, a transition between activation and passivation was observed.



Figure 10. Potentiodynamic polarization curves of 2205 DSS samples immersed in CO₂-containing environments for 168 h at various temperatures.

Table	3	Polarization	curve	fitting	results	of	the	2205	DSS	samples	immersed	in	CO ₂ -containing
	er	vironments f	or 168	h at va	rious ter	mp	eratu	ires					

<i>t</i> (°C)	$I_p(10^{-4}\text{A/cm}^2)$	$E_{corr}(V)$	Passivation zone(V)
30	0.013	-0.534	-0.494~0.095
90	0.231	-0.549	-0.473~-0.110
120	1.175	-0.559	-0.326~-0.111
150	2.879	-0.579	-0.450~-0.280

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3.4 Electrochemical Impedance Spectroscopy

Figure 11(a) and (b) show the Nyquist and Bode plots of the DSS specimens immersed at various temperatures. The diameters of the capacitive reactance arcs were closely related to the immersion temperature and appeared to decrease with increasing temperature. The smallest diameter of the capacitive reactance arc was obtained at 150 °C, suggesting that this passive film afforded the worst protection among the samples. The Nyquist plots obtained from the samples immersed at 90 °C and 120 °C showed the characteristics of capacitive reactance arcs, whereas an inductance arc appeared in the sample immersed at 150 °C. As shown in the Bode plots, the phase angle θ was greatest at 30 °C, approaching 70°, which indicated a stable passive film. However, the phase angle decreased with increasing temperature and was less than 30° at 150 °C, suggesting that this passive film covered less of the surface. The phase angle plots of the samples immersed at 30–120 °C showed two peaks, corresponding to two relaxation processes. The wide range of the phase angle peak at 150 °C was caused by the superposition of the two time constants.



Figure 11. EIS results of 2205 DSS samples immersed in CO₂-containing environments for 168 h at various temperatures, (a) Nyquist plots, (b) Bode plots



Figure 12. Equivalent electrical circuit used for quantitative evaluation of experimental impedance data, (a) 30°C–120 °C, (b) 150 °C

(°	t C) (Ω	$\begin{array}{ccc} R_s & Q \\ Q/cm^2 & (F/c) \end{array}$	$\frac{Q_f}{\mathrm{cm}^2}$ n_1	R_f (Ω/cm^2)	Q_{dl} (F/cm ²)	n_2	R_{ct} (Ω/cm^2)	L (H/cm ²)
3	0 4	5.85 1.14	×10 ⁻⁴ 0.79	4182	7.98×10 ⁻⁵	1	7607	
9	0 4	5.43 1.44	$\times 10^{-4}$ 0.75	2496	5.16×10 ⁻³	1	989.1	
12	20 4	4.35 6.59	$\times 10^{-4}$ 0.73	168.7	1.18×10^{-2}	0.95	122.6	
1:	50 3	3.66 3.85	×10 ⁻⁴ 0.41	3.7	1.66×10 ⁻²	0.83	151.8	84.56

Table 4. Fitted electrochemical parameters for impedance spectra of the 2205 DSS in CO₂-containing environments at various temperatures

The electrochemical impedance spectroscopy results were analysed by ZSimpWin software to confirm the electrochemical parameters quantitatively, and Figure 12 shows the equivalent electrical circuit models. Here, R_s is the solution resistance; R_f and Q_f are the resistance and the capacitance related to the passive film, respectively; R_{ct} and Q_{dl} are the charge-transfer resistance and the capacitance of the double-layer capacitance, respectively; and L is the inductance. The fitting results shown in Table 4 demonstrate that with increasing temperature, R_f decreased from 4182 to 3.7 Ω ·cm², and R_{ct} decreased from 7607 to 151.8 Ω ·cm², indicating that the corrosion resistance of the passive film was worst at 150 °C. The variable n in Table 4 is the dispersion coefficient (0 < n < 1), which reflects the dispersion effect caused by the surface roughness of the electrode[30]. The value of n decreased with increasing temperature, indicating that the corrosion level of the electrode surface was gradually aggravated.

3.5 Mott–Schottky

When a solid electrode with a passive film contacts an electrolyte solution, an electrical double layer will be formed at the solution-electrode interface[31]. When the double layer becomes depleted, the functional relationship between the capacitance *C* and potential *E* in the layer can be expressed by the Mott-Schottky equation. Equation (1) and (2) express the relationship between C^{-2} and *E* in passive films exhibiting n-type or p-type semiconductor characteristics, respectively [32].

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 e N_D} [E - E_{fb} - \frac{KT}{e}]$$
(1)
$$\frac{1}{C^2} = \frac{-2}{\varepsilon \varepsilon_0 e N_A} [E - E_{fb} - \frac{KT}{e}]$$
(2)

Here, ε_0 is the vacuum permittivity (8.85419 × 10⁻¹² F m⁻¹), ε is the dielectric constant of the passive film at room temperature (15.6 °C in this work), N_D is the donor density, N_A is the acceptor density, E_{fb} is the flat-band potential (V), E is the electrode potential (V), K is the Boltzmann constant (1.38 × 10⁻²³ J K⁻¹), T is the absolute temperature (K) and e is the electron charge (1.6 × 10⁻¹⁹ C). At room temperature, $KT e^{-1}$ is approximately 25 mV and can be ignored. N_A and N_D can be obtained from the slope of the line formed by C^{-2} versus E in the Mott-Schottky curve [33,34].

Passive films exhibit different semiconductor characteristics owing to the dominant defect type in the films. When a large number of metal ions are enriched or cation vacancies are missing, the passive film generally exhibits n-type semiconductor characteristics and the slope of the Mott-Schottky curve is positive; otherwise, the film exhibits p-type semiconductor characteristics, with a negative slope [35].

Figure 13 shows the Mott-Schottky results of 2205 DSS samples immersed at various temperatures. The curves exhibit four distinct regions. In region I (approximately -0.4–0 V), the negative slope of the line indicates that the passive film has p-type semiconductor characteristics. In region II (approximately 0–0.4 V), the line has a positive slope, and the passive film exhibits n-type semiconducting behaviour. In region III (approximately 0.4–0.7 V), the passive film on 2205 DSS exhibits p-type semiconductor again, which is caused by the increasing concentration of cation vacancies, such as ferric ions and chromium ions that these species become dominant within this potential range. Some scholars believe that the reason for the change in semiconductor characteristics in this linear region is related to the main component of the outer surface of the passive film being changed from an iron-rich oxide to a chromium-rich oxide or hydroxide[8]. In region IV (approximately 0.7–1.0 V), the slope of the line became positive again for the sample immersed at 30 °C, indicative of n-type semiconductor characteristics. This return to the positive slope is generally attributed to the presence of deep donor energy levels in the energy band structure of the passive film[36-38]. Hamadou [39] proposed that a rich iron(III) oxide-hydroxide layer could be supported by rich chromium(III) oxide and iron(III) oxide contents in the inner layer, and the capacitive behaviour in region IV may therefore have been induced by the presence of iron(III) oxide-hydroxide.



Figure 13. Mott-Schottky curves of 2205 DSS samples immersed in CO₂-containing environments for 168 h at various temperatures.

Table 5 Donor and	d acceptor	densities	and	flat-band	potential	of	2205	DSS	passive	films	at	various
temperature	S											

<i>t</i> (°C)	$N_A(\text{cm}^{-3})$	$N_D(\mathrm{cm}^{-3})$	$E_{fb}(v)$
30	3.01×10^{21}	3.58×10^{21}	-0.05
90	6.18×10^{21}	5.98×10^{21}	-0.05
120	1.81×10^{22}	1.20×10^{22}	0.05.
150	2.47×10^{22}	4.40×10^{22}	-0.2

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The acceptor densities N_A and donor densities N_D of the passive films under the different experimental conditions can be calculated by Equation (1) and (2), respectively. The calculation results are shown in Table 5. Both N_A and N_D increased and the slope of the Mott-Schottky curve in all four regions decreased with increasing temperature.

4. DISCUSSION

4.1 Corrosion Morphologies and Corrosion Products

The macroscopic corrosion morphology and SEM results showed that with increasing temperature, the DSS sample surfaces became tarnished, the corrosion degree gradually intensified and the pitting area increased, and the EDS results showed that the chromium content in the corrosion products decreased with increasing temperature. Passive films on stainless steel surfaces generally consist of iron oxides on the outer layer and chromium oxides on the inner layer[35,40], and this study's XPS results also indicated that the content of chromium(III) oxide in the passive film decreased continuously with increasing temperature. Chromium(III) oxide is a thin and dense passive oxide, with extremely hard and stable crystals [41], and as the chromium(III) oxide content of the passive film increases, the corrosion resistance of the film is enhanced[31]. In this study, when the temperature reached 150 °C, chromium(III) oxide no longer appeared in the passive film and chromium(III) hydroxide and chromium trioxide appeared, with the former being the main constituent substances of the film. Because the stability of chromium(III) hydroxide is lower than that of chromium(III) oxide, the degradation in the corrosion resistance of at 150 °C was mainly caused by the conversion of chromium(III) oxide into chromium(III) hydroxide in the passive film [42].

The XPS results also showed that iron was present in the passive film mainly as ferrous oxide and siderite. When the iron(II) and carbonate ion concentrations in the solution exceed the solubility product of siderite, siderite will begin to precipitate on the surface of the steel [43]. At 30 °C, the ratio of hydroxide ion to oxide ion was small, and hydroxides were difficult to generate. At this temperature, ferrous oxide and siderite were mainly present in the passive film. The content of siderite in the passive film decreases with increasing of temperature, which is related to the decrease of carbon dioxide solubility with the increase of temperature. The ratio of hydroxide ion to oxide ion in the passive film increased as the temperature increased, and when the temperature reached 150 °C, iron(III) oxide-hydroxide appeared in the passive film. In addition, ferrous oxide was thermally unstable in the passive film and was oxidized to iron(II,III) oxide, resulting in decreased corrosion resistance [44]. When the temperature was lower than 120 °C, nickel was present in the passive film mainly in the form of nickel(II) oxide, which converted to nickel(II) hydroxide when the temperature reached 150 °C. Therefore, at 150 °C, the proportion of hydroxide in the passive film increased, and the greater number of defects in hydroxide relative to oxide was considered to be the main mechanism leading to the degradation of the passive film at high temperature [29].

4.2 Electrochemical Results

Temperature affects the kinetics of the electrochemical reaction, and the polarization curves and electrochemical impedance spectroscopy results showed that as the temperature increased, the corrosion current density increased, and the polarization resistance decreased. The increase in the cathode current indicated that the cathodic depolarization was significant, and the cathodic reaction was significantly enhanced. In all samples, the polarization curves showed similar shapes in the cathode region, indicating that the cathodic corrosion mechanisms were the same. With increasing temperature, the number of active points on the DSS material surface increased, the ion diffusion in the solution was enhanced that caused the reaction rate increased, promoting the dissolution of the 2205 DSS material.

Passive films on DSS can exhibit different semiconducting characteristics, based on the film's chemical composition[45]. According to the XPS and Mott-Schottky results, in the potential interval from -0.6 to 0 V (Fig. 13, region I), the capacitive responses of the passive films on samples immersed at 30–120 °C were affected by chromium(III) oxide, which behaves as a p-type semiconductor. The capacitance response of the passive film immersed at 150 °C was affected by chromium(III) hydroxide, which behaves as a p-type semiconductor. Therefore, in the liner region I, the acceptors were chromium ion vacancies at 30-150 °C. In the potential interval from 0 to 0.4 V (Fig. 13, region II), at 30–120 °C, the capacitance response of the passive film was affected by ferrous oxide, which behaves as an n-type semiconductor. At 150 °C, the capacitance response of the passive film was affected by iron(II,III) oxide and iron(III) oxide-hydroxide, which behave as n-type semiconductors. In addition, the anode product chromium trioxide also exhibits n-type semiconducting behaviour [46,47]. The donors at 30–120°C were either iron(II) vacancies or oxygen vacancies caused by constricted motion inside the passive film resulting from the larger atomic radius of iron. At 150 °C, the donors were iron(II), iron(III), and oxygen vacancies. Because of the metallic properties of chromium that promotes series development of an inner chromium oxide p-type semiconductor and an outer n-type iron oxide, which explains the transition of semiconductor characteristics of regions I and II in the Mott-Schottky diagram. [40] The nickel oxide had no effect on the slope of the Mott-Schottky curves.

According to Fig. 13 and Table 5, as the temperature increased, the slopes of the Mott-Schottky curves and the donor and acceptor densities increased. The donor and acceptor densities can characterize the stability of the passive film [48]. According to the point defect model of passive film [49,50], a passive film with more donors and acceptors is more susceptible to damage. Table 5 shows that in the potential intervals of regions I and II, the amount of dopant at 120 and 150 °C was an order of magnitude larger than that at 30 and 90 °C. Therefore, the protective effect of the passive film on the substrate was significantly reduced in these two potential intervals at the higher temperatures. In region I, the acceptor density increased as the temperature increased, which can induce an increase in the anion concentration in the double layer in the passive film that in turn accelerates the intrusion of anion into the film[51]. As a result, the pitting potential decreases, and corrosion is more likely to occur, which is consistent with the SEM results. The slope of the curve in region II decreased with increased temperature, indicating that the donor density increased in the film. This was caused by the oxidation of iron(II) owing to the increased temperature, which thereby increased the valence

state in the film. In order to maintain electrical neutrality, the corresponding oxygen vacancy density in the film increased[52], resulting in the increased donor density N_D .

Figure 13 also shows a significant negative shift in the flat band in the sample immersed at 150 °C. This was attributed to the increase in the number of anions in the solution adsorbed onto the passive film, which in turn increased the amount of negative charge, thereby changing the potential distribution of the Helmholtz double layers and finally resulting in a decrease in the potential difference between the electrode surface and the outer Helmholtz layer. Because the potential difference between the semiconductor is zero at the flat band potential, the potential difference between the electrode surface and the outer Helmholtz layer reflects the change of the flat band potential. The relationship between the flat-band potential E_{fb} and the Fermi level E_F is [53]:

$$E_{fb} = -eE_F \tag{3}$$

Therefore, the increased temperature caused the Fermi level of the n-type semiconductor to shift to the higher energy, and the transition energy level difference decreased. In addition, the higher concentration of transition donor carriers can destabilise the passive film and aggravate the corrosion.



Figure 14. Corrosion mechanism of 2205 DSS in a carbon dioxide-containing environment at various temperatures: (a) 30 °C, (b) 90–120 °C and (c) 150 °C.

5. CONCLUSIONS

This study revealed the effects of temperature on the corrosion behaviour of 2205 duplex stainless steel (DSS) in in carbon dioxide-containing oil and gas fields. The main conclusions were drawn as follows:

(1) 2205 DSS showed pitting corrosion morphologies in an experimental environment that simulated a carbon dioxide-containing oil and gas field. With increasing temperatures, the corrosion products on the sample surfaces and the pitting area increased, and the chromium content in the passive film decreased. At 150 °C, the oxide film on the specimen surface was broken, and the pitting was dense, showing the most severe corrosion of all samples.

(2) At 30–120 °C, the passive film was composed of an inner layer of chromium(III) oxide and an outer layer of siderite and ferrous oxide; at 150 °C, the passive film was degraded into an inner layer of chromium trioxide and chromium(III) hydroxide and an outer layer of iron(II,III) oxide and

(3) As the temperature increased, the slopes of the Mott-Schottky curves and the donor and acceptor densities increased. The increase in acceptor density resulted in an increased anion concentration in the electrical double layer in the passive film, accelerating the intrusion of anions into the film. The increase in donor density resulted from the oxidation of iron(II) iron(III) owing to the increased temperature, which thereby increased the oxygen vacancy density in the film.

ACKNOWLEDGEMENTS

We are grateful to the Key Project of the Education Department of Liaoning Province of China (grant number: L2017LZD004) for their financial support.

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