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Investigation of Corrosion Behavior of X65 Steel in Simulated Deep-Sea Environment Using Electrochemical Techniques

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The corrosion behaviors of X65 steel in the simulated deep-sea environment at different temperatures are investigated using electrochemical techniques. The effect of temperature on corrosion products are also analyzed by X-ray diffraction. The results indicate that the corrosion current density decreases as the temperature decreases. The polarization resistance increases as the temperature decreases. The composition of the corrosion products formed on the surface of X65 steel remains the same as the temperature decreases, mainly composed of γ -FeOOH, γ -Fe₂O₃, and Fe₃O₄. The low temperature in the deep-sea environment retards the corrosion of X65 steel by inhibiting the anodic dissolution reaction.

Keywords: X65 steel, Deep-sea environment, Temperature, Electrochemical techniques, Corrosion

1. INTRODUCTION

Since the middle of the twentieth century, the offshore oil industry has achieved rapid development with the gradual acceleration of global industrialization [1]. The scope of offshore oil and gas exploitation has gradually expanded from shallow seas to deep seas in response to the depletion of shallow sea oil and gas resources in recent years [2]. For various metals or alloys used in the oil and gas industry, the deep-sea environment is a more severe corrosive environment than the shallow sea environment [3]. As one of the widely used deep-sea oil and gas pipeline materials, the corrosion resistance of X65 steel is closely related to the safety and stability of oil and gas transportation. The importance of research on corrosion behaviors and corrosion mechanisms of X65 steel in the deep-sea environment.

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Among the various environmental factors in the deep sea, the main factors affecting material corrosion include hydrostatic pressure, temperature, dissolved oxygen, and salinity [4-6]. In order to study the impact of these unique environmental factors on the corrosion process of materials, since the 1960s, researchers have carried out multiple in-situ exposure tests with the water depth up to 5100m. A large amount of long-term data have been obtained from the in-situ exposure tests of various structural materials [7-10]. The in-situ exposure test in the deep sea can reflect the most real corrosion data of materials in the actual deep-sea environment, but it still has disadvantages such as huge cost, long period, and high failure rate. The data obtained from the in-situ exposure test are the result of a combination of various environmental factors. It is impossible to study the influence of a single factor on the corrosion behavior and mechanism of materials in the deep-sea environment. Thus, laboratory simulation tests are performed. The influence mechanisms of the hydrostatic pressure on the enhancement of pitting susceptibility and the evolution of passivation film have been discussed [11-13]. For pipeline materials, Yang et al. have investigated the promotion of the high hydrostatic pressure in deep-sea environment on the pitting initiation and propagation of X70 steel. The hydrostatic pressure can accelerate the corrosion by promoting the transport and adsorption of chloride ions in the corrosion product layer [14].

For many years, the influence of deep-sea environment on corrosion has mainly focused on the effect of hydrostatic pressure. However, the deep-sea environment is a comprehensive and complex system. As the water depth increases, the hydrostatic pressure increases while the temperature decreases. At a depth of 3000m, the temperature is only about 2-3 °C [10]. In order to further study the influence of the deep-sea environment on the corrosion process of materials, the effect of temperature and hydrostatic pressure should be considered comprehensively.

In the previous study, the influence and the mechanism of hydrostatic pressure on the corrosion behavior of X65 steel in the artificial seawater have been investigated [15]. In this work, the objective is to investigate the corrosion behavior of X65 steel in the low temperature environment of the deep sea. Electrochemical measurements including potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and electrochemical noise (EN) are carried out at different temperatures. X-ray diffraction (XRD) is performed to analysis the corrosion products formed on the surface. Based on the analysis of the above measurement results, the influence mechanism of the low temperature in the deep sea environment on the corrosion behavior of X65 steel is explored.

2. EXPERIMENTAL

2.1 Materials

The chemical compositions of the X65 steel were 0.09%C, 0.26%Si, 1.30%Mn, 0.15%Ni, 0.04%Cr, 0.17%Mo, 0.13%Cu, 0.04%V, 0.03%Nb, and Fe balanced. X65 coupons were cut from a section of steel pipe and processed into different dimensions. For electrochemical measurements, the coupons were processed into the cylinder with the dimension of $\phi 6 \text{ mm} \times 20 \text{ mm}$. Internal threads were machined on the cylindrical coupons so that the coupons could be installed on the high-pressure device (as shown in the previous work [15]) to carry out electrochemical measurements in the simulated deep-

sea environment. For surface characterizations, the coupons were 20 mm \times 20 mm \times 3 mm. All the coupons were ground to 1500 grit by SiC paper. The ground coupons were cleaned with ethanol and dried for later use.

2.2 Electrochemical measurements

The corrosion behavior of the X65 steel were investigated using electrochemical techniques by an Autolab 302N electrochemical workstation. The electrochemical measurements were conducted with the three-electrode system in the literature [15]. For EN measurements, a coupon of X65 steel was used as the counter electrode instead of the platinum wire. All the electrochemical measurements were performed in the 3.5 wt% NaCl solution. The hydrostatic pressure was set to 0.1 MPa and the temperature was set from 5 °C to 25 °C to investigate the effect of low temperature in the deep-sea environment separately.

The coupons were first immersed in the solution at the open circuit potential (OCP) for 10 min as a pretreatment. The potential ynamic polarization measurements were applied by sweeping the potential from -300 mV vs. OCP towards the positive direction with a sweeping rate of 1 mV/s until the current density exceeded 1mA/cm^2 .

The EIS measurements were carried out at OCP with the frequency from 10^5 Hz to 0.01 Hz. The amplitude was set as 10 mV.

The EN measurements were conducted at OCP. The electrochemical potential noise (EPN) was recorded between WE and RE, and the electrochemical current noise (ECN) was recorded between WE and CE. The test frequency of EN was set to 2 Hz, and the duration of each EN measurement was set to 10 h. The EN data were decomposed into eight levels (d1-d8) by using the wavelet transform technology. The fraction of energy associated with each detailed crystal was calculated as follows [16],

$$E = \sum_{n=1}^{N/2} d_{1,n}^2 + \sum_{n=1}^{N/2^2} d_{2,n}^2 + \dots + \sum_{n=1}^{N/2^8} d_{8,n}^2$$
(Eq. 1)

2.3 Surface characterizations

By hanging in the high-pressure device, the X65 coupons for surface characterizations were immersed in the 3.5 wt% NaCl solution at 0.1 MPa for 3 days. The immersion test was set to two groups. The temperature of the two groups were 5 °C and 25 °C, respectively. The duration of the immersion test was 3 days. The corrosion products formed on the surface of the coupons were identified by XRD.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarization results

Fig. 1 illustrates the potentiodynamic polarization curves of the X65 steel in the artificial seawater at 5 °C, 10 °C, 15 °C, and 25 °C. As shown in Fig. 1, the anodic polarization curves at each

temperature exhibit activation characteristic, suggesting the dissolution of X65 steel under the conditions performed. The anodic current density decreases with the decreasing temperature, indicating an inhibited anodic dissolution rate of the X65 steel.

The corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) derived from the polarization curves are presented in Table 1. The E_{corr} obviously shows a trend to the negative direction as the temperature decreases. The i_{corr} decreases as the temperature decreases. The potentiodynamic polarization results suggest that the anodic reaction type of X65 steel remains unchanged with temperature, and the corrosion rate decreases as the temperature decreases.



Figure 1. Polarization curves of X65 steel exposed to the artificial seawater at 5 °C, 10 °C, 15 °C, and 25 °C with a sweeping rate of 1 mV/s.

Temperature (°C)	Parameters		
	$i_{\rm corr}$ (A·cm ⁻²)	$E_{\rm corr}({ m mV})$	
5	2.09×10^{-6}	-417	
10	2.46×10^{-6}	-485	
15	2.68×10^{-6}	-454	
25	$3.69 imes 10^{-6}$	-498	

Table 1. Evolutions of polarization parameters for X65 steel immersed in the artificial seawater under different temperatures.

3.2 EIS results

EIS measurements were conducted at 5 °C, 10 °C, 15 °C, and 25 °C. Fig.2 illustrates the impedance responses of X65 steel exposed to the artificial seawater at different temperatures. Fig. 2(a) and Fig. 2(b) are the Nyquist plots and the corresponding Bode plots, respectively. As shown in Fig. 2(a), the Nyquist plots display the characteristic of depressed capacitive loops. The diameter of the capacitive loops increases as the temperature decreases. The Bode plots confirm the characteristic of one time constant, as shown in Fig. 2(b). The impedance modulus increases from 892 $\Omega \cdot \text{cm}^2$ to 2571 $\Omega \cdot \text{cm}^2$ as the temperature decreases from 25 °C to 5 °C.



Figure 2. Electrochemical impedance spectra for X65 steel exposed to the artificial seawater at 5 °C, 10 °C, 15 °C, and 25 °C with a frequency range from 100 kHz to 0.01 Hz. (a) Nyquist plots, (b) Bode plots



Figure 3. The equivalent circuit model of one time constant used for EIS fitting analysis

Fig. 3 shows the equivalent circuit to extract the electrochemical parameters. As shown in Fig. 3, R_s is the solution resistance. R_p is the polarization resistance, and Q_{dl} is the constant phase element corresponding to the R_p . The fitted values of the element parameters are listed in Table 2. As shown in Table 2, R_p increases as the temperature decreases (from 994 $\Omega \cdot cm^2$ to 2953 $\Omega \cdot cm^2$), indicating the corrosion resistance of X65 steel is improved by the decreasing temperature. The EIS results suggest that the corrosion rate of X65 steel is retarded by the decreasing temperature, which is consistent with the results of the potentiodynamic polarization.

Parameters	Temperature (°C)			
	5	10	15	25
$R_{\rm s} \left(\Omega \cdot { m cm}^2 ight)$	4.5	7.1	6.5	5.2
α	0.79	0.81	0.79	0.80
$Q_{\rm dl} (\mu {\rm F} \cdot {\rm cm}^{-2})$	682.9	603.0	736.4	794.4
$R_{\rm p}(\Omega\cdot{ m cm}^2)$	2953	2646	2452	994

Table 2. Evolution of electrochemical impedance parameters with temperature for X65 steel immersed in the artificial seawater.

3.3 EN results

Fig. 4 illustrates the EN records of the X65 steel exposed to the artificial seawater at 5 °C and 25 °C. The records of EPN and ECN are shown in Fig. 4(a) and Fig. 4(b), respectively. As shown in Fig. 4(a), the potential of X65 steel at 5 °C and 25 °C gradually decreases with time. At 25 °C, the potential rapidly decreases during the initial stage, and quickly stabilizes at approximately -0.60 V vs. Ag/AgCl. The potential at 25 °C is lower than the potential at 5 °C with a higher decrease rate. As shown in Fig. 4(b), the current at 5 °C is lower than the current at 25 °C. The current fluctuates with time, and the signals are smooth without typical transient shape representing localized corrosion. Similar characteristic of the typical EN signals have been reported in other researches [17, 18].

The noise resistance R_n of X65 steel at 5 °C and 25 °C are calculated by the corresponding EN data. Fig. 5 illustrates the scatter diagram of R_n at different temperatures. As shown in Fig. 5, the R_n at 5 °C is larger than the R_n 25 °C during the whole measurement, indicating a lower corrosion rate at 5 °C. The increasing trend of corrosion with temperature is verified again by the EN results.

The EN data is analyzed by using the Db4 wavelet. Generally, activation-controlled processes are fast processes with short time scales, and diffusion-controlled processes are slow processes with long time scales [19, 20]. Fig. 6 illustrates the energy distribution plots (EDPs) of X65 steel in the artificial seawater at 5 °C and 25 °C. As shown in Fig. 6, at both 5 °C and 25 °C, the crystals d7-d8 accumulate the main relative energy during the whole measurement. The result indicates the corrosion type of X65 steel in the artificial seawater is not affected by the temperature. The reaction of the electrode surface for X65 steel in the artificial seawater is mainly controlled by diffusion processes.



Figure 4. EN records of X65 steel immersed in the artificial seawater at 5 °C and 25 °C with a sampling frequency of 2 Hz. (a) EPN, (b) ECN



Figure 5. The variation of R_n with time at 5 °C and 25 °C.



Figure 6. The variation of EDPs with time corresponding to the EN data of X65 steel in the artificial seawater at (a) 5 °C and (b) 25 °C

3.4 Corrosion products analysis

Fig. 7 illustrates XRD spectra of the corrosion products after 3 d of immersion in the artificial seawater at 5 °C and 25 °C. As shown in Fig. 7, at both 5 °C and 25 °C, the corrosion products are composed of the same components, lepidocrocite (γ -FeOOH), maghemite (γ -Fe₂O₃), and magnetite

(Fe₃O₄). The results indicates that the composition of corrosion products formed on the surface of X65 steel in the artificial seawater is not affected by the low temperature. The corrosion products mainly consist of γ -FeOOH, γ -Fe₂O₃, and Fe₃O₄, which is consistent with the previous findings in the literature [10].



Figure 7. XRD spectra of the corrosion products after 3 d of immersion in the artificial seawater at 5 °C and 25 °C.

For electrochemical reactions, the increase in temperature is beneficial to promote the corrosion reaction rate, especially to accelerate the anodic dissolution of metals [21, 22]. Generally, most of the increase in reaction rate caused by temperature follow the Arrhenius equation. According to the Arrhenius equation, the relationship between the corrosion rate and the temperature can be described as follows,

$$\log(i_{\rm corr}) = \log(A) - \frac{E_{\rm a}}{2.303RT}$$
(Eq. 2)

where *A* is the pre-exponential factor, a constant for each reaction, E_a is the activation energy for the corrosion reaction, *R* is the universal gas constant, and *T* is the absolute temperature (in kelvin). E_a can be calculated from the slope of $\text{Log}(i_{\text{corr}})-1/T$ curve.

Fig. 8 illustrates the variation of i_{corr} with temperature. As shown in Fig. 8, the data are fitted by using the Eq. 3. The fitting result indicates that, in the artificial seawater, the relationship between the corrosion rate of X65 steel and the temperature follows the Arrhenius equation. Combined with the previous results, the temperature influence mechanism on the corrosion behavior of X65 steel in the artificial seawater can be inferred. The influence of temperature in the deep-sea environment follows the Arrhenius formula. The decrease in temperature inhibits the anodic dissolution reaction of X65 steel, leading to a decrease in the corrosion rate. The low temperature in the deep-sea environment has no effect on the corrosion type and the corrosion product composition.



Figure 8. Dependence of i_{corr} on the temperature according to the Arrhenius equation.

4. CONCLUSIONS

The corrosion rate of X65 steel in the simulated deep-sea environment decreases as the temperature decreases. The decrease in temperature lead to the increase in R_p and R_n . At both 5 °C and 25 °C, the corrosion products formed on the surface of X65 steel mainly consist of γ -FeOOH, γ -Fe₂O₃, and Fe₃O₄. The decrease of temperature has little effect on the composition of the corrosion products. The temperature does not change the corrosion type of X65 steel in the artificial seawater. The decrease in temperature inhibits the anodic dissolution reaction of X65 steel, leading to a decrease in the corrosion rate.

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