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EFFECTS OF ANODIC PROTECTION ON SCC BEHAVIOR OF X80 PIPELINE STEEL IN HIGH-pH CARBONATE-BICARBONATE SOLUTION

WPŁYW OCHRONY ANODOWEJ NA NAPRĘŻENIOWE PĘKANIE KOROZYJNE STALI TYPU X80 Z ZASTOSOWANIEM NA RUROCIĄGI W ROZTWORZE BUFOROWYM O WYSOKIM pH

The potentiodynamic polarization test and slow strain rate tensile tests of X80 pipeline steel were performed in 0.5M Na_2CO_3-1M $NaHCO_3$ solution to study the electrochemical and stress corrosion cracking properties. The results of potentiodynamic polarization test show that there is an obvious stable passive region, about from 0v to 0.8V (SCE), indicating that anodic protection is feasible. The results of slow strain rate tensile tests show that the stress corrosion cracking sensibility is high and cathodic protection effect is restricted due to the hydrogen permeation. However, the elongation, yielding strength and tensile strength all increase with anodic protection. The higher anodic protection potential in the stable passive region is benefit to improve tensile strength and yielding strength. However, the higher elongation is obtained at 0.5V (SCE) anodic protection potential.

Keywords: X80 pipeline steel, stress corrosion cracking, high-pH solution, anodic protection

Badania polaryzacji potencjodyniamicznej oraz próby powolnego rozciągania (SSRT) przeprowadzono na stali typu X80 w roztworze 0,5M Na_2CO_3-1M $NaHCO_3$. Określono odporność na korozję elektrochemiczną oraz zbadano zjawisko naprężeniowego pękania korozyjnego. Rezultaty badań polaryzacji potencjodynamicznej wykazały istnienie stabilnego obszaru pasywacji w zakresie potencjału od 0V do 0,8V (SCE: półogniwo odniesienia – elektroda kalomelowa). Próby powolnego rozciągania pokazały wysoką wrażliwość materiału na naprężeniowe pękanie korozyjne i ograniczenia ochrony katodowej w związku z przenikaniem wodoru. Ochrona anodowa natomiast, zwiększa znacząco wydłużenie próbki, granicę plastyczności oraz wytrzymałość na rozciąganie. Ponadto zwiększanie wartości potencjału w stabilnym obszarze pasywacji dodatkowo poprawia te właściwości.

1. Introduction

X80 pipeline steel, as a kind of high strength low alloy (HSLA) and high-grade steel which is produced by thermo mechanical control process (TMCP), has been used more and more widely to transport oil and natural gas all over the world due to its outstanding properties [1-3]. However, on the other hand, stress corrosion cracking (SCC) has becoming one of the most important factor causing failures and disastrous. The SCC behavior and safeguard measures of X80 pipeline steels should be paid much attention for the sake of the security of pipeline.

Generally speaking, pipelines mainly experience two types of SCC, high-pH and near-neutral-pH SCC respectively, though SCC in acid environment has been found in recent years [4,5]. The mechanism of high-pH SCC is mainly attributed to anodic metal dissolution and repeated rupture and re-passivation of passive films that form over the crack tip [6-10]. The suggesting simulated solution in laboratory test is 0.5M Na_2CO_3-1M $NaHCO_3$ [11]. Previous studies have indicated that the crack growth increases exponentially with stress in the simulated solution and the passive film formed at the surface of pipeline steel behaves like an n-type semiconductor, whose properties would be quite influenced by the applied stress [11]. Cathodic protection, used widely in the pipeline transportation, can prevent anodic dissolution efficiently. However, hydrogen permeation is induced at the same time and the passive film at the surface of pipeline steel would be breakdown due to the cathodic current so that the likelihood of SCC increases [11,12]. Anodic protection, meaning adding an additional anodic potential which is chosen from stable passivity regions in polarization curve, can promote the formation of passive film and re-passivity after rupture of passive films produced on the steels surface effectively. Compared with cathodic protection, the hydrogen permeation can not be induced by anodic protection so that it has high potential to be used to prevent high-pH SCC.

Previous studies have shown that the electrochemical methods and slow strain rate tensile (SSRT) tests are the effective ways to study the corrosion resistance with or without

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applied stress [4, 5, 13, 14]. In this study, polarization curve of X80 pipeline steel in high-pH solution was tested, from which the corrosion potential and the stable passivity region can be determined. One cathodic potential near the corrosion potential and four anodic potentials in stable passivity region were chosen to be used as protection potential of the X80 pipeline steel in simulated solution. And then the slow strain rate tensile (SSRT) tests were carried out to study the effect of cathodic and anodic protection on SCC behavior.

2. Experimental

2.1. Materials

The chemical composition of X80 pipeline steels, used in this study, is (wt.%): C 0.046, Si 0.305, Mn 1.76, P 0.007, S 0.001, Al 0.058, Nb 0.079, V 0.008, Ni 0.225, Cr 0.023, Mo 0.226, B 0.00025, Ti 0.015, Ca 0.001, Cu 0.215 and Fe balance. The effect of many alloying elements is precipitation hardening and grain refined crystalline strengthening. The main microstructure of X80 steel is composed of polygonal ferrite and granular bainite.

2.2. Test solution

In this study, the classical solution system of 0.5M Na_2CO_3+1M $NaHCO_3$ was used to investigate the SCC behavior of X80 pipeline steel. All experiments were performed at about 25°C and the pH is maintained about 9.4.

2.3. Electrochemical measurements

A three-electrode electrochemical cell system was employed with the use of the studied material, X80 pipeline steel, as the working electrode, platinum plate as the counter electrode, and saturated calomel electrode (SCE) of +0.241 V_{SHE} as the reference electrode. In this study, all potentials are all relative to SCE. Prior to electrochemical tests, the samples were ground up to 800 grit silicon, then soldered to copper wires, mounted in silica gel, rinsed with deionized water, degreased in acetone, cleaned ultrasonically with ethyl alcohol for 15 min and then air dried. Potentiodynamic polarization scans were obtained at 1 mV/s sweep rate from -1.2 V to 1.2V.

2.4. Slow strain rate tensile (SSRT) tests

The SCC behavior of X80 and the effect of cathodic or anodic protection in high-pH solution were investigated using SSRT methods. The Schematic diagram of specimens for the samples of SSRT tests is shown in Fig. 1. Prior to testing, the gauge lengths of the specimens were polished to 1200 grit emery paper along the tensile direction, then degreased with alcohol, acetone in an ultrasonic cleaner, and then washed with distilled water, finally with hot air. In SSRT tests, the platinum plate and saturated calomel electrode (SCE) were also immersed in the solution to test the changes of corrosion potential of samples or apply an additional potential. However, the counter electrode was removed in the solution in the SSRT tests without additional potential. The strain rate was

controlled at 1×10^{-6} s^{-1}, which was suggested in reference [11,15].
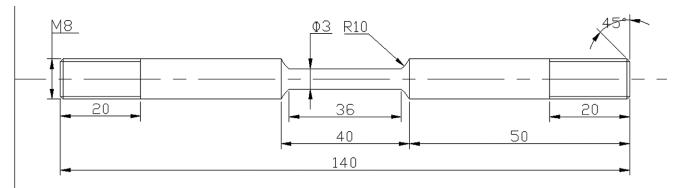

Fig. 1. Schematic diagram of specimens for the samples of SSRT tests

In this study, seven group experiments were designed. No.1 is in the air, No.2 is in the solution without any protection. And No.3-7 is in the solution with additional protection potential of -0.9V, 0V, 0.25V, 0.5V and 0.75V respectively. And there are 5 samples in each group to assure the repeatability of the test results. The test values were the average.

To investigate the SCC susceptibilities of X80 steels in high-pH solution, sensibility indexes were put forward using the following equations:

$$I_{SCC} = (1 - \frac{I_{corr}}{I_0}) \times 100\% \qquad (1)$$

where I_0 is the test parameters in the air, and I_{corr} is the test parameters in high-pH solution. I_0 and I_{corr} can be yield strength (σ_s), tensile strength (σ_b), elongation rate (A), and so on.

In addition, the effect index of protection (I_{effect}) was also put forward to investigate the effect of cathodic or anodic protection in high-pH solution using the following equation:
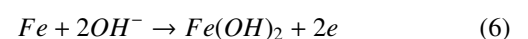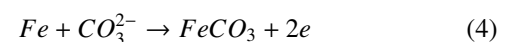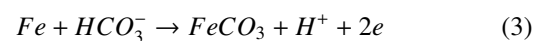
$$I_{effect} = (1 - \frac{I_{protection}}{I_{corr}}) \times 100\% \qquad (2)$$

where $I_{protection}$ is the test parameters with additional cathodic or anodic potential in high-pH solution.

3. Results and analysis

3.1. Electrochemical tests

Fig. 2 showed potentiodynamic polarization curve of X80 in 0.5M Na_2CO_3-1M $NaHCO_3$ solution. It is shown that the corrosion potential is about -0.84V, indicating that the applied cathodic protection potential should be smaller than -0.84V, -0.9V is ok for instance. When the potential increased to -0.67V, the current density began to drop, which can be called passive phenomenon. This may be due to the production by corrosion products, $FeCO_3$ and $Fe(OH)_2$ [3,16], as follows:
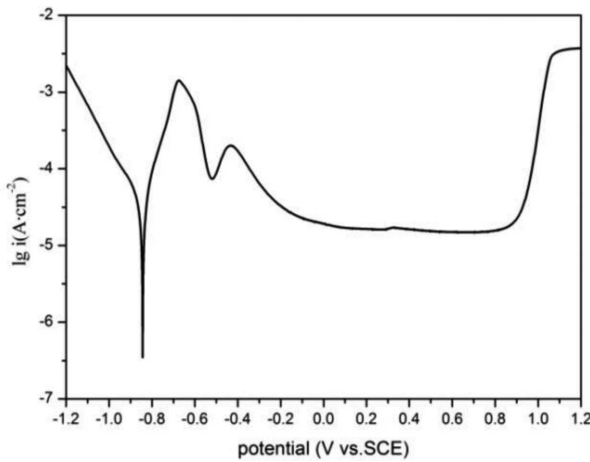
$$Fe + HCO_3^- \rightarrow FeCO_3 + H^+ + 2e \qquad (3)$$

$$Fe + CO_3^{2-} \rightarrow FeCO_3 + 2e \qquad (4)$$

$$Fe(OH)_2 + HCO_3^- \rightarrow FeCO_3 + H_2O + OH^- \qquad (5)$$

$$Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e \qquad (6)$$

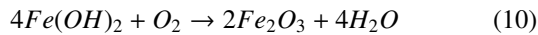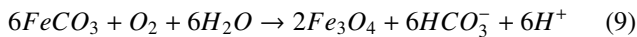Fig. 2. The potentiodynamic polarization curve of X80 in 0.5M Na$_2$CO$_3$-1M NaHCO$_3$ solution

Fig. 3. Curves of SSRT tests of X80 in air and in high-pH with or without cathodic protection

Moreover, the current density began to increase again when the potential increased to about -0.51V which may be induced by the dissolution of Fe(OH)$_2$ in HCO$_3^-$, as follows:

$$4Fe(OH)_2 + HCO_3^- \rightarrow CO_3^{2-} + OH^- + Fe^{2+} + H_2O \quad (7)$$
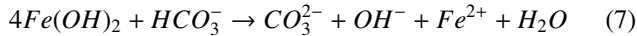
In addition, the second anodic peak is observed at -0.43 V vs. SCE. This phenomenon can be called "re-passive phenomenon", which is due to oxidation of FeCO$_3$ and Fe(OH)$_2$ to Fe$_2$O$_3$ and Fe$_3$O$_4$ by O$_2$ [3,16]:

$$4FeCO_3 + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 4HCO_3^- + 4H^+ \quad (8)$$

$$6FeCO_3 + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 6HCO_3^- + 6H^+ \quad (9)$$

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 + 4H_2O \quad (10)$$
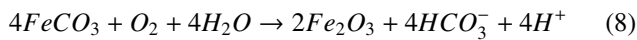
When the potential increased to about 0V, the current density began to keep stable until about 0.9V which can be called "stable passivity region". The appearance of stable passivity region provides possibility of anodic protection. The anodic protection potential can be chosen from this region. In this study, four anodic protection potentials of 0V, 0.25V, 0.5V and 0.75V were chosen to be applied as the anodic protection potential.

3.2. SCC analysis

3.2.1. Cathodic protection

Fig. 3 shows the results of SSRT tests of X80 pipeline steel in air and in high-pH with or without cathodic protection of -0.9V. The main values of yielding strength, tensile strength, elongation and protection effect index I$_{protection}$ were shown in Table 1. It is shown that samples in solution exhibits lower yielding strength, tensile strength, and elongation in high-pH solution than that of in the air, and there is an obvious yielding zone from about 1.2% to 1.9%. The SCC sensibility of X80 in high-pH solution is about 5.66% (I$_A$), 27.09%(I$_{\sigma b}$) and 19.64%Ł·I$_{\sigma s}$Ł$_{\sigma s}$, showing that much attention should be paid to the SCC failure of X80 in high-pH solution. Compared to the elongation loss, the yielding strength and tensile strength loss are much higher indicating that the ability to resist deformation is much lower in high-pH solution than in the air.
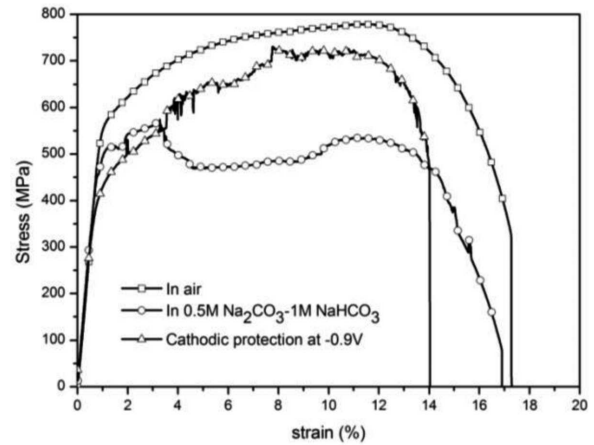
TABLE 1

The specific values of SSRT tests results. Applied potential means the cathodic or anodic protection potential. A, σ_b and σ_s are elongation, tensile strength and yielding strength. I$_{protection}$ is cathodic and anodic protection index. Sample of No.1 is in the air, No.2 is in the simulated solution without any protection. And others are in the simulated solution with additional protection potential. There are three columns of I$_{protection}$, they are the protection index in elongation, tensile strength and yielding strength respectively

No.	applied potential (V)	A (%)	σ_b (MPa)	σ_s (MPa)	I$_{protection}$		
					A(%)	σ_b(%)	σ_s(%)
1	—	17.29	779	560	—	—	—
2	—	16.91	568	450	—	—	—
3	-0.9	14.03	725	370	-17.03	27.64	-17.78
4	0	16.76	664	510	-0.89	16.90	13.33
5	0.25	17.11	698	510	1.18	22.88	13.33
6	0.5	18.27	765	530	8.04	34.68	17.78
7	0.75	17.70	776	550	4.67	36.62	22.22

Fig. 4 shows the changes of the potential of X80 in high-pH solution with the strain increases in SSRT test. At the start, the potential is -320mV, much higher than the corrosion potential of -840mV, indicating that there is a self-passive phenomenon of X80 in the simulated solution. Moreover it is shown that the change regular of potential is like the stress. In the elastic deformation zone, the potential increase linearly with the strain, from -320mV to -275mV, and this is very different from the results in near-neutral pH solution [17]. It is indicated that the potential of X80 in high-pH solution increases during the deformation process due to the continuous generation of passive film in the sample surface. However, in the plastic deformation process, a mass of pores and cracks may be introduced due to the permanent deformation, and the repeated rupture of passive films is inevitable resulting in the increase rate of potential becomes lower than the elastic deformation process and even there is a decline area.

Cathodic protection can effectively prevent the anodic dissolution in the crack tip, however, the passive film would also be breakdown and permeate hydrogen would be induced at the same time. In the high-pH solution, the possible cathodic

electrochemical reactions taking place on the sample surface with cathodic protection potential are as follows:

$$H_2O \rightarrow H^+ + OH^- \tag{11}$$

$$H^+ + e \rightarrow H \tag{12}$$

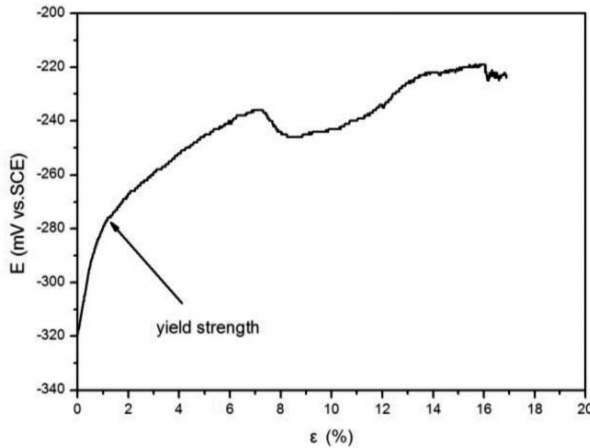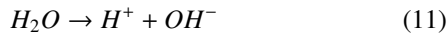$$H + H \rightarrow H_2 \tag{13}$$

Fig. 4. The effect of strain on potential in high-pH solution

The potential of hydrogen reaction can be calculated as follows:

$$E_H = -0.059pH = -554.6mV_{SHE} = -795.6mV_{SCE} \tag{14}$$

Though further drop of ohmic potential would take place due to the electrical reduction of the solution itself, leading a more negative potential during the hydrogen reduction. However, the potential of -900mV is negative enough for hydrogen evolution, hence, the hydrogen atoms will penetrate into the X80 pipeline steel, hence they will be captured in the trapping sites, such as non-metallic inclusions, pores and micro-cracks. In addition, hydrogen embrittlement dominates SCC when the concentration of hydrogen reached a critical value. The results of SSRT with -0.9V cathodic protection prove the analysis. Although the σ_b was elevated to about 725MPa, about 27.64% higher than without protection, however, the σ_s and elongation was descend to 370Mpa and 14.03%, about 17.78% and 17.03% lower than without protection. It is indicated that adding cathodic protection can only improve the tensile strength and enhance the resistance of plastic deformation. The protection effect is restricted so that cathodic protection would not be an effective way to be applied for X80 in high-pH solution.

3.2.2. Anodic protection

The SSRT results with anodic protection were shown in Fig. 5, and the specific values were also shown in Table1. In addition, the relationship between $I_{protection}$ and the applied protection anodic potential were shown in Fig. 6. It is shown that the protection effect is much better than cathodic protection. Both yielding strength and tensile strength increase obviously at four anodic protection potentials, and protection

effect index increases with the applied anodic potential increases indicating that the ability of resist deformation increases. However, the results of elongation are not completely same with yielding strength and tensile strength. Except at 0V (the elongation is little lower than without protection), the $I_{protection}$ of elongation are all positive, indicating that it is better for elongation with anodic protection. At first, the elongation effect index increases with the applied anodic potential, obtaining the maximum value at 0.5V of 18.27%, and then drops a little at 0.75V. It is indicated that 0.5V is the better potential which can be chosen as the anodic protection potential.
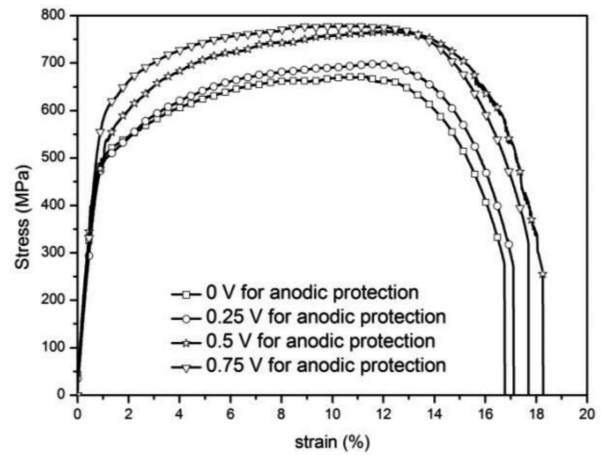

Fig. 5. Effect of anodic protection on curves of slow strain test of X80 pipeline steel
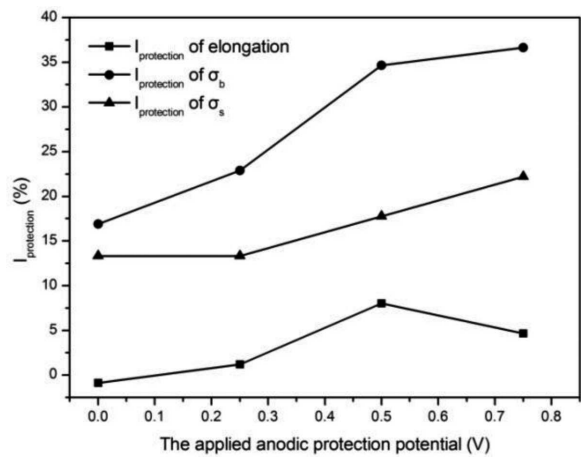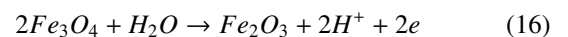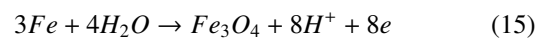

Fig. 6. The relationship between protection effect index and applied protection anodic potential

In stable passivity region, Fe can be oxidized to Fe_3O_4 directly at the sample surface, and then Fe_3O_4 can be further oxidized to Fe_2O_3 – more stable oxide, as follows:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e \tag{15}$$

$$2Fe_3O_4 + H_2O \rightarrow Fe_2O_3 + 2H^+ + 2e \tag{16}$$

The equilibrium potentials of equation Eq. (15) and (16) are -0.459V and -0.219V respectively in the simulated solution, calculated by Nernst equation. It is shown that the four protection potentials are positive enough for Eq. (15) and (16),

indicating that Fe_3O_4 and Fe_2O_3, as main components of passive film, can be formed at the sample surface directly and the ability of re-passivity of passive film at the crack tip after rupture is enhanced compared to without protection. On the other hand, the rapid repairing of passive film prevents the anodic dissolution at the crack tip. What's more, penetrate hydrogen would be less than with cathodic protection and without protection because the hydrogen would move to the counter electrode due to the anodic reaction at the surface of pipeline. Because of these reasons, anodic protection with four anodic protection potentials presents satisfying results.

What's more, the more positive the applied potential is, the bigger driving force of Eq. (15) and (16) is and re-passivity of passive film so that the protection effect of yielding strength and tensile strength increases with the applied potential increases. However, the reason why the elongation with 0.75V protection is smaller than with 0.5V protection remains unclear and need further studies.

4. Conclusion

1. Electrochemical tests show that there's broad passive region of X80 pipeline steel in simulated high-pH solutions.
2. Slow strain tensile tests demonstrate that X80 pipeline steel encounters serious SCC in high-pH solution. It is found that the cathodic protection effect is restricted. However, the elongation, yielding strength and tensile strength all increase with anodic protection.
3. The higher anodic protection potential in the stable passive region is benefit to improve tensile strength and yielding strength. However, the higher elongation is obtained at 0.5V anodic protection potential.

Received: 20 February 2014.

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