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THE INFLUENCE OF OXYGEN ON CORROSION AND TRIBOCORROSION OF LOW CARBON STEEL IN HYDROGEN SULFIDE ENVIRONMENT

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Abstract: *Corrosion, hydrogenation and tribocorrosion of 17Mn1Si pipe steel in a chloride-acetate solution bubbled with H_2S, air and their mixture at the pressure ratio P_{H_2S}: P_{air} = 1:1 were investigated. The ingress of oxygen into the hydrogen sulfide environment causes steel destruction due to a combination of anodic dissolution and hydrogen cracking mechanisms. In the presence of oxygen in the solution, the combined effect of pitting corrosion, hydrogen cracking, iron oxides and hydroxides in the corrosion products determines the abrasive nature of friction. The effect of elemental sulfur on the friction process was not detected.*

Keywords: *oxygen, hydrogen sulfide, corrosion, tribocorrosion, steel, chloride-acetate solution.*

1. INTRODUCTION

Natural gas from gas condensate fields, as a rule, contains impurities of hydrogen sulfide and moisture. A solution of H_2S in water exhibits corrosive activity. It intensifies corrosion and hydrogenation of steels, what accelerates their corrosion-mechanical destruction. These processes are significantly affected by sulfide-containing films formed on the surface of the corroding metal. Depending on the chemical composition and density, sulfides can localize corrosion, reduce hydrogen overvoltage, and also increase hydrogen absorption and embrittlement of steels.

Oxygen can enter the transported environment during repair work, due to poor deaeration, poor-quality seals, etc. Oxygen contamination of environments containing H_2S can sharply (up to two orders of magnitude) increase the corrosion rate of steels [1–5]. Oxygen significantly complicates corrosion processes, activating them as a depolarizer, it can react with H_2S and sulfide-containing corrosion products, changing its action. As a result of the reactions, oxides, sulfides, elemental sulfur and trivalent iron are formed, which also have an ambiguous effect on corrosion. Oxygen can also reduce the release of hydrogen and hydrogenation of the metal. Corrosion processes are very sensitive to changes in temperature, the ratio of partial pressures of H_2S and O_2. In the presence of oxygen, friction and wear processes in H_2S environments are complicated.

To date, corrosion and tribocorrosion processes on steels in hydrogen sulfide environments in the presence of oxygen have not been studied sufficiently [1–7]. The electrochemical features of

steel corrosion in environments containing different concentrations of O_2 and H_2S, the influence of corrosion products containing both oxides and sulfides on hydrogenation, embrittlement and tribocorrosion of steels have been poorly studied. Therefore, it is important to investigate the resistance of pipe steels to corrosion and tribocorrosion in environments with the presence of oxygen and hydrogen sulfide in relation to the nature of corrosion, the composition of their products and hydrogenation.

2. EXPERIMENTAL PROCEDURE

Ferritic-pearlite steel 17Mn1Si was studied (mass. %: 0.17 C; 0.47 Si; 1.4 Mn; <0.3 Cr; 0.3 Ni; <0.3 Cu, Fe – the rest). The electrochemical characteristics of corrosion processes were studied in a 5% NaCl+0.5% CH_3COOH solution, bubbled with H_2S, air and their mixture at a ratio of partial pressures P_{H_2S}: P_{air} = 0:1; 1:1; 1:0. The tests were carried out in a standard cell using a PI-2MK-10A potentiostat. The reference electrode was silver chloride type EVL-1M1, the auxiliary electrode was platinum. The hydrogen concentration in the samples was determined by a LECO DH 603 analyser.

Tribocorrosion tests were performed in the same solution, bubbled with H_2S and air at a ratio of partial pressures P_{H_2S}: P_{air} = 1:1; 1:0. Friction scheme "ball-plane". Load 10 N, counter body Al_2O_3 ball Ø9 mm, duration of the test 1200 s. The tests were performed in freshly prepared solutions and in solutions after samples were aged for 300 and 720 h. The duration of tribocorrosion test was 1200 s. The change in the friction coefficient during reciprocating motion was determined using specially developed software. The width of the friction track was determined using a scanning electron microscope EVO-40XVP. An optical microscope METAM PB-2 was used for metallographic studies.

3. RESULTS AND THEIR DISCUSSION

Based on the polarization curves, in a hydrogen sulfide-saturated solution, the corrosion potential of steel is measured at -0.643 V, and the corresponding corrosion rate is 3.26 mm/year. For the ratio P_{H_2S}: P_{air} = 1:1, the change in the corrosion potential is insignificant, and the corrosion rate decreases by ~30%. Corrosion of steel in the presence of hydrogen sulfide is controlled by cathodic processes. Dissolved oxygen interacts with hydrogen sulfide:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O, \quad (1)$$

therefore, the concentration of H_2S and O_2 in the solution decreases and corrosion slows down. In a solution bubbled with air, the corrosion rate increases to 3.25 mm/year (Fig. 1, table), the corrosion potential shifts to the anodic region to -0.593 V. Corrosion is controlled by anodic processes.

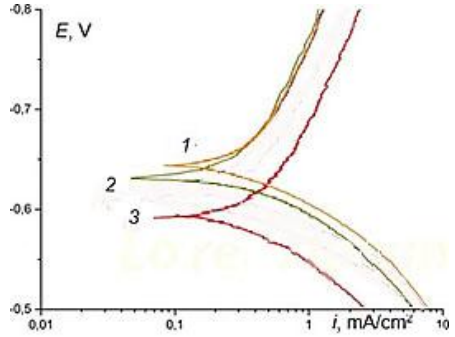

Figure 1. Polarization curves of 17Mn1Si steel in a solution of 5%NaCl+0.5%CH_3COOH, bubbled with hydrogen sulfide and air at the ratio of partial pressures P_{H_2S}: P_{air}: 1 – 1:0; 2 –1:1; 3 – 0:1.

Table 1. Corrosion currents and potentials of 17Mn1Si steel in a solution with H_2S and air

P_{H_2S}: P_{air}	E_{corr} [V]	i_{corr} [mA/cm^2]
0:1	-0,593	0,281
1:1	-0,635	0,182
1:0	-0,643	0,282

During long-term tests (720 h) in a hydrogen sulfide-saturated solution, corrosion slows down during the first ~ 70 h, and increases after ~ 300 h, reaching 4.8 mm/year in the test end (Fig. 2a, curve 1).

The decrease in the corrosion rate is associated with the formation of a dense surface film of mackinawite $Fe_{(x+1)}S_x$. Over time, mackinawite

transforms into porous troilite, which does not protect from corrosion.

At the ratio P_{H_2S}: P_{air} =1:1, the corrosion rate decreases to 1.3 mm/year within 200 h, and increases after ~450 h. The slowdown in corrosion is associated with a decrease in the concentration of H_2S and O_2 in the solution (reaction (1)).

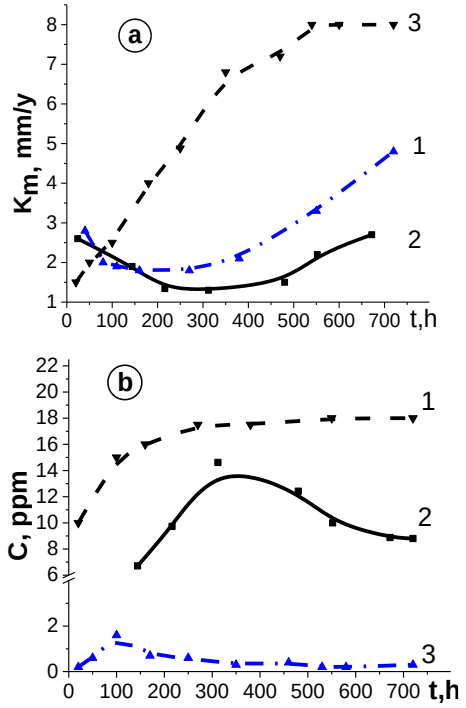

Figure 2. The corrosion rate (a) and the concentration of absorbed hydrogen (b) in 17Mn1Si steel after exposure in a chloride-acetate solution at the ratio P_{H_2S}: P_{air}=1:0 (1), 1:1 (2), 0:1 (3).

The oxidation and transformation of the sulfide film impair its protective effect. After 720 h corrosion rate is half as low as in a hydrogen sulfide-saturated solution. In a solution bubbled with air, the corrosion rate increases almost linearly with time, reaching 8 mm/year after 550 h (see Fig. 2a). Corrosion occurs with the formation of iron oxides and hydroxides.

Corrosion of steel in the presence of hydrogen sulfide-contained solution is accompanied by hydrogenation. In a saturated solution, the maximum concentration hydrogen is ~18 ppm (Fig. 2b). At the ratio P_{H_2S}: P_{air} =1:1, the concentration of absorbed hydrogen reaches a maximum after ~300 h (~14 ppm), and decreases overtime to ~8 ppm. Hydrogen absorption is not observed in solution without H_2S.

Hydrogen penetration into the metal is facilitated by the action of specific adsorbates (H_2S, HS^-). These compounds react with oxygen with the formation of sulphur and sulphate and hydrogen absorption slows down.

Blisters, ulcers and cracks were detected on the steel surface after exposure in a hydrogen sulfide-saturated solution (Fig. 3a). Sharp ulcers appear on the steel surface after exposure in a solution with P_{H_2S}: P_{air} =1:1. Cracks extending into the metal are visible at the base of the ulcers (Fig. 3b). In a solution bubbled with air, corrosion proceeds with the formation of iron oxides and hydroxides, without ulcers and cracks.

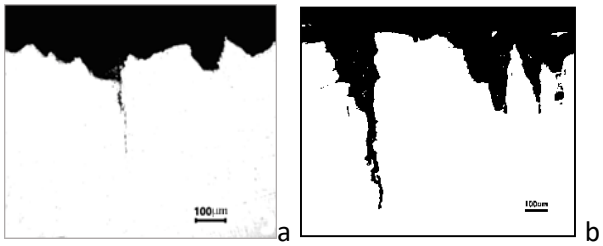

Figure 3. Cross-section of 17Mn1Si steel after corrosion in a chloride-acetate solution at the ratio P_{H_2S}: P_{air}=1:0 (a), 1:1 (b)

Tribocorrosion of 17Mn1Si steel in a chloride-acetate solution at the ratios P_{H_2S}: P_{air}=1:0 and 1:1 was studied. In a freshly prepared hydrogen sulfide-saturated solution, the friction coefficient does not exceed 0.1, the friction track width is 270 μm. After exposure of steel in the environment for 10 and 30 days, the friction coefficient increases by 4 and 4.5 times (Fig.4), the track width - by 2.5 and 5 times. At the beginning of the exposure, corrosion damage of the surface is insignificant, the mackinawite surface film is formed. Multilayer flake-shaped crystals of mackinawite can act as a solid lubricant in the friction zone, and improve the wear resistance of steel. Over time, mackinawite transforms into porous troilite, and pitting corrosion accelerates. The hard needle-shaped crystals of troilite in the friction zone can play the role of an additional abrasive and deteriorate the wear resistance of steel [8].

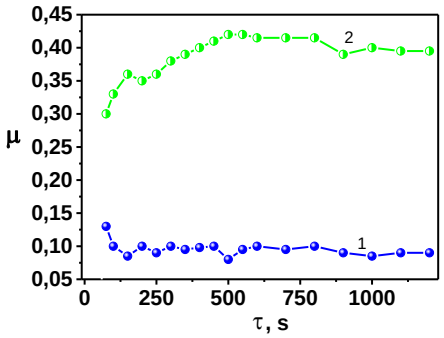

Figure 4. The coefficient of friction at the beginning (1) and after 10 days (2) of exposure of 17Mn1Si steel in solution of 5% NaCl + 0.5% CH_3COOH, saturated by H_2S

In a freshly prepared solution containing a mixture of hydrogen sulfide and air at P_{H_2S}: P_{air}=1:1, the friction coefficient increases in a jump-like manner from 0.1 to 0.2. It indicates the presence of ulcers and abrasive on the friction surface. During friction, the electrode potential shifts to the cathodic region. After corrosion of steel in the environment for 300 and 720 h, the friction coefficient is more stable, but increase to 0.27 and 0.37, respectively, the electrode potential of the friction surface decreases by ~30 and ~50 mV, the width of the friction track increases from 250 μm by 1.7 and 3.4 times, respectively.

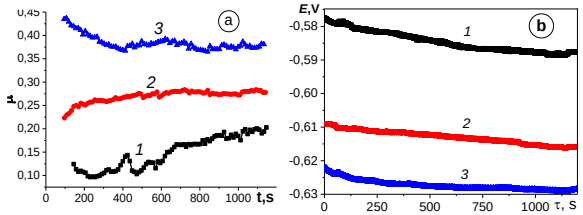

Figure 5. Change in friction coefficients (a) and electrode potential (b) at the friction of 17Mn1Si steel in a chloride-acetate solution at a ratio of P_{H_2S}: P_{air}=1:1. Exposure time of steel in the solution before friction: 1 – 0; 2 – 360 h; 3 – 720 h

After 300 h of corrosion tests, the steel surface is covered with a dense layer of corrosion products containing ~17.0 mass. % O, 52.6 mass. % Fe, 0.18 mass. % S, which indicates the predominant formation of oxide rather than sulfide phases. Numerous ulcers and grooves as the result of abrasive wear are detected on the friction track. After 720 h of corrosion tests the number and size of ulcers significantly increase. The width of the friction track doubles.

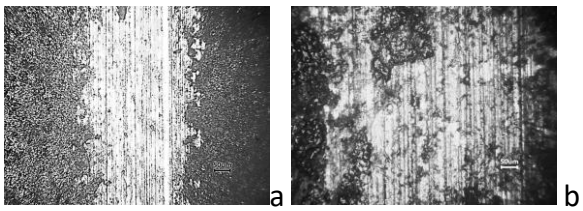

Figure 6. Friction surface of 17Mn1Si steel after exposure in a chloride-acetate solution at a ratio of P_{H_2S}: P_{air}=1:1. Exposure time: 300 (a); 720 h (b)

The ingress of oxygen into the hydrogen sulfide environment causes steel destruction due to a combination of anodic dissolution and hydrogen cracking mechanisms. The effect of elemental sulfur on the friction process has not been detected. The combined effect of pitting corrosion, hydrogen cracking, iron oxides and hydroxides in the corrosion products determines the abrasive mechanism of tribocorrosion.

4. CONCLUSION

Corrosion, hydrogenation and tribocorrosion of 17Mn1Si pipe steel in a chloride-acetate solution bubbled with hydrogen sulfide , air and their mixture at the pressure ratio P_{H_2S}: P_{air}=1:1 were investigated.

1. In the short-term test, the corrosion rate of steel in the solution at the pressure ratio P_{H_2S}: P_{air} =1:1 slows down due to the interaction between H_2S and O_2, as well as the reduction in the concentration of both components in the solution.

2. In the long-term corrosion test, pitting corrosion and hydrogen-initiated cracking were detected on the steel surface. The ingress of oxygen into the hydrogen sulfide environment causes steel destruction due to a combination of anodic dissolution and hydrogen cracking mechanisms.

3. At the beginning of the tribo-corrosion tests of steel in a H_2S-saturated solution, the flake-shaped mackinawite acts as a solid lubricant, and decrease the wear. Over time, mackinawite transforms into hard needle-shaped troilite, and wear increases by 4-5 times.

4. In the presence of oxygen in the solution, the combined effect of pitting corrosion, hydrogen cracking, iron oxides and hydroxides

in the corrosion products determines the abrasive nature of friction. The effect of elemental sulfur on the friction process was not detected.

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