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EFFECT OF HYDROGEN SULFIDE ON CORROSION AND TRIBOCORROSION OF STEEL 07Cr16Ni6

M.S. Khoma, V.A. Vynar, N.B. Ratska, Ch.B.Vasyliv [1], V.R.Ivashkiv, B.M. Datsko, M.R.Chuchman, S.Halaichak
Karpenko Physico-Mechanical institute, National Academy of Ukraine, Ukraine

Abstract: the influence of hydrogen sulfide concentration (0…1500 mg/dm^3) in chloride-acetate solution on corrosion processes, hydrogenation and corrosion-mechanical wear of 07Cr16Ni6 steel has been studied. Hydrogen sulfide in solution, regardless of concentration, significantly reduces the corrosion resistance of steel. The wear resistance of steel in solution at hydrogen sulfide concentrations 100…500 mg/dm^3 do not change significantly, and it decreases by ~30% at the concentrations 1000…1500 mg/dm^3. It is associated with hydrogenation of friction surface.

Keywords: *steel 07Cr16Ni6, corrosion, hydrogenation, tribocorrosion, chloride-acetate solution, hydrogen sulfide, concentration.*

1. INTRODUCTION The reliability and durability of equipment in the oil and gas industries significantly depends on its resistance to corrosion and mechanical damage caused by hydrogen sulfide. Hydrogen sulfide accelerates continuous and ulcerative corrosion, and causes cracking of steels [1-4]. Such corrosion-mechanical destruction of steels is one of the most dangerous in the oil and gas industries. Much attention is paid to study mechanisms of hydrogen sulfide corrosion of steels, corrosion products morphology and their influence on the corrosion rate and hydrogen penetration. The corrosion and mechanical failure ability of steels depends on many factors: the hydrogen sulfide partial pressure, pH, temperature, chemical composition and structure of steels and corrosion products, mechanical stresses [5-7]. The efficiency of oil and gas equipment is increased comprehensively, in particular, using various technological methods, coatings, corrosion inhibitors, etc. [4,5]. However, these approaches do not always ensure reliable and efficient operation of friction units. Therefore, it is necessary to comprehensively assess and study the patterns of influence of hydrogen sulfide on the tribological properties of steels, which is important to increase the life of oil and gas refining units. The tribocorrosion of friction elements is determined by physicochemical and mechanical processes on the surface [6]. Friction changes the sensitivity of the material to corrosion, and corrosion alters the conditions of friction, and this interaction depends on surface processes during frictional contact. Corrosion of friction surfaces in aggressive hydrogen sulfide-containing environments is accompanied by formation of sulfide films of different stoichiometric composition and hydrogenation. It significantly affects the nature of wear and the durability of friction elements. Therefore, it is necessary to study the relationship between corrosion processes in the frictional contact and mechanical factors that cause surface destruction of materials [7-10]. Corrosion, hydrogenation and corrosion cracking of steels in hydrogen sulfide-containing environments have been studied in great detail, but the results of their tribocorrosion are limited.

The influence of hydrogen sulfide concentration in chloride-acetate solution on the corrosion resistance, hydrogenation and tribological properties of 07Cr16Ni6 steel was investigated.

2. EXPERIMENTAL Steel 07Cr16Ni6 (% mass: 0.07 C; 5.3 Ni; 0.38 Ti; 17 Cr; <0.8 Si and Mn; <0.02 S; 0.035 P, the rest - Fe) samples were tested in a standard NACE solution (mass %: 5% NaCl +

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[1] Author for contacts: Chrystyna Vasyliv
E–mail: chrystyna.vasyliv@gmail.com

0.5% CH_3COOH (pH = 2.7)) with a concentration of H_2S: 0; 100; 500; 1000; 1500 mg/dm^3. The solutions were purged with gas mixture of hydrogen sulfide and argon of appropriate concentrations for 2 h. H_2S was obtained by hydrolysis of aluminum sulfide, which guaranteed its purity. The concentration of H_2S up to 50 mg/dm^3 in the solution was determined by photocolorimetric method using N, N-dimethyl-p-phenylenediamine; and iodometric method was used at higher concentrations of H_2S.

PI-2MK-10A potentiostat, silver chloride reference electrode and auxiliary platinum electrode were used. Tafel coefficients were determined by graph analytical method. The mass index of corrosion rate K_m was calculated according to the formula: $K_m = K_i \cdot k_e$, where, g/(m^2·h); K_i - electrochemical corrosion index, A/m^2; $k_e = M/(z \cdot F)$ - electrochemical equivalent of the metal, g/(A h); M is the atomic mass of the metal, g; z is the number of electrons involved in the redox reaction; F – Faraday constant, A·h. The corrosion rate was determined gravimetrically after long-term exposure of the samples in the environment.

A hydrogen concentration in steels was determined by the vacuum extraction method. Samples were heated in vacuum and a volume of released hydrogen was fixed at 200 ºC (C_{H200}) and 800 ºC (C_{H800}). The total volume of absorbed hydrogen was determined as $C_\Sigma = C_{H200} + C_{H800}$.

A scanning electron microscope EVO 40XVP with a system of micro X-ray spectral analysis on the energy-dispersive spectrometer INCA ENERGY 350 was used for metallographic investigation of the surface layers.

Tribocorrosion tests in hydrogen sulfide solution were performed in an electrochemical cell. The sample (10×50×2 mm) was installed on the frame, the electrochemical cell was fixed by pressing it to the rubber seal. Load on the counterbody (ball Ø9 mm with Al_2O_3) was 10 N. Material loss was determined by the width of the friction track. The change in the coefficient of friction was recorded by strain gauges glued to the rod and connected to a computer via an analog-digital device. During the reciprocating movement, the values of the coefficient of friction in different directions were recorded and its average value $(\mu + |-\mu|) / 2$ was calculated.

3. RESULTS AND DISCUSSION The electrochemical parameters of steel 07Cr16Ni6 in chloride-acetate solution with hydrogen sulfide were analyzed. Steel 07Cr16Ni6 is passivated in a solution without hydrogen sulfide, (Fig. 1, curve 1). The current of complete passivation is equal to 0.012 mg/dm^3 at the corrosion potential. The corrosion rate is determined by cathodic processes, which proceed more slowly (Fig. 1, table 1).

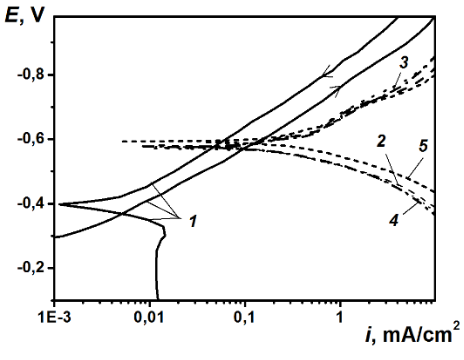
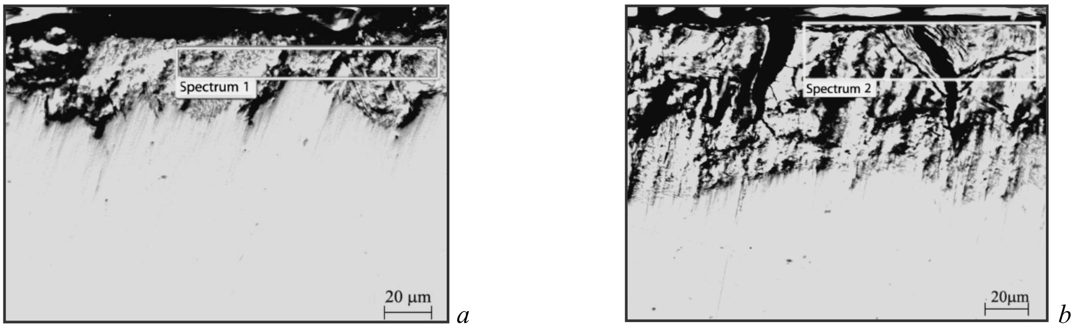


Figure 1. Polarization curves of steel 07Cr16Ni6 in 5% NaCl + 0.5% CH_3COOH solution at 20 °C, scan rate 1 mV/s and different concentrations of hydrogen sulfide, mg/dm^3: *1* – 0, *2* – 100, *3* – 500, *4* – 1000, *5* – 1500.

Table 1. Electrochemical parameters of steel 07Cr16Ni6 corrosion in a solution of 5% NaCl + 0,5% CH_3COOH with various concentration of hydrogen sulfide

Concentration H_2S, mg/dm^3	E_{corr}, V	I_{corr}, mA/cm^2
0	-0.21	0.012
100	-0.57	0.182
500	-0.55	0.170
1000	-0.56	0.182
1500	-0.57	0.178

The corrosion potentials of steel shift in the cathode region from -0.21 to -0.55… -0.57 V, and corrosion currents increase from 0.012 to 0.170…0.182 mA/cm^2, when the concentration of H_2S in a solution changes from 100 to 1500 mg/dm^3. Corrosion occurs under cathodic control. The steel is not passivated, porous black corrosion products are formed on the surface, which can contain sulfides of different chemical composition (Fig.2). Maquinavit $Fe_{1+x}S$ is firstly formed during corrosion under such conditions. It is further transformed into sulfides with a higher sulfur content with deteriorated protective properties [13, 14]. The film thickness increases from 40 ... 55 to 70 ... 80 when the concentration of hydrogen sulfide in a solution increases from 100 to 1500 mg/dm^3. The cracking of sulfide layer is observed at a concentration of H_2S 1500 mg/ dm^3 (Fig.2, b) [15].



a *b*

Element	Spectrum 1		Spectrum 2	
	mass.%	at.%	mass.%	at.%
O K	12.31	36.43	24.25	47.77
S K	2.03	2.66	18.38	18.44
Cr K	17.80	14.37	4.12	2.55
Fe K	60.26	45.27	36.87	21.25
Ni K	7.60	5.43	16.38	8.98
Total	100.00	100.00	100.00	100.00

c

Figure 2. Metallography of the near-surface layer of 07Cr16Ni6 steel after tests in a solution of 5% NaCl + 0,5% CH_3COOH with a concentration of hydrogen sulfide, mg/dm^3: *a* –100, *b* –1500 (σ = 0 MPa, τ = 720 h) and their typical composition (*c*).

The formation of iron sulfides is accompanied by the release of hydrogen [11]. Steel 07X16H6 absorbs 4.2, 8.0 and 17.5 ppm of hydrogen after 720 h corrosion in chloride-acetate solution at C_{H2S} = 100, 500, and 1500 mg / dm^3 (Fig.3). Mostly it is diffusion-active hydrogen (C_{200} = 62… 70%), contained in traps with low activation energy. At C_{H2S} = 1500 mg/dm^3, hydrogenation increases significantly. Defects of the corrosion layer can be a "reservoir" for hydrogen.

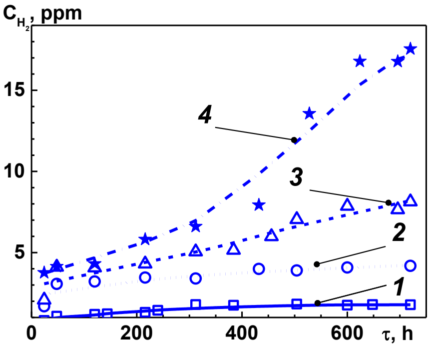
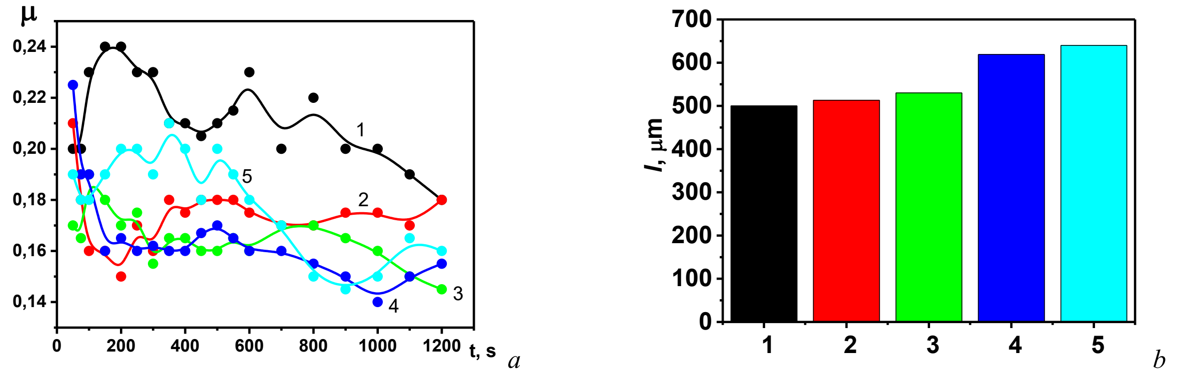


Figure 3. Hydrogen desorption of steel 07Cr16Ni6 in a solution of 5% NaCl + 0.5% CH_3COOH + H_2S. Concentration of hydrogen sulfide (mg/dm^3): 1 – 0; *2* ~100; *3*– ~500; *4* – ~1500.

The tribological characteristics of 07Cr16Ni6 steel in a solution of 5% NaCl + 0.5% CH_3COOH without hydrogen sulfide and with its different concentrations were studied. The coefficient of friction gradually decreases from 0.24 to 0.19 in a solution without hydrogen sulfide (Fig. 4a). The coefficients of friction reduce by 10-15% with increasing of H_2S concentration from 100 to 500 mg/dm^3. There is a decrease in the oscillations of the friction coefficient, a slight difference between its average values too. The values and oscillations of the friction coefficient increase at the H_2S concentration >1000 mg/dm^3. The secondary structures on the surface change and depend on the hydrogen sulfide concentration in the environment. The width of the friction track almost does not increase at concentrations of hydrogen sulfide 100…500 mg/dm^3, compared to the solution without hydrogen sulfide, and at higher concentrations increases by 30% (Fig. 4b).



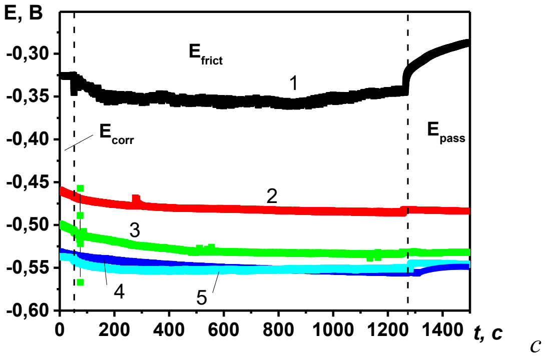


Figure 4. Tribological characteristics of steel 07Cr16Ni6 in the solution of 5% NaCl + 0.5% CH_3COOH without hydrogen sulfide (*1*), with a concentration of hydrogen sulfide: 100 (*2*), 500 (*3*), 1000 (4) and 1500 mg/dm^3 (*5*).
a - friction coefficient; *b* - width of the wear track; *c* - change of electrode potential during the friction.

The electrode potentials of steel surface shift to the cathode region at the beginning of friction and return to the anode section by 0.06 V after unloading the contact pair. The electrode potentials during stable friction depends on hydrogen sulfide concentration. The potentials are maximal in solution without H_2S (-0.350 V) and shift to the cathode region from -0.470 V at 100 mg/dm^3 H_2S to -0.550 V at 1500 mg/dm^3 (Fig.4, c). It is associated with passivation processes in the friction-activated areas. This indicates the intensification of anodic reactions, which probably take place at maximum anodic oxidation currents and are controlled by diffusion processes.

The plastic deformation and local areas of oxides were observed on the track surfaces after friction in the chloride-acetate solution without hydrogen sulfide. It indicates the heterogeneity of the surface films (Fig. 5a). Accelerated oxidation of the surface during friction contributes to a slight chipping of the grains. Wear of steel under these conditions occurs by a mixed mechanism - tribochemical (oxidative) and abrasive [12, 13].

There is a plastic deformation of the friction surface and uniform wear of steel after the friction in the environment with hydrogen sulfide. Small ulcers were found on the friction track at a concentration of hydrogen sulfide of 1500 mg/dm^3, probably due to hydrogenation of the surface layer, but no traces of brittle fracture were recorded (Fig. 5b).

Therefore, the corrosion and wear resistance of steel 07X16H6 gradually decreases when hydrogen sulfide concentration increases in chloride-acetate environment. The tribochemical mechanism of wear is definitely influenced by corrosion processes and hydrogenation of steel. The wear of the steel is insignificant at the hydrogen sulfide concentration in the solution of 100 and 500 mg/dm^3. It can be explained by the greater homogeneity of the oxide-sulfide films. The effect of hydrogen is most noticeable in a corrosive environment with a hydrogen sulfide content of 1000 and 1500 mg/dm^3. The wear resistance of steel decreases at the hydrogen sulfide concentration > 1000 mg/dm^3.

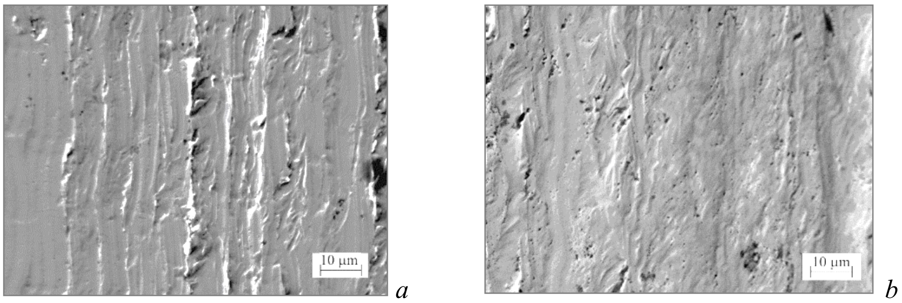


Figure 5. Microstructure of the friction surface of steel 07Cr16Ni6 in chloride-acetate solution without hydrogen sulfide (a) and with a hydrogen sulfide concentration of 1500 mg/dm^3 (*b c*).

This explains the increase in the oscillations of the coefficient of friction, and a significant increase in wear compared to environment with a lower concentration of hydrogen sulfide. In addition, the oxide-sulfide films are intensively restored and partially cover single ulcers during the frictional interaction. When homogeneity of surface films decreases due to the formation of sulfides with larger number of defects, the tribocorrosion resistance of steel deteriorates [2].

CONCLUSIONS

07Cr16Ni6 steel is passivated in a chloride-acetate solution without hydrogen sulfide. Surface of steel is in an electrochemically active state and the corrosion resistance of steel is 10…30% lower in solutions with hydrogen sulfide. Corrosion products with oxide-sulfide compounds are formed on the steel surface. The corrosion film thickness increases from 40 ... 55 to 70 ... 80 when the concentration of hydrogen sulfide in a solution increase from 100 to 1500 mg/dm^3. The cracking of upper sulfide layer is observed at a concentration of H_2S 1500 mg/dm^3. Steel absorbs, respectively, 4.2; 8.0 and 17.5 ppm of hydrogen in the environment at a hydrogen sulfide concentration of 100; 500 and 1500 mg/dm^3. 75...85% of hydrogen is diffusional mobile.

It was established, that uniform corrosion-mechanical wear without significant local damage dominates as a result of corrosion-mechanical wear of steel in a solution of 3% NaCl + 0.5% CH_3COOH with different content of hydrogen sulfide. The adhesive-cohesive interaction between secondary structures and surface layers is weakened in the presence of hydrogen sulfide, which is illustrated by a decrease in the coefficient of friction. The change in electrode potentials during tribocorrosion indicates, that the processes of formation and destruction of secondary structures are more intensive in the chloride acetate solution compared to the one containing hydrogen sulfide.

Tribocorrosion processes reduce the wear resistance of 07Cr16Ni6 steel due to the activation of corrosion by an acidic solution by ~40%. The wear resistance of steel in solution at hydrogen sulfide concentrations 100…500 mg/dm^3 do not change significantly, and it decreases by ~30% at the concentrations 1000…1500 mg/dm^3. It is associated with hydrogenation of friction surface.

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