with 34% nickel, possibly owing to the higher chromium content of this steel. In alloys 20Cr—25Ni and 22Cr—34Ni, in a number of cases crevice corrosion is accompanied by intercrystalline corrosion. The latter is observed in all the compositions with 72% nickel.

CONCLUSIONS

1. The authors have investigated the mechanical corrosion strength of steels 07Kh18N10T, 04Kh20N25T, 02Kh22N34T, and 03Kh17N72T in relation to the content of Group V elements — arsenic, antimony, and bismuth.

2. At stresses greater than the yield stress, the stress corrosion cracking resistance of alloys of type 07Kh18N10T and 03Kh17N72T is practically independent of the content of these elements and is determined by corrosion behavior of the host metal.

3. It has been shown that an adverse influence is exerted on the CC resistance of steels 04Kh20N25T and 02Kh22N34T by arsenic at a concentration greater than 0.02% and by antimony at a concentration of 0.1%.

4. Within the concentration range 0.00002-0.001%, bismuth does not have an adverse influence on the mechanical corrosion strength of these steels and alloys.

5. Limitation of the arsenic and antimony contents to 0.002% and 0.001%, respectively, makes alloy 20Cr—25Ni resistant to stress corrosion cracking in chloride-containing media.

6. Regardless of the content of As, Bi, and Sb, alloy 03Kh17N72T exhibits a tendency to pitting formation, crevice corrosion, and intercrystalline corrosion in a current of high-parameter water containing 100 mg/kg Cl^- and 0.2 mg/kg O_2 at 320°C and 150 atm.

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MECHANISM OF THE EFFECT OF HYDROGEN SULFIDE AND INHIBITORS ON IRON CORROSION IN ACID SOLUTIONS

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Stimulation of iron corrosion by hydrogen sulfide is due to catalyzing of the cathodic and anodic reactions. Being anionic bridges, the adsorbed HS^- ions promote adsorption of cation-type inhibitors. The latter, by blocking the catalysts and creating a positive adsorption ψ_1 potential, retard the electrochemical reactions. Organic compounds with negative groups (alcohols, acids, sulfo acids, etc.) are weakly adsorbed in the presence of hydrogen sulfide and create a negative ψ_1 potential, leading to stimulation of iron corrosion.

It is known that hydrogen sulfide is a strong stimulator of corrosion of iron and steel, particularly in acid solutions in which iron oxides and sulfides are soluble.

It will be seen from the polarization curves of zone-melted cast iron in 1 N H_2SO_4 [1, 2] (Fig. 1) that hydrogen sulfide accelerates both the anodic and cathodic reactions, the anodic reaction being more strongly stimulated, with a negative shift of the steady potential.

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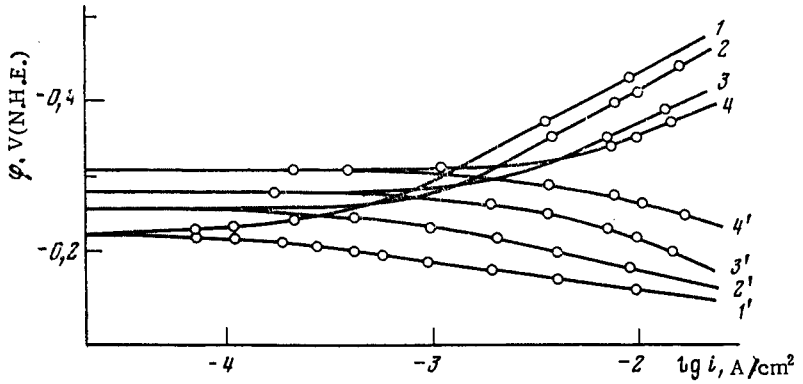

Fig. 1. Polarization curves of pure zone-melted cast iron in 1 N H_2SO_4 without addition (1, 1') and with addition of Na_2S (M): 2, 2') 10^{-6}; 3, 3') 10^{-4}; 4, 4') 10^{-2}.

The acceleration of the anodic reaction by hydrogen sulfide, similar to the known influence of pH, may be due to occurrence of a catalytic process on the iron surface [3, 4]:

$$H_2S+H_2O=H_3O^++HS^- \quad (1)$$

$$Fe+HS^-=Fe(HS^-)_a \quad (2)$$

$$Fe+H_2S+H_2O=Fe(HS^-)_a+H_3O^+ \quad (3)$$

$$Fe(HS^-)_a \rightarrow Fe(HS)_a+e \quad (4)$$

$$Fe(HS)_a \rightarrow FeHS^++e \quad (5)$$

$$FeHS^+\cdot H_3O^+ \rightarrow Fe^{2+}+H_2S+\dot{H}_2O\,* \quad (6)$$

In stages (2) and (3), HS^- is adsorbed on iron and a surface catalyst $Fe(HS^-)_a$ is formed and then oxidized to $FeHS^+$ cations in subsequent electrochemical reactions (4) and (5); with H^+ ions the $FeHS^+$ cations give Fe^{2+} and H_2S (6).†

Calculating the concentration of the catalyst $Fe(HS^-)_a$ from the equilibrium equation for quasireversible reaction (3), we obtain:

$$i=k[H_2S]/[H_3O^+]\exp[2\beta(\varphi-\psi_1)]F/RT; \quad (7)$$

$$\varphi=a+\psi_1+RT/2\beta F\{\ln[H_3O^+]-\ln[H_2S]+\ln i\}, \quad (8)$$

where ψ_1 is the potential arising during adsorption of ions or dipole molecules, and β is a constant. As follows from (7) and (8), with a positive sign of the ψ_1 potential the anodic reaction is retarded. From Eq. (8) it follows that when $\psi_1 = 0$, $\beta = 0.75$, $(\partial\varphi/\partial \log i)_{pH,H_2S} = 39$ mV, $(\partial\varphi/\partial pH)_{H_2S,i}$ and $(\partial\varphi/\partial \log [H_2S])_{pH,i} = -39$ mV. The experimental values of these derivatives are 35-40, −40, and −(35-25) mV, respectively, depending on the acid concentration. The latter value is less than the theoretical one, probably due to the incomplete reversibility of reaction (3).

It appears that the acceleration of the cathodic reaction in the presence of hydrogen sulfide is also due to occurrence of a catalytic reaction on the electrode surface [2, 6]. The surface compound $Fe(HS^-)_a$ formedby reactions (1), (2), adds on protons from the H_3O^+ ions, giving a molecular complex — the catalyst $Fe(H\!-\!S\!-\!H)_a$. In the cathodic reaction its protons are readily reduced to adsorbed H atoms, which recombine as molecules and are evolved as gas or diffuse into the metal. ‡ As a result of this reaction the adsorbed HS^- ions are regenerated:

*In certain experiments, instead of H_2S we used Na_2S, bearing in mind its hydrolysis to H_2S in acid solutions.

†Experiments with labeled sulfur atoms showed that from acid solutions there are adsorbed on iron not H_2S molecules but HS^- ions [5, 6], despite their very low equilibrium concentration. Clearly, as adsorption of HS^- ions progresses (reaction (2)) dissociation of H_2S molecules continues until adsorption equilibrium is attained.

‡Here we do not examine the mechanism of the action of inhibitors in the presence of H_2S on diffusion of hydrogen into the metal, or embrittlement of iron and steels.

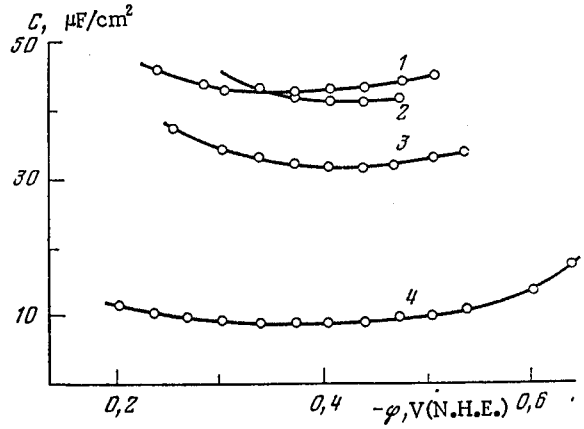

Fig. 2. Differential capacitance of iron in 1 N H_2SO_4 without an additive (1) and with additives: 2) 10^{-4} M Na_2S; 3) 0.2 g/liter Katapin; 4) 0.2 g/liter Katapin + 10^{-4} M Na_2S.

$$Fe+HS^-=Fe(HS^-)_a \qquad (a)$$

$$Fe(HS^-)_a+H_3O^+=Fe(H-S-H)_a+H_2O \qquad (b)$$

$$Fe(H-S-H)_a+e\rightarrow Fe(HS^-)_a+H_a\rightarrow {}^1/_2\,H_2 \qquad (c)$$

(c) → diffusion into the metal

Stages (a) and (b) are quasireversible; stage (c) governs the rate of the whole process. Calculating the catalyst concentration from equilibrium equation (b), we obtain:

$$i=k[HS^-][H_3O^+]\cdot\exp[-\alpha(\varphi-\psi_1)-\psi_1]F/RT, \qquad (d)$$

$$\varphi=a+\frac{1-\alpha}{\alpha}+RT/\alpha F\{\ln[H_3O^+]+\ln[HS^-]-\ln i\}. \qquad (e)$$

A ψ_1 potential arises during adsorption of ions or dipole molecules; when it has a positive value, the cathodic reaction is retarded.

The surface concentration and the strength of the bond of the HS^- ions with the surface iron atoms decrease with an increase in the cathodic potential, but the catalyst activity and concentration increases because the hydrogen ions come closer to the electrode and the protons are readily attached to the adsorbed HS^- ions. At lower cathodic potentials the strength of the bond between the HS^- ions and the metal increases, a fairly labile complex is not formed, and the catalytic cathodic process is retarded; this explains the retardation of the cathodic reaction by hydrogen sulfide at low currents (Fig. 1). Thus, with strengthening of the bond between the HS^- ions and iron, they begin to behave like halide ions.

The catalytic mechanism of the cathodic reaction is confirmed by the data of experiments with a rotating disk electrode [2], according to which hydrogen sulfide is not discharged during the cathodic reaction but accelerates the reaction of hydrogen ion discharge.

The decrease in the slope of the Tafel straight lines (from 120 to 80 mV, Fig. 1) with an increase in the H_2S concentration is probably due to an increase in the concentration of the catalyst and its activity as the negative potential increases.

These mechanisms of the anodic and cathodic reactions permit an explanation of the action of inhibitors in the presence of hydrogen sulfide. It reduces to the following independent effects: 1) intensification of adsorption of the cation-type inhibitor on iron in the presence of hydrogen sulfide — synergic adsorption effect; 2) blocking of the anodic and cathodic catalysts by the adsorbed inhibitor and prevention of catalytic processes; 3) the above-mentioned appearance of a positive ψ_1 potential, retarding the electrochemical reactions.

On iron the adsorbed HS^- ions form dipoles with their negative ends facing the solution; these dipoles serve as anionic transition bridges, promoting adsorption of cation-type inhibitors (R^+). The latter follows from the curves of the differential capacitances vs potential (Fig. 2). The decrease in the capacitance, ΔC, which characterizes the degree of

TABLE 1. Decrease in Differential Capacitance and Coefficient of Corrosion Retardation γ*

Solution	1N H_2SO_4		1 N H_2SO_4 + 10^{-3} M Na_2S	
	ΔC, μF/cm²	γ	ΔC, μF/cm²	γ
1N. H_2SO_4	–	1	3	0,2
The same + $2 \cdot 10^{-3}$ M $(C_4H_9)_4N^+$	4	6	30	400
» + $5 \cdot 10^{-3}$ M $(C_6H_5)_3CH_2N^+$	4	6	31	400
» + $5 \cdot 10^{-3}$ M $(C_6H_5CH_2)_3N$	3	5	30	360
» + 0,2 g/liter Katapin	10	20	32	460

*The coefficient of retardation $\gamma = \rho_o/\rho_i$, where ρ_o is the corrosion rate without an inhibitor, and ρ_i is the corrosion rate with an inhibitor or stimulator.

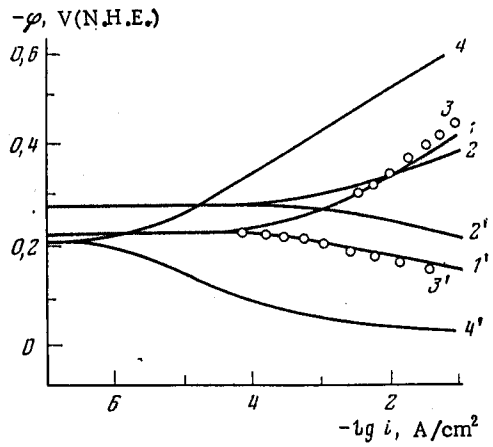

Fig. 3. Cathodic and anodic polarization curves of pure iron in 1 N H_2SO_4 (1) and with additives: 2) 10^{-3} M Na_2S; 3) $2 \cdot 10^{-3}$ M tribenzylmethylammonium sulfate; 4) 10^{-3} M Na_2S + $2 \cdot 10^{-3}$ M tribenzylmethylammonium sulfate.

adsorption, in the presence of hydrogen sulfide or Katapin in the solution is very small (2-3 and 10 μF/cm², respectively). However, when present simultaneously in the same concentrations, ΔC = 33 μF/cm², i.e., a synergic adsorption effect is observed.

The above-mentioned blocking of the catalyst is due to adsorption of the inhibitor R^+ on it with formation of a strong molecular complex $Fe(HSR)_a$ not readily oxidized by reactions (4) and (5); this retards the anodic reaction and cannot transfer protons from the solution to the electrode, slowing down the cathodic reaction (Table 1, Fig. 3) [3, 9, 10]. Low H_2S concentrations (~10^{-6} M) can intensify the action of the inhibitor, and low concentrations of the latter prevent the stimulating effect of H_2S (Fig. 4).

Among cation-type inhibitors belong tetraalkylammonium compounds, pyridine derivatives, and a number of onium compounds, the molecules of which can attach protons from acid solutions and undergo conversion to cations:

$$R_3X + H^+ \rightarrow [R_3XH]^+$$
$$R_2SO + H^+ \rightarrow [R_2SOH]^+$$
$$R_3AsO + H^+ \rightarrow [R_3AsOH]^+$$
$$(RNH)_2CS + H^+ \rightarrow [(RNH)_2CSH]^+,$$

where R is a radical of the aliphatic or aromatic series, and X denotes atoms of N, P, or As. In the presence of H_2S these compounds also exhibit a synergic inhibitor effect. However, at high H_2S concentrations and in concentrated acid solutions their inhibiting effect is greatly reduced.

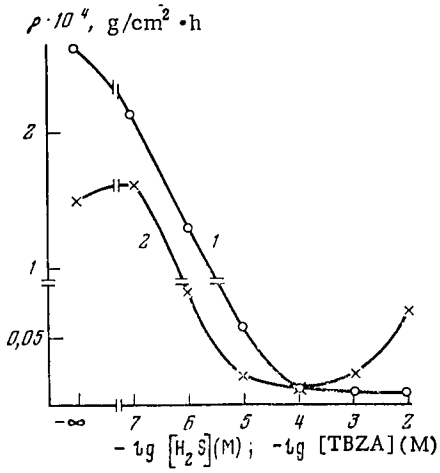

Fig. 4. Corrosion rate of Armco iron in 1 N H_2SO_4 + 10^{-3} M Na_2S vs tribenzylamine concentration (1), and in 1 N H_2SO_4 + 10^{-3} M tribenzylamine vs Na_2S concentration (2).

TABLE 2.

Solution	1 N H_2SO_4		1 N H_2SO_4 + 10^{-3} M Na_2S	
	ΔC, μF/cm²	γ	ΔC, μF/cm²	γ
1 N H_2SO_4	–	1	3	0,22
The same + $C_6H_{13}OH$ (sat.)	0	1	3	0,05
» + $C_5H_{11}COOH$ (sat.)	2	1,2	2	0,05
» + 0,05 M $CH_3(CH_2)_3COOH$	3	1,1	2	0,22
» + 0,1 M CH_3CHO	8	7,8	4	0,30
» + 0,1 M CH_3CH_2CHO	10	7,6	4	0,15
» + 0,01 M $C_6H_5SO_3Na$	10	0,5	6	0,27
» + 0,01 M $C_6H_{13}SO_3Na$	11	0,3	7	0,05

In the presence of H_2S we observe a different picture for the behavior of organic compounds of anionic character (alcohols, organic acids, sulfo acids, and aldehydes [3, 9, 10]) as a result of the presence of negative groups (–OH, –COOH, SO_3OH, –CHO). When they are adsorbed, repulsion occurs at the ends of the negative dipoles of $Fe(HS^-)_a$ [11], and these compounds cannot prevent the catalytic action of hydrogen sulfide. Furthermore, their adsorption is accompanied by formation of a negative ψ_1 potential, accelerating the electrochemical reactions. As a consequence these compounds intensify the stimulating effect of hydrogen sulfide, the increase being greater the higher their concentration (Table 2).

During corrosion in acid solutions, sulfur-containing compounds — thiourea and its derivatives, sulfonic oxide derivatives, thiocyanates, etc. — decompose and are reduced with formation of sulfides and H_2S [9, 13]. Depending on the acid concentration, the degree of reduction, and the overall concentration of the H_2S formed, they either inhibit or stimulate iron corrosion [9-15]. With an increase in the added hydrogen sulfide concentration we observe transition from inhibition to stimulation of iron corrosion. Therefore, the action of each of these sulfur-containing compounds requires a separate investigation in lengthy experiments.

CONCLUSIONS

1. Acceleration of corrosion of iron in the presence of hydrogen sulfide is induced by its catalytic effect on the anodic and cathodic reactions.

2. Low hydrogen sulfide concentrations in an acid solution promote adsorption of an onium inhibitor. The author suggests a mechanism of the effect of a cation-type inhibitor which retards corrosion of iron in the presence of hydrogen sulfide.

3. Organic compounds containing negative groups are weakly adsorbed in the presence of hydrogen sulfide and intensify the effect of hydrogen sulfide as a result of the appearance of a negative ψ_1 potential.

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INFLUENCE OF FLOW RATE ON STEEL CORROSION IN SODIUM

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On the basis of allowance for the reaction of sodium-dissolved oxygen with the components of steels the authors collate and classify experimental data on the influence of the flow rate of sodium on corrosion of austenitic stainless steels. They have obtained relations permitting an estimate of the corrosion of various steels in relation to the flow rate of sodium.

Corrosion of structural materials in liquid-metal heat-transfer agents increases with the flow rate. With a decrease in the thickness of the diffusion sublayer, control of corrosion gradually passes from the diffusion region to the kinetic region, where the influence of the flow rate is insignificant [1]. The critical value of the flow rate ω_c at which corrosion acquires a kinetic regime depends on the type of heat-transfer agent, the hydrodynamics of the flow [1], and the nature of the metal.

For chromium–nickel steels in sodium, ω_c is defined as from 3-4 [2, 3] to 6-7 m/sec [4], but for pure iron andnickel, $\omega_c > 12$ m/sec [2, 3].

We have investigated the influence of the flow rate of sodium on corrosion of steel 08Kh16N15M3B at 700°C.

Tubular specimens were tested on a test-bench with forced circulation of sodium. Sodium flowed through an annular gap, formed by the outer surface of the specimen and the concentric inner surface of the tube, at a rate of 1.7-12.3 m/sec. The flow rate and the cross section of the annular gap were varied. The oxygen content of the sodium (8-10 mg/kg) was kept constant by a cold trap.

*Deceased.

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