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Hua Bao-ding, Shen Xin-su, Z. A. Iofa, and E. I. Mikhailova

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Fig. 1. Dependence of the dissolution rate of 18-8 steel in 10 N H_2SO_4 on the concentration of added salt: a—NaCl, b—KBr

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Abstract

Full Text

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EFFECT OF HALIDE IONS ON THE CORROSION OF 18-8 STAINLESS STEEL IN SULFURIC ACID

(Presented by Academician A. N. Frumkin on 30 VII 1959)

The corrosion resistance of stainless steels, as is known, is connected with their ability to passivate. In sulfuric acid, 18-8 steel, in the absence of oxidizing agents, dissolves at a considerable rate ⁽¹⁾. S. M. Babitskii and Kh. L. Tseitlin ⁽²⁾ found that the addition of small amounts of halide salts substantially decreases the rate of dissolution of 18-8 stainless steel in solutions of sulfuric acid.

The inhibiting action of halide ions on the acid corrosion of pure iron, first discovered by Walpert ⁽³⁾, was studied in detail by Z. A. Iofa and co-workers ⁽⁴⁻⁷⁾. It has been shown that halide ions are adsorbed on the surface of iron from acid solutions and form with them strongly bound, non-monolayer-filling chemisorbed layers, which slow the rate of electrochemical reactions on iron, especially the discharge reaction of hydrogen ions. The change in the electrochemical properties of the iron surface that occurs in the presence of halide ions (probably a shift of the zero-charge potential of iron toward positive values) facilitates the adsorption of inhibitors—organic compounds of basic character, owing to which these inhibitors become effective.

Fig. 1. Dependence of the dissolution rate of 18-8 steel in 10 N H_2SO_4 on the concentration of the added salt: a—NaCl, b—KBr.

The transfer of these conclusions to stainless steels encounters difficulty, since halide ions, and first of all chlorine ions, have the ability to destroy the passivating film ^(1, 8-10) and, consequently, it would seem, should increase the rate of dissolution of stainless steel in sulfuric acid.

In order to elucidate the mechanism of action of halide ions, experiments were carried out at the Institute of Applied Chemistry of the Academy of Sciences of

Fig. 2

Figure 2: Fig. 2

the PRC and at the Department of Electrochemistry of Moscow State University named after M. V. Lomonosov to measure the rate of dissolution of 18-8 stainless steel* in 10 *N* H₂SO₄ as a function of the concentration of added salts NaCl, KBr, and KJ, by the decrease in the weight of the specimen and by the rate of hydrogen evolution; polarization curves were also taken.

* The steel used in the last series of experiments contained (in %): Ni 9.3, Cr 16.8, C 0.14, Si 0.25, Mn 0.84, Ti < 0.05, S 0.019, P 0.013.

in pure 10 *N* H₂SO₄ and with the addition of the indicated salts in a hydrogen atmosphere at room temperature. The curves shown in Figs. 1 and 2 were obtained in China, and those in Figs. 3 and 4—in Moscow.

In Figs. 1 and 2 the curves give the dependence of the dissolution rate of steel ρ (in g/cm²·h) on the concentration of the added halide salt in percent, from which it is seen that halide ions slow the dissolution rate of 18-8 steel in acid; moreover, there is an optimal concentration of the halide salt at which the strongest effect of the indicated action is observed. Table 1 gives approximate values of the optimal concentrations of halide salts and the corresponding dissolution rates of 18-8 steel in 10 *N* H₂SO₄.

Fig. 2. Dependence of the dissolution rate of 18-8 steel in 10 *N* H₂SO₄ on the logarithm of the concentration of added KI

When the concentration of the halide salt is below the optimum, the corrosion rate increases with time, while at concentrations above the optimum it decreases. From Table 1 it is seen that in the series Cl—Br—J the concentration of halide salt at which the strongest suppression of corrosion is observed decreases, and the inhibition effect increases significantly.

From the polarization curves shown in Fig. 3, it follows that at the stationary potential 18-8 steel in 10 *N* H₂SO₄ is active; passivation begins at a more positive potential and at an anodic current density that is higher than the self-dissolution current. Chloride ions added to the acid depassivate the steel; it cannot be passivated at all values of i_a indicated in Fig. 3. Chloride ions, moreover, accelerate the anodic process in the range of potentials where, in the absence of chloride ions, the steel is active. From comparison of the cathodic curves it is seen that chloride ions increase the hydrogen overvoltage and shift the stationary potential toward more negative values. The slowing of corrosion at the stationary potential is entirely caused by the increase in hydrogen overvoltage. Owing to the latter, the depassivating action of chloride ions does not lead to acceleration of the self-dissolution of the steel.

Table 1

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Added salt	Optimal concentration, mol/l	Corrosion rate, g/cm ² · h	Corrosion retardation coefficient
Without additive	—	$3 \cdot 10^{-3}$	1
NaCl	0.1	$5 \cdot 10^{-5}$	60
KBr	0.008	$5 \cdot 10^{-6}$	600
KJ	0.0006	$7 \cdot 10^{-7}$	4000

Fig. 4 shows the polarization curves in pure 10 N H₂SO₄ (curves 1, 1') and with the addition of KBr and KJ at concentrations close to the optimal ones (curves 2, 2' and 3, 3'). At the stationary potential in these cases as well the steel is active; however, in contrast to chloride ions, bromide and iodide ions at the indicated small concentrations slow the anodic reaction of metal ionization, which in the case of iodide ions leads to a shift of the stationary potential toward more positive values. In the presence of these ions passivation occurs, although at more positive potentials, but at lower values of i_a than in pure H₂SO₄. The slowing of the anodic process and the increase in hydrogen overvoltage lead to a significant decrease in the corrosion rate. Thus, a chemisorbed layer of halide ions, which increases the hydrogen overvoltage and evidently does not disappear at more positive potentials, promotes passivation of the steel during anodic polarization in the case of ions

bromine and iodine and prevents the establishment of the passive state in the case of chlorine ions.

The fact that, in the presence of chlorine ions, in contrast to bromine and iodine ions, the passive state is not established under anodic polarization shows that exchange adsorption between the passivator—chemisorbed oxygen¹⁰—and chlorine ions occurs much more readily than with bromine and iodine ions. With a considerable increase in concentration

Fig. 3. Polarization curves on an electrode of stainless steel 18-8: 1, 1'—in 10 N H₂SO₄; 2, 2'—in 10 N H₂SO₄ + 0.1 N NaCl

Fig. 4. Polarization curves on an electrode of stainless steel 18-8: 1, 1'—in 10 N H₂SO₄; 2, 2'—+0.01 N KBr; 3, 3'—+0.001 N KJ; 4, 4'—+0.2 N KJ above the optimum, bromine and iodine ions, like chlorine ions, facilitate ion-

ization and prevent passivation of steel 18-8 under anodic polarization. With increasing KJ concentration, a decrease in hydrogen overvoltage is also observed (Fig. 4, 4') and a decrease in the inhibitory action on corrosion (Fig. 2).

A similar increase in the rate of self-dissolution upon addition of large concentrations of KJ to the acid solution is also observed in the case of pure iron. For example, in 4 N H₂SO₄ the dissolution rate of Armco iron changes with the KJ concentration as follows:

KJ concentration	0.001N	0.02N	0.1N	1.0N
ρ , g/cm ² · h	$4.2 \cdot 10^{-5}$	$2.2 \cdot 10^{-7}$	$2.0 \cdot 10^{-7}$	$5.2 \cdot 10^{-7}$

It may be assumed that the reversal of the effect upon addition of large KJ concentrations is associated with the formation, in addition to the chemisorbed layer, of another, weakly bound layer of iodine anions on the metal, which acts

Table 2

Dissolution rate of steel 18-8 in 10 N H₂SO₄

Additives	ρ , g/cm ² · h	Corrosion retardation coefficient
Without additive	$1.5 \cdot 10^{-3}$	1
0.0005 N KJ	$8 \cdot 10^{-7}$	1800
0.001 M [N(C ₄ H ₉) ₄] ₂ SO ₄	$9.4 \cdot 10^{-4}$	1.60
0.001 M [N(C ₄ H ₉) ₄] ₂ SO ₄ + 0.0005 N KJ	$1.2 \cdot 10^{-7}$	12000
0.003 N Na ₂ S	$7.2 \cdot 10^{-4}$	2.1
0.003 N Na ₂ S + 0.001 M [N(C ₄ H ₉) ₄] ₂ SO ₄	$5.6 \cdot 10^{-6}$	270

acts on the hydrogen overvoltage in the opposite direction, i.e., in the same way as in the case of adsorption of these anions on mercury (11). In the case of the anodic process, the participation of adsorbed anions in the elementary act of metal ionization is also possible, with the primary formation of complex anions.

A similarity in the behavior of 18-8 steel and iron is also observed in other processes; for example, the presence of halide ions (6) or sulfides (12) in the acid solution increases the inhibiting action of organic cations. Table 2 gives the dissolution rate of steel in 10 N H₂SO₄.

The data obtained in the present work—especially the facilitation of passivation by bromine and iodine ions—are, in our opinion, of interest for the general theory of passivity, since they are incompatible with the conception of the obligatory

phase nature of adsorption layers and confirm the significance of adsorption phenomena.

Institute of Applied Chemistry
Academy of Sciences of the PRC
Changchun

Moscow State University
named after M. V. Lomonosov

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