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The Depassivating Action of Halide Ions on Iron-Based Alloys

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The role of halide ions in the process of dissolution of metals in electrolyte solutions may differ depending on the nature of the metal and the magnitude of its potential. For passivating metals in the range of potentials in which the metal is passive in the absence of halide, the introduction of halide ions into the solution may lead to its depassivation. It is known that activation of the metal in this case is, as a rule, accompanied by the formation of pitting cavities on its surface. Such a phenomenon is characteristic, in particular, of iron and of some alloys based on it, for example Fe—Cr and Fe—Cr—Ni alloys ($^{1-7}$).

In order to obtain data necessary for a correct interpretation of the phenomenon of pitting formation, we carried out a systematic study of the influence of various factors on the ability of passive iron—chromium* and iron—chromium—nickel alloys to pass into the active state under the action of halide ions. As a criterion for evaluating this ability, the values of the activation potential of the alloys φ_a were used. The values of φ_a were determined either from potentiostatically measured anodic polarization curves (Fig. 1a), as the potentials at which the current begins to rise sharply in a solution containing halide (curve 2), in the potential region between the passivation potential φ_p and the transpassivation potential φ_r of the alloy, characteristic of it in a solution without halide (curve 1), or from curves of the change in alloy potential with time at constant values of the anodic current (Fig. 1b), as the stationary values reached after the potential had passed through the minimum φ_m. Using steel 1Kh13 as an example, we showed that the values of φ_a obtained by the second method depend on current density in accordance with the Tafel equation, shifting, upon a tenfold increase in current density, by 50 mV in the positive direction, and at sufficiently low current densities are close to the values of φ_a determined from polarization curves. The values of φ_a cited by us were obtained from potential—time curves at a current density of $2.5 \cdot 10^{-3}$ A/cm^2.**

The dependence of φ_a on the concentration and nature of halide ions at constant pH, and on pH at constant halide concentration, was determined in solutions of composition KHal + HHal. The corresponding data for steel 1Kh13 are given in Fig. 2***. As follows from these data,

Fig. 1 and Fig. 2 schematic plots

Figure 1: Fig. 1 and Fig. 2 schematic plots

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* As iron—chromium alloys, steels of grades 1Kh13, Kh17, and Kh28 and binary alloys of Armco iron with chromium (99.9%) containing 12, 20, 27, and 35% chromium were used.

** Strictly speaking, the activation potential of an alloy in a given solution should be taken as the values of φ_a obtained by extrapolating them to current densities equivalent to the rate of dissolution of the alloy from the passive state. However, for determining the dependence of the activation potential on various parameters, one may also use values of φ_a obtained at higher current densities.

*** Here, as below, potentials are given relative to the normal hydrogen electrode.

the activation potential of steel shifts, with increasing concentration C of the halide ion in the solution, in the negative direction, and the curves $\varphi_a - \lg C_{\mathrm{Hal}^-}$ (curves 1 and 2) are linear and have a slope of 200 ± 5 mV. Activation of the passive alloy is facilitated on going from bromide to chloride, as evidenced by the shift of the curve obtained for chloride (curve 1) by 200 mV in the negative direction as compared with the corresponding curve for bromide (curve 2).

Fig. 1. Schematic anodic curves (*a*—polarization curves, *b*—potential—time) for determining the activation potential of steel: 1—in sulfuric acid solution (for comparison), 2, 3—in solutions containing halide ions

Fig. 2. Dependence of the activation potential of steel 1Kh13 on the concentration of Cl^- ions (1), Br^- ions (2) at pH 2 and on pH in a 0.1 *N* bromide solution (3)

With increasing pH of the solution in the pH range from 1.6 to 12.7 at $C_{\mathrm{Hal}^-} =$ const, the activation potential of steels 1Kh13, Kh17, and Kh28 changes very little, shifting with an increase in pH by one unit by no more than 10 mV in the positive direction (Figs. 2, 3). This dependence, however, holds only up to a certain pH value. Upon reaching pH 14, the linear course of the curve is disturbed: depassivation of steels under the action of halide ions practically ceases. The ability of halide ions to exert a depassivating action on alloys depends substantially on the presence of extraneous anions in the solution. As is evident from the data of Fig. 3, obtained in measurements on steel 1Kh13 in solutions of $\mathrm{KHal} + \mathrm{H_2SO_4}$, as the ratio of the concentrations $\mathrm{SO_4^{2-}}$ and Hal^- increases at constant C_{Hal^-} and pH, the activation potential shifts in the positive direction, reaching, at some critical value of $C_{\mathrm{SO_4^{2-}}}/C_{\mathrm{Hal}^-}$, the repassivation potential of the steel characteristic of it in a solution not containing halide ions. This indicates the cessation of the activating action of halide ions in solutions containing a certain excess of extraneous anions.

Fig. 3 and Fig. 4: graphs

Figure 2: Fig. 3 and Fig. 4: graphs

The effectiveness of the action of halide ions on alloys also depends on their composition. Figure 4 gives the activation potentials of Fe—Cr alloys as a function of their chromium content P_{Cr} (curve 1), and also as a function of the amount of nickel P_{Ni} added to alloy Kh22T (curve 2). The data presented show that increasing the chromium or nickel content in the alloy as a whole leads to a weakening of the depassivating action of halides. However, in quantitative terms this effect changes noticeably on going from relatively small contents of alloying additions to some critical value. In the region of low concentrations (from 12 to 20-27% chromium in the Fe—Cr alloy and from 2 to 12% nickel in Fe—Cr—Ni alloys), with increasing content of additions in the alloy the activation potential shifts only slightly in the positive direction. At higher chromium and nickel concentrations the effect is intensified and

upon reaching a nickel concentration (as an addition to the Kh22T alloy) of 14% and a chromium concentration in the Fe—Cr alloy of 35%, the depassivating action of the halides ceases, as a result of which the course of the curves φ_a—P_{Cr} and φ_a—P_{Ni} changes sharply. In agreement with these results are also the data for pure chromium, which under the conditions studied, as experiment showed, is not depassivated by halide ions.

Fig. 3. Dependence of the activation potential of steel 1Kh13 on the ratio of the concentrations of SO_4^{2-} and Hal^- ions in solutions with constant $C_{\mathrm{Hal}^-} = 0.01\,N$ and pH 2: 1 —for Cl^-; 2 —for Br^-

Fig. 4. Dependence of the activation potential of Fe—Cr alloys on their chromium content (1) and on the addition of nickel to alloy Kh22T (2) in 0.1 N chloride solution at pH 2

Comparison of the electrochemical behavior of the alloys studied with the behavior of zirconium in solutions containing halide ions, previously studied in our laboratory ([8],[9]), indicates the existence of a certain similarity in the activating action of halides on zirconium, on the one hand, and on iron-based alloys, on the other. In both cases, the activating action of halide ions appears only upon the attainment of a certain critical potential, which shifts toward positive values as the concentration of halide is decreased, and also upon transition from chlorides to bromides, and ceases completely when the concentration of foreign anions (sulfate and hydroxyl ions) is increased to a certain limit. Such similarity indicates the applicability of the mechanism of the activating action of halide ions, developed for zirconium, also to iron-based alloys. According to this mechanism, the activating action of halide ions is associated with complete or partial displacement, from the metallic surface, of passivating oxygen, as a result of which the metal acquires the ability to pass into solution in the form of its complex with the halide. Such a reaction, however, becomes possible only upon the attainment of a certain potential and on those surface areas where the concentration of halide ions has reached a certain critical value*.

Despite the existence of a number of common features testifying to a single mechanism of action of halide ions on zirconium and on iron-based alloys, the transition from zirconium to these alloys is accompanied by a quantitative change in some regularities of their activation. Thus, for example, the slope of the curves φ_a— $\lg C_{\mathrm{Hal}^-}$ for Fe–Cr alloys is three several times exceeds the corresponding slope for zirconium, which apparently indicates the participation of different numbers of halide ions in the elementary acts of dissolution of metals of different nature. The dependence of φ_a on i, calculated from the φ–t curves measured at different current densities i, obeys the Tafel equation with a slope of 50 mV, in contrast to the corresponding data for zirconium, for which a strict independence of φ_a from i is characteristic. The indicated differences, however, are not in contradiction with the concepts developed above, since, according to these concepts, the activating action of halide ions must change substantially in passing from one metal to another, because such a transition must lead to a change in the strength of the adsorption bond between passivating oxygen and the surface atoms of the metal, as well as in the chemical affinity of these atoms for the halide ions themselves.

The role of the nature of the metal in the process of its depassivation under the action of halides can be traced especially clearly from the example of data on the dependence of the activation effect on the quantitative composition of an alloy. It is known that an increase in the chromium content in an alloy generally facilitates passivation, expressed in a shift of the passivation potential in the negative direction, which is accompanied by an increase in the strength of the bond of the metal with oxygen at a given potential. In this connection, with an increase in the chromium concentration in the alloy, the onset of the adsorption displacement of oxygen by halide ions shifts toward more positive potentials, at which the adsorption capacity of halide ions becomes sufficiently high. Taking into account that, as the potential shifts in the positive direction, not only the adsorption capacity of the halide ion increases, but also the strength of the bond of the metal with adsorbed oxygen, in order to explain the depassivating action of halides on alloys it is necessary to assume that the former quantity increases with potential more rapidly than the latter. As a result, as the chromium concentration in the alloy increases, the activation potential shifts in the positive direction, and the interval between the potentials of passivation and activation under the action of halide ions expands considerably, which is of interest for practical purposes, making it possible, in particular, to broaden the possibilities of applying anodic protection of alloys in halide solutions.

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* The latter in our work is confirmed by data on determining the quantity of electricity that must be passed through the electrode to shift its potential from φ_1 to φ_m (see Fig. 1b). As was found for steel 1Kh13 in halide solutions, this quantity of electricity, to a first approximation, does not depend on the density of the polarizing current during measurement of the φ—t curve.

In considering the question of the influence of halide ions on the electrochemical behavior of alloys, it is necessary to take into account that their surface layers consist of heterogeneous atoms. In this connection, cases are in principle possible in which atoms of one kind are predominantly subjected to the action of halide ions, while the passivating adsorption of oxygen takes place mainly on atoms of another kind. In this case, when evaluating the activating role of halide ions it is necessary to take into account the structure of the surface layer of the alloy and, in particular, to consider the possibility of an additional hindrance to the adsorption of halide ions on some atoms when the relative number of other atoms capable of being passivated on the alloy surface is significantly increased. It is possible that the sharp change in the course of the curves φ_a–P_{Cr} and φ_a –P_{Ni} upon reaching a certain chromium and nickel content in the alloys is also connected with this cause.

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