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Abstract

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ON THE QUESTION OF THE ACTIVATION OF IRON BY HALIDE IONS

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A substantial feature of the electrochemical behavior of passivating metals in solutions of halide salts is the activation of the metal that arises under certain conditions, which, as a rule, is associated with the development of pitting corrosion. In works devoted to the study of the activation of zirconium ([1]), aluminum ([2]), magnesium ([3]), Fe–Cr alloys ([4]), and a number of technical stainless steels, it was observed that dissolution of this type occurs only at potentials whose value is not lower than a certain critical value (E_{cr}). The existence of such a potential is of primary importance both for understanding the mechanism of the process itself and for finding effective methods of protection against pitting corrosion.

However, the experimental data relating to such an important technical metal as iron are not unambiguous. Thus, L. V. Vanyukova and B. N. Kabanov ([5]), studying the dependence of the Fe potential in alkaline solutions on the amount of electricity passed, found that at a concentration of Cl' ions of 0.5-2 N, under certain conditions, a constant value of the metal dissolution potential was established. An analogous phenomenon, observed by the authors ([5]) upon additions of ClO_4' ions to alkali, was later studied in detail in works ([6-8]), in which, by means of the potentiostatic method, it was shown that activation of iron by ClO_4' ions in a large number of cases occurs at potentials not lower than $\simeq 1.4$ V.

Along with this, Engel and Stolica ([9]), on the basis of a study of the activation of iron by Cl' ions at concentrations of the latter of $3 \cdot 10^{-4}$—$4 \cdot 10^{-3}$ N in a solution of sulfuric acid, expressed the opinion that there is no critical activation potential. Later, a similar opinion was expressed by Frank ([10]).

One might think that the absence of a critical potential in the experiments of Engel and Stolica is connected not with the fact that activation proceeds by a chemical mechanism, as was assumed in ([9]), but with the fact that, under the conditions of the measurements, the value of E_{cr} was more negative than the potentials at which the measurements were carried out. Indeed, since the value of E_{cr} over a wide pH interval does not depend on pH ([1, 2, 4, 7, 8]), while the passivation potential of iron increases substantially with decreasing

Fig. 1

Figure 1: Fig. 1

pH, then at a definite concentration of Cl′ ions in a sufficiently acidic solution the passivation potential may prove to be more positive than the activation potential. Under these conditions the metal can no longer passivate, and the addition of the corresponding amount of Cl′ ions to an acid solution in which the iron potential is maintained in the passive region should always cause the development of pitting corrosion; this, apparently, is what is connected with the results obtained in similar experiments by Engel and Stolica.

On the basis of an assessment of the available data, one could think that the existence of a critical activation potential at concentrations of Cl′ ions close to those used in the experiments of the authors ([9]) would be found in neutral solutions. In connection with this, we studied the activation of iron (Hilger grade) in borate buffer sol–

in solutions (pH 7.4 and 8.4) at concentrations of Cl′ ions from 0.001 to 0.1 N.* For comparison, the effect of additions of Br′, J′, F′, and ClO_4' ions was also studied.

Polarization measurements in the experiments were carried out mainly by means of the nonstationary potentiostatic method–the electrode potential was shifted (from the value established without polarization) in the positive direction in steps of 50 mV. The hold time at each potential was 2 min. In individual experiments, both shorter and longer hold times were used, and galvanostatic measurements were also applied.

Fig. 1. Effect of KCl concentration on the activation potential of iron (pH 8.4). KCl concentration: 1–0; 2–0.001 N; 3–0.003 N; 4–0.01 N; 5–0.1 N. Segment A–B of curve 1–oxygen evolution

The polarization curves obtained for solutions with pH 8.4 (0.11 M H_3BO_3 + 0.023 M $Na_2B_4O_7$) at various KCl concentrations are presented in Fig. 1. At a salt concentration of 0.001 N, activation under the experimental conditions was expressed only in an increase in the dissolution rate in the passive state at potentials from 0.4 to 1.0 V (curve 2). However, at higher concentrations the dissolution rate, upon reaching a certain potential, increased sharply, which was expressed in the appearance on the polarization curves of almost horizontal sections (curves 3-5), characteristic of activation at the critical potential (1). At the same time, with a tenfold increase in the concentration of Cl′ ions, the value E_{cr} shifted in the negative direction by approximately 0.15-0.2 V, which agrees satisfactorily with the corresponding data for Fe–Cr alloys[4]. In the nonstationary measurements performed, the obtained activation potentials were shifted in the positive direction from the stationary values of E_{cr}, determined, for example, at constant current density. For a 0.1 N KCl solution, according to the galvanostatic-measurement data (Fig. 2), the value of E_{cr} is close to −0.2

Fig. 2

Figure 2: Fig. 2

V, so that the magnitude of the indicated shift is $\simeq 0.25$ V.

It is evident that the activation potential for a 0.003 N KCl solution (+0.2 V), even without introducing a correction for the nonstationarity of the measurements, is more negative than the lowest potential value (+0.35 V) at which the authors[9] observed activation of passive iron in sulfuric acid at the same concentration of Cl′ ions. This agrees with the supposition stated above concerning the interpretation of the corresponding data.

* The use of boric acid and sodium tetraborate additions for buffering raised the question of the influence of these solution components on the passivation of iron under the experimental conditions. Experimental data of Mayne and Menter[11] and Nagayama and Cohen[12] indicate that in the corresponding solutions phase films of borates are not formed on the surface of iron. In order to check the possibility of adsorption passivation of the metal by components of borate buffer solutions, anodic polarization curves were recorded in solutions in which the concentrations of the buffering additions were varied by a factor of 10 at pH $\simeq 8.4$ and by a factor of 3 at pH $\simeq 7.4$. Increasing the concentration under these conditions had a very weak effect on the measurement results, which, contrary to expectation, was expressed in a certain increase in the critical passivation current and in the dissolution rate in the passive state. At the same time, the indicated changes were not especially large and could have been caused by experimental error. Thus, it may be assumed that no substantial interaction of iron with the buffering additions occurred under the experimental conditions. Similar conclusions regarding the passivation of nickel in borate solution were drawn by Davis and Barker[13].

The polarization curves for 0.01 N solutions of salts of various halides, presented in Fig. 3, show the influence of the nature of the anion under activation conditions. In accordance with the literature data for other metals, the value of E_{cr} increases in the series Cl′ < Br′ < J′, the difference between the activation potentials for neighboring ions in this series being $\simeq 0.1$ V.

Fig. 2. Change in potential in 0.1 N KCl solution with increasing current density (pH 8.4)

At the same time, the activation potential in $NaClO_4$ solutions (curves 6, 7) is shifted in the positive direction by more than 1 V relative to the activation potentials by halide ions. This shows that ClO_4' anions possess a significantly lower activating ability not only in comparison with Cl′ ions, as was noted earlier (8), but also in comparison with Br′ and J′ ions.

Despite the differences in activation potentials, the signs of dissolution of activated iron in KCl, KBr, KJ, and $NaClO_4$ solutions are identical: iron passes into

Fig. 3

Figure 3: Fig. 3

solution in the form of Fe^{+2} ions, and ferric hydroxide forms on the electrodes in the form of white nodules and hanging threads. Corrosion

Fig. 3. Polarization curves in buffer solution (pH 8.4) with additions of various salts. 1—without additions; 2—0.01 N KCl; 3—0.01 N KBr; 4—0.01 N KJ; 5—0.01 N NaF; 6 and 7—portions of the polarization curves corresponding to activation for solutions of, respectively, 1 and 0.1 N $NaClO_4$

has a localized character; upon reaching sufficiently high current densities, separate large pits are observed on the metal surface*. Since under the experimental conditions activation by ClO_4' ions occurred in the region of oxygen evolution, then in 1 N $NaClO_4$ and especially

* Since all experiments were carried out with electrodes made of wire (diameter 1 mm), these data, together with the data of (8), show that, contrary to the opinion expressed by the authors of (7), pitting corrosion can develop both on the surface of rolled metal and on a surface formed under drawing conditions.

in a 0.1 N solution of $NaClO_4$ (because of the more positive activation potential), the ferric hydroxide formed was partially oxidized to ferric oxyhydroxide by the oxygen evolved.

In contrast to the indicated anions, the addition of 0.01 N F' ions did not cause activation of iron (curve 5). At a higher concentration of NaF or KF (0.1 N), there was a substantial increase in the critical passivation current and in the rate of dissolution in the passive state.

It is still difficult to indicate ways of explaining such an essential fact as the considerable difference in the activating properties of Cl', Br', and I' ions, on the one hand, and of ClO_4' or F' anions, on the other. Apparently, as Piontelli and Seravalle noted in general form ([14]), to explain such differences it is insufficient to take into account any one property of the ions, for example ionic radius or polarizability. Most likely, it is necessary simultaneously to take into account, along with the noted quantities, a number of physicochemical characteristics: the solubility of compounds with the metal, the tendency toward complex formation, and others.

At the same time, the data obtained make it possible to suppose that iron is characterized by the same distinctive features of activation by halide ions as are other metals: the presence of a critical activation potential, and its dependence on the nature and concentration of halide ions. This makes it possible to regard the electrochemical theory of activation ([1]), which connects this process with the displacement of passivating oxygen by halide ions and with the participation of the latter in the first stage of the dissolution reaction, as a general basis for explaining the activation of metals by halide ions.

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CITED LITERATURE

[1] Ya. M. Kolotyrkin, V. A. Gilman, DAN, **137**, 642 (1961).
[2] N. D. Tomashov, V. N. Modestova, in the collection *Investigations on the Corrosion of Metals*, Publishing House of the Academy of Sciences of the USSR, 1951, p. 75; H. Kaesche, Zs. Phys. Chem., N. F., **26**, 138 (1960).
[3] B. N. Kabanov, D. V. Kokoulina, DAN, **112**, 682 (1957); **120**, 558 (1958).
[4] Ya. M. Kolotyrkin, G. V. Golovina, G. M. Florianovich, DAN, **148**, 1106 (1963).
[5] L. V. Vanyukova, B. N. Kabanov, DAN, **59**, 917 (1948).
[6] V. D. Kashcheev, B. N. Kabanov, D. I. Leikis, DAN, **147**, 143 (1962).
[7] B. N. Kabanov, V. D. Kashcheev, DAN, **151**, 883 (1963).
[8] L. I. Freiman, Ya. M. Kolotyrkin, DAN, **153**, 886 (1963).
[9] H. J. Engell, N. D. Stolica, Zs. Phys. Chem., N. F., **20**, 113 (1959).
[10] U. F. Frank, In: I Intern. Congr. on Metallic Corrosion, London, 10–15 April, 1961, Butterworths, 1961, p. 197.
[11] J. E. O. Mayne, J. W. Menter, J. Chem. Soc., 1954, p. 99.
[12] M. Nagayama, M. Cohen, J. Electrochem. Soc., **109**, 781 (1962); **110**, 670 (1963).
[13] D. E. Davies, W. Barker, Corrosion, **20**, No. 2, 47 (1964).
[14] R. Piontelli, G. Seravalle, Zs. Elektrochem., **62**, 759 (1958).

Note: Figure translations are in progress. See original paper for figures.