EFFECT OF ANIONS ON THE PASSIVATION OF IRON IN NEUTRAL SOLUTIONS

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The electrochemical and corrosion behavior of a metal depend on the nature of the electrolyte and, above all, on the type of anions and pH of the electrolyte. The effect of anions on the dissolution and passivity of iron has been investigated mainly in alkaline and acid solutions. The interpretation of the results concerning the effect of a given anion in an acid solution is complicated by the presence of the anions of the acid proper. In a number of cases where the galvanostatic method is used to study the passivity it is difficult to obtain a clear picture of the behavior of the metal in the passive region. Electrochemical measurements at intermediate values of pH, necessary for an understanding of the corrosion behavior of steels in neutral solutions, have been made in very few investigations.

In what follows we describe the results of our study of the passivation and activation of iron in neutral solutions with different anions.

EXPERIMENTAL PART

We used samples of pure iron (Hilger) prepared from wire 1 mm in diameter with a total working area $\simeq 0.1$ cm^2. The samples were polished (the final polishing done with KZM-14 corundum powder), degreased with ethyl alcohol, etched with distilled sulfuric acid, and then washed and placed quickly in the cell. The tests were made at 20°C in an atmosphere of pure nitrogen.

We used borate buffer solutions to keep the pH at a constant value during the experiments. The anions investigated were SO_4^{-2}, ClO_4^{-1}, NO_3^{-1}, Cl^{-1}, Br^{-1}, I^{-1}, and F^{-1}. They were added to the solution in the form of calcium or sodium salts of the respective acids. We used reagents recrystallized three times and also chemically pure reagents. The chemically pure reagents were used only in cases where it was shown by special experiments that additional purification by recrystallization had no significant effect on the results. The solutions were prepared with bidistilled water and the samples were washed with bidistilled water.

Polarization measurements were made mainly by the nonsteady potentiostatic method: the potential of the electrode was displaced toward positive values (from that stabilized without polarization) by jumps of 50 mV. The sample was kept for 2 min at each value of the potential. In separate experiments we used longer or shorter times and we also made galvanostatic measurements.

The use of buffered solutions (with borates) as the background for the study of the effect of anions required additional study of the effect of the buffers (boric acid and sodium tetraborate) on the passivation of iron under the experimental conditions. The possibility of passivation with films of iron borate was excluded, since as was shown in [1] and [2], only oxide films are formed on the surface of iron in solutions containing borate. In order to determine the possibility of adsorptional passivation of iron by buffers we drew anodic polarization curves in buffer solutions (without any additional elements) in which the concentration of the components was varied by a factor of 10 at pH 8.4 ± 0.1 and by a factor of 3 at pH 7.4 ± 0.1. The increase of the concentration within this range has little effect on the results. The effect consists of a certain increase of the critical passivation current and a slight increase of the dissolution rate in the passive state, but these were within the limits of the experimental error and were considerably lower than the effects induced by changes in the concentration of other anions, including OH^{-1} ions. Thus, we may assume that the passivation of iron under the conditions examined here is due to the interaction between the

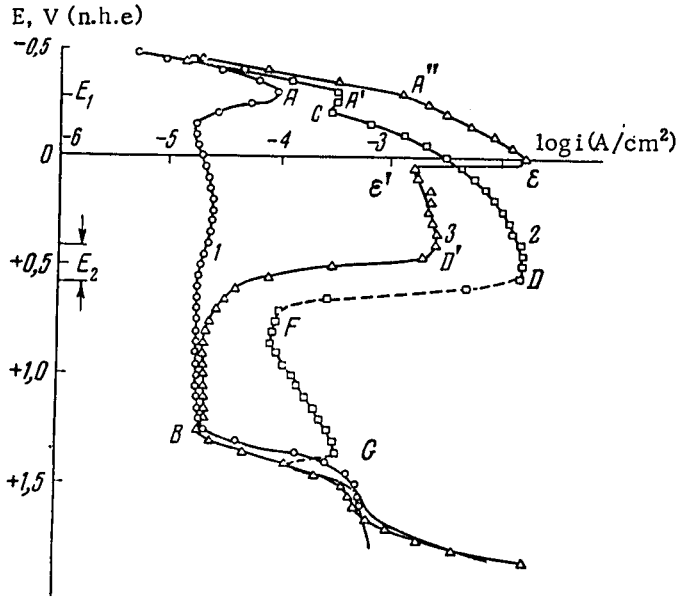

Fig. 1. Polarization curves in Na_2SO_4 solutions. Concentrations of Na_2SO_4 are as follows: 1) 0; 2) 0.1; 3) 1.0 N.

metal and water molecules or OH^{-1} ions. Similar conclusions relative to the passivation of nickel in borate solutions were derived in [3].

EXPERIMENTAL RESULTS

The effect of the concentration of SO_4^{-2} ions on the passivation of iron at a pH of 7.4 is shown in Fig. 1. In the absence of SO_4^{-2} ions the polarization curve has a simpler shape—one current maximum at the passivation potential $E_1 \simeq -0.3$ V (point A on curve 1) and a passive region between -0.15 and +1.25 V. At higher potentials oxygen begins to evolve. The addition of SO_4^{-2} ions slows down the passivation at the potential E_1, and this decelerating effect increases with increasing concentrations of sulfate ions. When 0.1 g-eq/liter of SO_4^{-2} is added (curve 2) then the decrease of the dissolution rate which begins at point A' covers only a narrow range of potentials (section A'C). In the solution containing 1.0 N SO_4^{-2} ions (curve 3) the passivation at $E = E_1$ is manifest only in the increase of the Tafel slope of the polarization curve (bend at the A" point).

At potentials between 0.4 and 0.55 V the dissolution rate decreases sharply in solutions containing Na_2SO_4 (points D and D'). For brevity, we shall indicate this potential range as E_2.

After passivation at E_2 the dissolution rate in 0.1 N Na_2SO_4 solution is higher than in the 1.0 N Na_2SO_4 solution, but the section of the polarization curve relative to this range of potentials is not very reproducible (dashed line DFG).

Figure 2 shows the polarization curves obtained in different solutions at a pH of 8.4. In the buffer solution (without any additional elements—curve 1) the critical passivation current and the dissolution rate in the passive state are lower than at a pH of 7.4 and the passivation potential E_1 is more negative (-0.38 V). This value is in satisfactory agreement with the results obtained in [2]. As in the case where the pH = 7.4, the SO_4^{-2} ions as well as the ClO_4^{-1} and NO_3^{-1} ions slow down the passivation at the potential $E = E_1$, and the higher their concentration the greater the deceleration. This effect of the concentration remains at all potentials $E > E_1$ in the case of NO_3^{-2} ions. An increase of the concentration of SO_4^{-2} ions between 0.1 and 1.0 N at some potentials between E_1 and E_2 and at potentials $E > E_2$ decreases the solution rate as it does at a pH of 7.4. We did not succeed in obtaining consistent results on the effect of the concentration of ClO_4^{-1} ions at these potentials.

Section ab of curve 3 in Fig. 2 (1.0 N $NaClO_4$) reflects the activation of iron by ClO_4^{-1} ions at high anodic potentials, which was studied recently [4-6]. The characteristic of this activation is the fact that it begins only after a certain critical potential (~1.4 V) is reached. For a number of metals and alloys it was found that halogen ions induce dissolution of this type [7-10].

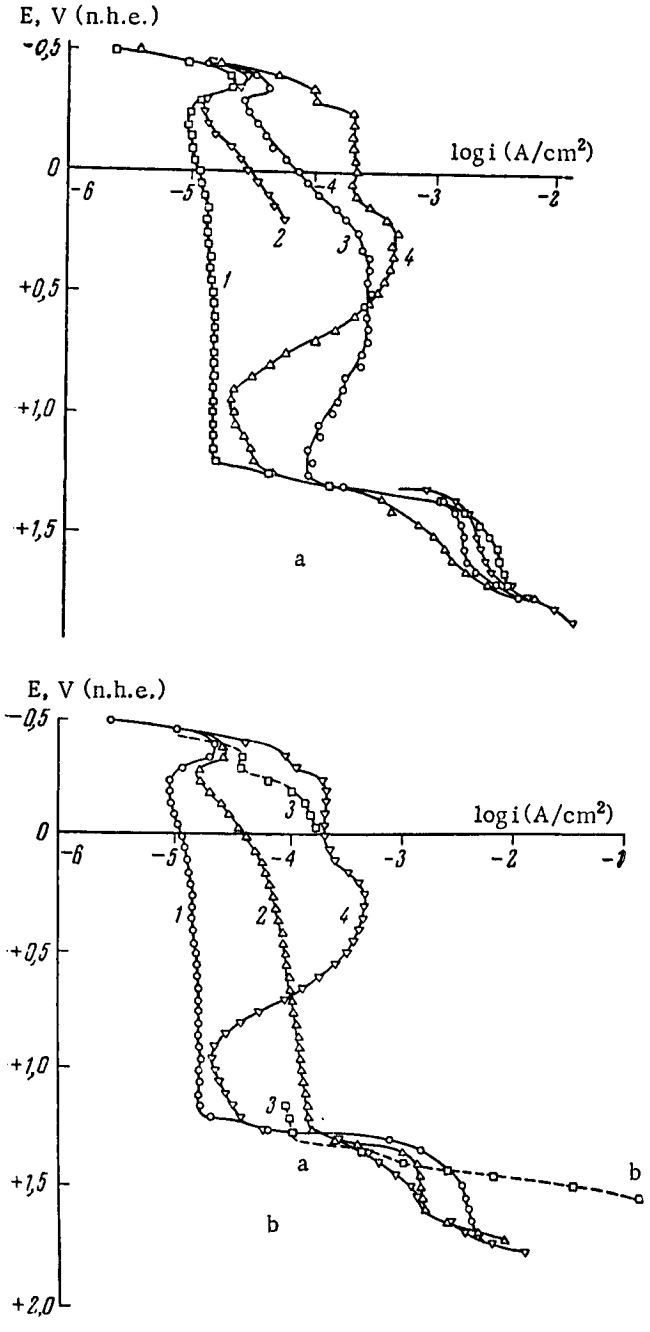

Fig. 2. Polarization curves in buffer solutions (pH = 8.4) at different concentrations of sodium nitrate (a) and with the addition of different salts to a concentration of 1.0 N (b). a: 1) 0; 2) 0.03 N; 3) 0.1 N; 4) 1.0 N. b: 1) without additional salts; 2) $NaNO_3$; 3) $NaClO_4$; 4) Na_2SO_4.

Experimental results show that halogen ions activate passive iron in the same way.

The effect of the concentration of Cl^{-1} ions on the activation of iron was investigated at a pH of 8.4 in solutions in which the concentration of Cl^{-1} was varied from 0.001 to 0.1 N. The smallest amount of Cl^{-1} leads only to a slight increase of the dissolution rate in the passive state at potentials between 0.4 and 1.0 V. However, at concentrations equal to or greater than 0.003 N the dissolution rate increases sharply after a certain potential E_{cr} is reached, and this can be seen by the occurrence of almost horizontal sections on the polarization curves. These sections are

characteristic of activation at the critical potential (see [7], for example). At the same time, a ten-fold increase in the concentration of Cl^{-1} ions displaces the value of E_{cr} toward more negative values by about 0.15-0.2 V, and this agrees satisfactorily with the results obtained in [9] for Fe-Cr Alloys.

The polarization curves in Fig. 3 indicate the effect of the type of anion. The value of E_{cr} increases in the sequence $Cl^{-1} < Br^{-1} < I^{-1}$ and the difference between the activation potentials of the neighboring ions in this series is $\simeq$ 0.1 V. Comparison of curve 3 in Fig. 2b (section ab) with the curves 2-4 in Fig. 3 shows that the activation potential of iron is shifted by the ClO^{-1} ions more than 1 V toward more positive values from the activation potential by the ions of the series indicated. This result indicates that in this type of activation the ClO_4^{-1} ions have a much lower activation capacity not only as compared to that of Cl^{-1} ions, as was noted before [6], but also as compared to Br^{-1} and I^{-1} ions.

In spite of the difference in the activation potentials, the results of the dissolution of activated iron are the same in KCl, KBr, KI, and $NaClO_4$ solutions; iron passes into the solution in the form of Fe^{+2} ions and $Fe(OH)_2$ is formed on the electrodes in little hills and hanging threads. The corrosion is of the pitting type; at a sufficiently high current density separate large lesions occur on the surface of the metal.

The addition of F^{-1} ions (0.01 N), unlike the addition of the anions, does not activate iron (curve 5, Fig. 3) [at higher concentrations of NaF or KF (0.1 N) the solution rate increases significantly within a wide range of potentials]. Similar results were obtained for aluminum [8].

DISCUSSION OF RESULTS

The results concerning the activation of iron by halogen ions differ from the results obtained in [11], where the authors concluded that the activation of iron in 1 N sulfuric acid is not related to any specific potential when the concentration of Cl^{-1} ions is between $3 \cdot 10^{-4}$ and $4 \cdot 10^{-3}$ N.

This difference is understandable if we take into account the value of E_{cr} at the concentrations of Cl^{-1} ions used. Since this value is independent of the pH within a wide range of pH values [6-9], we may assume that in the acid containing 0.003 N Cl^{-1} the activation potential is close to that we determined in neutral solution ($\simeq$ +0.2 V). Even if we do not take into account the fact that this value can be displaced toward positive values as the result of unsteady measurements, it is clear that it is much more negative than the passivation potential in the 1.0 N H_2SO_4 solution (+0.56 V). Therefore, iron should not be passivated in the acid with the indicated concentration of Cl^{-1} ions. If the Cl^{-1} ions are added after the passivation (keeping the potential in the passive region), as was done in the experiments described in [11], then pitting corrosion must develop within the whole range of potentials of the passive region. Thus, the results obtained in [11], contrary to the assumption made by the authors, should be explained not by the chemical mechanism of pitting corrosion but by the fact that the measurements were made at potentials more positive than E_{cr}.

Consequently, we may assume that when passive iron is activated by Cl^{-1}, Br^{-1}, I^{-1}, and ClO_4^{-1} ions, the same relationship holds true as in the case of the activation of metals by halogen ions; there is a critical activation potential and it is dependent on the nature and concentration of the anions. This makes it possible to examine the electrochemical theory [1] relating the occurrence and the development of passivation with the expulsion of the passivating oxygen by the halogen ions and their participation in the first stage of the dissolution reaction as a general basis for the explanation of the activation of metals undergoing passivation.

On the other hand, the anions mentioned may increase the dissolution rate of the passive metal also at potentials more negative than E_{cr}. The NO_3^{-1}, F^{-1}, and SO_4^{-2} ions also have the capacity to increase the dissolution rate of passive metals. The cause of this activation may be either the decrease of the protective properties of the whole passivating layer or the occurrence in the layer of separate centers with a low degree of passivity as the result of the effect of anions. The experimental results do not allow us to choose between these alternatives.

The experimental results concerning passivation in Na_2SO_4 solutions (pH = 7.4) indicate that during the increase of the potential the solution rate decreases within a narrow range of potentials E_2 and that this decrease is particularly clear at high concentrations of SO_4^{-2} (0.1-1.0 N). At a pH of 8.4 (Fig. 2a) there is also a region E_2 (0.4-0.5 V) where the solution rate is decreased even more, but not as much as at pH = 7.4.

In the absence of SO_4^{-2} ions, iron can be passive at potentials between E_1 and E_2. Therefore, we can assume that in this case SO_4^{-2} ions activate iron and that this activation is in some way due to the decrease of the degree of

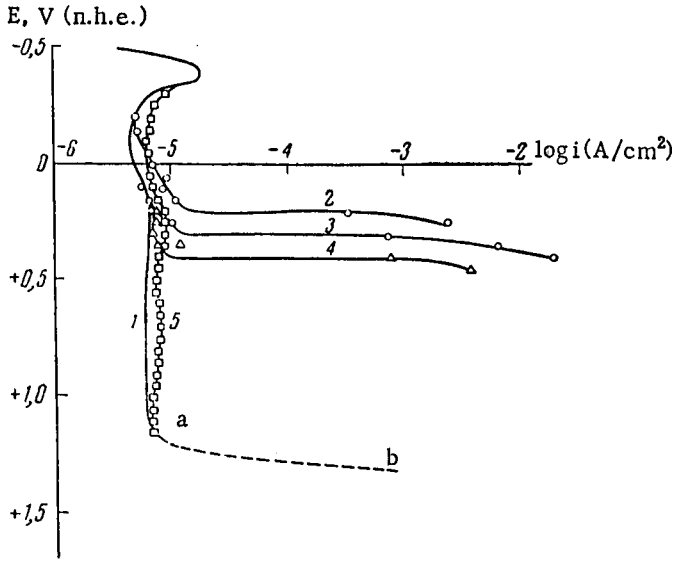

Fig. 3. Polarization curves in buffer solutions (pH = 8.4) containing halides at a concentration of 0.01 N. 1) Without additional salts; 2) KCl; 3) KBr; 4) KI; 5) NaF. Section ab of curve 1 corresponds to the oxygen evolution.

passivation of the whole surface or of separate areas of the surface. Then we may logically conclude that the decrease of the solution rate in the vicinity of E_2 is due not to the fact that the electrode is passivated first, but to the fact that there occurs a new deeper passivation related to the formation of a passive layer with greater protective properties. We may also assume that under the conditions investigated there exist two passivation potentials E_1 and E_2, which can be called the first and second passivation potentials.

The results obtained in solutions with pH = 7.4 are to some extent similar to the results of potentiostatic measurements with Fe electrodes in sulfuric acid. To explain the results of these measurements (see [12], for example) it is often considered that the deceleration of dissolution at potentials between the active and passive regions is due to the effect of the precipitate of iron sulfate, whose dissolution rate is limited by diffusion in the electrolyte. This assumption is improbable as an explanation of the deceleration of dissolution between potentials E_1 and E_2 in our case for the following reasons: 1) under the experimental conditions the solubility of iron hydroxides is much lower than that of the sulfates; 2) special experiments showed that mixing does not increase but somewhat decreases the solution rate; 3) the increase in the concentration of SO_4^{-2} ions (0-0.1 N) increases the solution rate; 4) the deceleration of the dissolution in Na_2SO_4 solution begins at the same E_1 potential as in the solution not containing SO_4^{-2} ions (the potentials at the points A, A', and A" on the curves in Fig. 1 practically coincide).

It should be noted that a number of hypotheses [13-16] which explain the passivation of iron in sulfuric acid contain the premise that the anions of the acid do not affect the passivation process. The results described exclude this assumption in the case of neutral solutions.

We may assume, on the contrary, that at potentials between E_1 and E_2 (region of the first passive state) the low solution rates exist only in the absence of significant amounts of SO_4^{-2} anions in the solution. In the second passive state ($E > E_2$) the low solution rates can exist also in the presence of considerable amounts of SO_4^{-2} anions in the solution.

A more detailed discussion of these problems together with additional experimental results will be given in the next publication.

CONCLUSIONS

1. We investigated the passivation of iron in borate buffer solutions to which different salts were added.

2. It was shown that halogen ions and also SO_4^{-2}, NO_3^{-1}, and ClO_4^{-1} ions increase the solution rate of metals within the passive region, while the Cl^{-1}, Br^{-1}, I^{-1}, and ClO_4^{-1} ions also activate the metal at certain potentials and induce pitting corrosion at certain activation potentials.

3. We discussed some problems of passivation of iron in neutral solutions and the activating action of anions of the solutions. It was noted that there exist two passivation potentials of iron in sodium sulfate solutions.

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