THE ELECTROCHEMICAL BEHAVIOR OF IRON IN NEUTRAL SOLUTIONS OF PHOSPHATES

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Phosphates are used in many cases for inhibiting corrosion of metals in neutral aqueous solutions. The mechanism of the protective effect of these compounds is debatable, but it is usually attributed to passivation of metals in media containing phosphates.

Mayne and Menter [1] showed that the surface film formed on iron during passivation in an aerated 0.1 M solution of Na_2HPO_4 consists mainly of γ-Fe_2O_3 and contains several percent of $FePO_4 \cdot 2H_2O$. The authors of [2-4] suggested that in this case the formation of γ-Fe_2O_3 is due to reaction of the metal with dissolved oxygen or oxidizing agent, the role of phosphate consisting in reduction of the rate of solution of the passivating oxide layer. In the opinion of these authors the iron phosphate in the surface film is formed by precipitation on the metal's surface of corrosion products from the solution as a whole and does not have protective properties. Furthermore, it is assumed that deposition of this salt impedes access of oxygen to the corresponding areas of the metal surface and thereby impedes formation of a continuous layer of γ-Fe_2O_3.

Therefore, it follows that the inhibiting effect of phosphates can only be displayed in the presence of a different type of oxidizing agent; this agrees with experimental data in [2, 5-7]. However, it is forgotten that the passivating effect of an oxidizing agent is not necessarily connected with its direct participation in oxide layer formation. Kolotyrkin and Bune [8] have shown that this effect may also be due to simple reduction of the oxidizing agent on the metal surface, leading to displacement of the metal's electrode potential to values more positive than the passivation potential.

It therefore seemed of interest to study the electrochemical behavior of iron in aqueous solutions of phosphates without an oxidizing agent.

METHOD

For the major part of the experiments we used the potentiostatic method for obtaining the anode polarization curves. Beginning with the stationary potential, the electrode potential was shifted towards the positive side at intervals of 50 mV, the residence time at each value being 30 minutes*. The measurements were performed in a three-electrode cell, using a P2B automatic electronic potentiostat as designed at the Karpov Institute. Some of the experiments were performed in flowing or mixed solutions. The rate of flow was 250 ml/h (the volume of solution in the cell was 40 ml). A magnetic stirrer was used for mixing the solutions.

For this work we used iron specimens of Hilger grade, with surface area 0.2 cm^2, made from 0.5 mm diameter wire. Before an experiment the specimen was cleaned with ethyl alcohol, etched in H_2SO_4 and washed twice with distilled water. The measurements were preceded by cathode polarization of the electrodes at potential -1.0 V for 5 minutes. The experiments were performed at 20° in purified nitrogen.

Buffer phosphate mixtures were used to keep the solution pH constant. In some experiments we used borate buffer solutions for studying the effect of phosphate ions on the solution kinetics of iron because Freiman and Kolotyrkin [9] have indicated that borate ions do not react with the surface of iron. The solutions were prepared from twice recrystallized KH_2PO_4 and Na_2HPO_4, boric acid, sodium borate and bidistillate. Changes in the borate concentration at constant pH were obtained by diluting

* In some experiments the curves were determined at a higher rate. These cases are dealt with separately below.

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with stronger solutions; changes in pH at constant overall borate content were obtained by changing the KH_2PO_4/Na_2HPO_4 ratio. The potential was measured with respect to a palladium electrode and converted to a n.h.e.

The rate of solution of iron was determined from the value of the anode current and in some cases was monitored by weighing the electrode and by photocolorimetric analysis of the solution for the iron content (using thioglycollic acid). In all cases it was found that the current is completely expended on iron solution (transfer of iron to solution, and formation of a film on the electrode).

During the process of solution the iron specimens were covered by films. To determine the nature of these films we subjected them to visual examination and metallographic and x-ray analyses. In this connection we used rolled specimens of Armco iron plate with surface area 2.5 cm^2.

EXPERIMENTAL RESULTS: DISCUSSION

Figure 1 shows the effect of phosphate on the anode behavior of iron in a borate solution at pH 7.1. In a pure borate solution (curve 1) electrode passivation begins at $\varphi_{pas} = -0.2$ V, the rate of solution being independent of potential in the range −0.05 to 1.4 V. At more positive potentials, evolution of oxygen begins. Addition of 0.033 g. mole/liter phosphate to this solution shifts the passivation onset potential (φ'_{pas}) 200 mV towards the negative side, with a simultaneous marked reduction in the critical passivation current. In this connection a characteristic feature is the appearance on the polarization curve of an additional break at the point φ''_{pas} demarcating the primary passivation range (I on curve 2), specific only for phosphate solutions, from the normal passivation range (II on curve 2), which is also observed in the absence of phosphate. The existence of a specific passivation range in phosphate solutions was also noted in a report by K. Z. Rajogopalan and others at the 3rd International Congress on Corrosion of Metals.

Therefore, in phosphate solutions the transition of iron to the normal passive state precedes its primary passivation (specific for the given solutions), which begins at markedly more negative potentials. It is logical to assume that the inhibiting effect of phosphate on iron corrosion is governed by the metal's behavior in the range of primary passivation potentials.

The character of this behavior depends on many factors, including the rate of potential displacement towards the positive side, phosphate concentration, and the mixing intensity.

Figure 2 shows the curves obtained in a mixed borate-phosphate solution at different rates of application of potential. Curves 1 and 3 were obtained at 100 and 400 mV/h respectively. A rate of

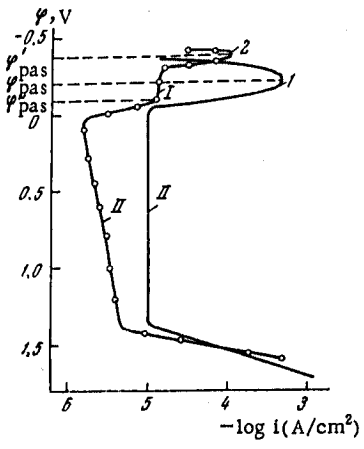

Fig. 1. Polarization curves measured on iron in buffer solutions (pH 7.1) of borate (1) and borate containing 0.033 M phosphate (2).

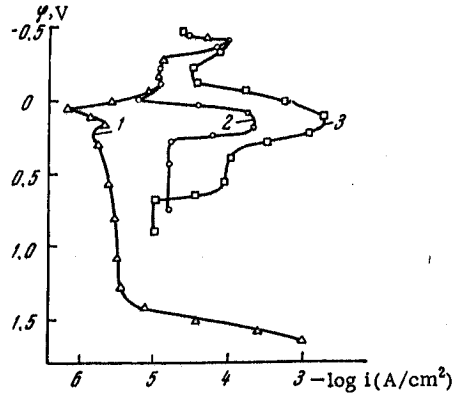

Fig. 2. Polarization curves measured on iron in 0.191 M borate + 0.033 M phosphate (pH 7.1) at the following rates (m/h): (1) 100; (2) 100 (below $\varphi = 0.1$ V) and 400 (at potentials more positive than −0.1 V); (3) 400.

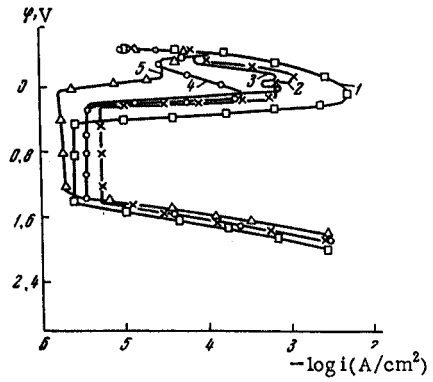

Fig. 3. Polarization curves measured on iron in buffer phosphate solutions at pH 5.9. Overall Na_2HPO_4 and KH_2PO_4 concentration (mole/liter): 1) 0.0165; 2) 0.033; 3) 0.066; 4) 0.0825; 5) 0.165.

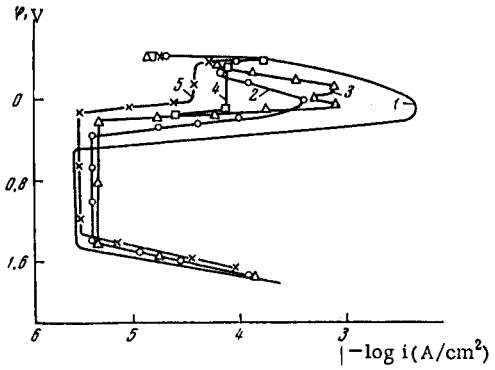

Fig. 4. The effect of mixing on polarization curves measured on iron in phosphate solutions of different concentration (pH 5.9): (1), (2) 0.0165 M; (3) - (5) 0.066 M. Curves 1 and 3 were measured without mixing of the solution; (4) in a flowing solution.

100 mV/h was also used for obtaining the initial sector of curve 2, the remainder of this curve (with potentials more positive than −0.1 V) was obtained at 400 mV/h. It will be seen that at the given phosphate concentration, over the whole potential range between φ'_{pas} and φ''_{pas} effective passivation of iron is observed only at a fairly low rate of potential application (100 mV/h). At higher rates only partial passivation is observed (in a narrower range of potentials); this is replaced by marked activation, beginning at a potential whose negative value increases with the rate of potential application. Activation is then replaced by passivation; however, it begins at markedly more positive potentials than in pure borate solutions with the same pH.

At constant rate of potential application and constant solution pH, the passivating efficiency of phosphate depends markedly on concentration. It will be seen from Fig. 3 that, beginning at a certain concentration, a decrease in phosphate content in the solution is accompanied by narrowing of the primary passivation range, with simultaneous widening of the activation range. At a sufficiently low phosphate concentration (in this case 0.0165 M) primary passivation is absent altogether. The same effect is observed with a fall in the solution pH. It will be seen from a comparison of curves 2 in Figs. 1 and 3, relating to the same phosphate concentration and rate of potential application, that a decrease in pH from, say, 7.1 to 5.9 is also accompanied by a narrowing of the primary passivation range and by the appearance of an activation sector on the polarization curve.

The relationship between the primary passivation efficiency and hydrodynamic conditions is very important for understanding the mechanism governing the effect of phosphates. It will be seen from Fig. 4 that by agitating the solution with a stirrer or making it flow we greatly extend the primary passivation range and impede or eliminate activation.

When electrodes are kept in phosphate solutions at potentials corresponding to the primary passivation range, compact phase films are formed on the metal surface, differing in external appearance from the loose porous films formed in the activation range. This difference is illustrated by the photomicrographs in Fig. 5. X-ray structural analysis showed that these films correspond in composition to the crystalline salt $Fe_3(PO_4)_2 \cdot 8H_2O$, the film obtained under iron activation conditions also displaying an admixture of an amorphous substance. No iron oxides were observed in the film. It was also established that the salt precipitate formed during solution of iron was amorphous.

From the x-ray structural analysis of the film, and not forgetting that retardation of iron solution in phosphate solutions begins at markedly more negative potentials than in borate solutions with the same pH, it is logical to infer that in this case primary passivation is due not to formation of oxide layers but to coating of the metal surface by an iron phosphate film.

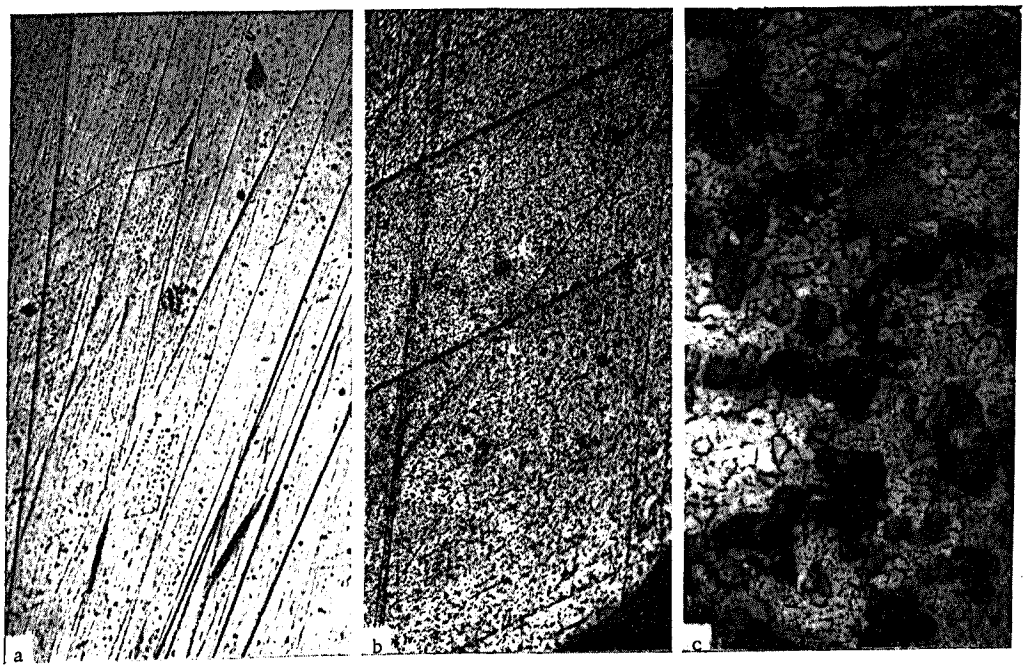

Fig. 5. Photomicrograph of the surface of iron after residence in a 0.066 M phosphate solution (pH 5.9) at steady potential (a) and in anode polarization conditions at the following potentials: (b) $\varphi = -0.32$ V; (c) $\varphi = -0.2$ V (× 225).

The formation of such a film can have one of two possible mechanisms. The simplest case is precipitation of iron phosphate from the solution owing to supersaturation of the near-electrode layers with solution products. However, this mechanism does not agree with the effect exerted by mixing on phosphate efficiency in the primary passivation range. If the mechanism were the true one, mixing would obviously promote removal of the solution products from the metal surface and thereby impede, rather than assist, formation of a phosphate film [10,11].

The other mechanism, clearly the most probable one, is direct formation of a phosphate film on the surface of the dissolving metal by adsorption of the corresponding ions and their subsequent reaction with the surface atoms of the metal, as follows:

$$\text{Fe} + (\text{phosphate-ion})^{n-}_{ads} \rightarrow \text{Fe(II) phosphate} + m\bar{e}\,. \qquad (1)$$

The authors of [12-14] have already indicated that such reactions can lead to formation of salt layers with protective properties, in contrast to the layers deposited from solution. This hypothesis readily explains both the effect of mixing and the relationship (established by the present authors) between the primary passivation potential and the phosphate concentration. Separate experiments showed that an

Concentration of the solution studied, mole	Electrode potential, V	Duration of expt., h	Increase in wt of specimen, g	Amount of Fe^{2+} combined in the precipitate in the solution as a whole (from colorimetric analysis data)	Amount of Fe^{2+} in the film on the specimen's surface, from colorimetric and gravimetric analysis data (in terms of $Fe_3(PO_4)_2 \cdot 8H_2O$), g
0.066	-0.32	4.0	$1.6 \cdot 10^{-3}$	$5.35 \cdot 10^{-4}$	$1.22 \cdot 10^{-3}$
"	"	2.5	$2.3 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$	$1.61 \cdot 10^{-3}$
"	"	4.5	$1.7 \cdot 10^{-3}$	$4.11 \cdot 10^{-4}$	$1.07 \cdot 10^{-3}$
0.165	-0.2	4.5	$2 \cdot 10^{-4}$	$2.96 \cdot 10^{-3}$	$1.59 \cdot 10^{-3}$

increase in concentration by a factor of 10 is accompanied by displacement of φ'_{pas} by 40 mV towards the negative side*. This mechanism also agrees with data of Brasher [15], who concluded that a phosphate-ion adsorption potential is present on iron (−0.43 V for 0.1 M Na_2HPO_4).

An appreciable amount of iron phosphate deposit is formed not only on the metal surface but also in the solution. This indicates that under these conditions iron solution is effected not only by reaction (1) but also by the usual mechanism†:

$$Fe \rightarrow Fe^{+2} + 2e \quad (2)$$

$$3Fe^{+2} + 2PO_4^{-3} + 8H_2O \rightarrow [Fe_3(PO_4)_2 \cdot 8H_2O]_{\text{precipitate}} \quad (3)$$

Owing to possible deposition of part of the precipitate on the electrode surface, we cannot separate analytically the iron ions formed from (1), on the one hand, and from (2) and (3), on the other. However, if we assume (as above) that the surface layer formed from (1) has a protective effect on iron, its thickness may be assessed from the potential decay curve after the current has been switched on. These curves show that displacement of the potential to a value equal to the steady potential (established immediately after the iron has been placed in the phosphate solution) is rapid and is not accompanied by the appearance of lags on the curves; this evidently indicates that the protective layer is very thin.

Nevertheless, various determinations showed that the amount of iron salt on the electrode surface after its polarization in phosphate solutions is fairly high (cf. the table). Bearing in mind the above hypothesis regarding the thickness of the protective effect, this result means that the protective layer on iron consists of two layers: a thin protective layer, and a thicker layer without passivating properties. The deposit composition, as determined by x-ray analysis, corresponds to the upper layer. Therefore, in a general case the composition of the passivating layer cannot be identified with that found by x-ray analysis.

Reactions (2) and (3) must inevitably lead to a fall in phosphate-ion concentration at the metal surface and therefore to retardation of (1), which is the reaction leading to passivation. Bearing this in mind, we can evidently explain the activation of iron. We need to assume only that all the factors favoring the appearance of the activation effect increase the proportion of the current consumed on solution of iron in accordance with (2). This leads in turn to faster and more extensive depletion of the phosphate ions near the electrode, thanks to formation of iron phosphate by (3).

These hypotheses obviously cannot explain the marked positive shift of the ensuing iron passivation potential. Such a shift is logical if we assume that it is caused or accompanied by a marked fall in pH of the solution near the electrode.

It will be shown in the next paper that our results and the arguments developed enable us to explain why phosphates are effective corrosion inhibitors only in the presence of an oxidizing agent, no appeal being made to direct participation of the latter in the formation of the passivating layer.

SUMMARY

1. In neutral phosphate solutions transition of iron to the optimum passivation state precedes its primary passivation at potentials more negative than the normal passivation potential of iron in a phosphate free solution at the same pH.

2. In certain conditions, iron present in the primary passive state may be activated.

3. Primary passivation of iron is promoted by an increase in phosphate concentration and residence time, and by mixing of the solution.

4. Factors promoting passivation impede the activation of passive iron.

5. It is concluded that phosphate ions participate directly in formation of the passive layer, and a mechanism is proposed for this process.

* In Fig. 3 the scale selected does not allow this effect to be observed.

† (2) is given in general form without allowing for participation by the anions.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.
