BRIEF COMMUNICATIONS

INFLUENCE OF THE ACIDITY OF THE MEDIUM ON THE PASSIVATION POTENTIAL OF IRON

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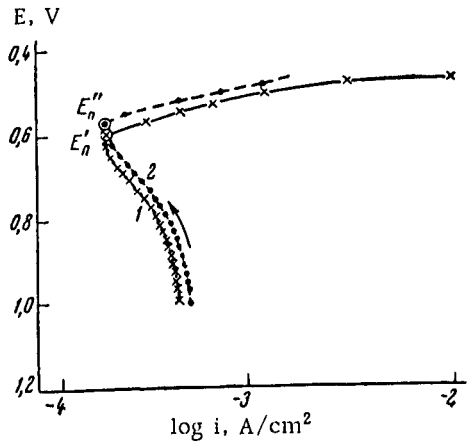
Authors of various investigations have based their studies on the influence of the pH of the solution on the passivation potential of iron on the explicit or implicit assumption that the passivation process is determined only by a given interaction in the metal-water system in which the anions of the solution do not play any significant role. Therefore, in selecting media for experimental determination of the dependence of the passivation potential (E_p) on the value of the pH the anion composition of the solution was not kept constant. The dependence of E_p on the pH of the solution found in [1] under these conditions is as follows: $E_p = 0.58 - 0.058$ pH. Later, the authors in [2] obtained a similar equation with the difference that the coefficient of the second term was larger (0.10). In these investigations the value of E_p was considered to be identical to the potential of the point at which the rate of change of the potential slows down before it drops after the anodic polarization is turned off, i.e., it was identified with the so-called Fladepotential. The experimental dependence of E_p on the pH was one of the starting points of the phase theory of passivity according to which the passivation process was assumed to be a reaction of the following type:

$$n\,\mathrm{Me} + m\,\mathrm{H_2O} = \mathrm{Me}_n\mathrm{O}_m + 2m\mathrm{H}^+ + 2me.$$



Anodic polarization curves of iron in a 1 N Na_2SO_4 solution with the following values of pH: 1) 1.95; 2) 8.5.

According to the data in [3], one would expect the Frank equation to be valid for both acid and neutral solutions. However, it was shown in [4] that the second iron passivation potential in a neutral solution of sodium sulfate determined by the method of polarization curves and by the curves of the drop of potential is close to + 0.5 V. Such a high value of E_p, close to the mentioned data for acid solutions, leads us to doubt the validity of the Frank equation in the case where the anion composition of the solution is constant.

Therefore, we made experiments in order to measure the value of E_p at a constant concentration of SO_4^{2-} ions in the solution equal to 1 g-eq/liter. Iron samples after ordinary preparation were passivated in a 1% solution of $K_2Cr_2O_7$ for 10 min, were then connected to a potentiostat, and were then introduced into the cell at a given potential equal to +1.0 V with respect to the normal hydrogen electrode. After the current was relatively stable we drew the polarization curves by shifting the potential toward negative values by a jump of 20 mV and then kept the sample at this potential for 2 min. The measurements were made at 20°C in an atmosphere of nitrogen. By

pH	Experimental value of E_p, V	Values of E_p calculated by Frank's equation, V
1.95	0.60	0.467
3.3	0.57	0.389
5.3	0.57	0.273
7.3	0.58	0.157
8.5	0.57	0.087

special experiments we showed that when the treatment with potassium bichromate was excluded or when the rate of displacement of the potential was reduced the value of E_p (potential of the beginning of the sharp increase in the current – see figure) does not change.

The results of the experiments summarized in the table show that at values of pH between 2 and 8.5 the passivation potential is practically independent of the acidity of the solution. At pH $\ll$ 2, for example, in a 1 N H_2SO_4 solution the condition under which the concentration of SO_4^{2-} ions is constant is apparently satisfied – HSO_4^- ions predominate in the solution.

It seems to us that the result obtained here should be considered more correct than the result obtained in the publication cited above, where the variation of the pH was accompanied by a change in the anion composition of the solution. The independence of E_p on the pH in a solution of sodium sulfate sharply contradicts the existing concepts concerning the passivation of iron by an oxide film. This indicates the necessity of reexamining the theory for conditions in which anions present in the solution can strongly interact with the metal.

LITERATURE CITED

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