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Abstract

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Pitting Corrosion of Iron by Perchlorate Ions

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Literature data on the influence of ClO_4^- ions on the corrosion and electrochemical behavior of metals are quite few and do not provide a clear picture of this question. In corrosion experiments, Hoar (^{1,2}) observed that, under certain conditions, in the presence of an oxidizing agent, ClO_4^- ions cause pitting corrosion of tin and iron. On the basis of these data, Hoar proposed the so-called acid theory of pitting development, which relates the growth of pits to the fact that such anions as ClO_4^- and Cl^- give the corresponding strong acids inside the pits. On the other hand, according to Piontelli' s theory (^{3}), developed on the basis of studies of the influence of anions on the electrochemical behavior of metals under weak polarizations, ClO_4^- ions should exert an inhibiting effect on the dissolution of metals owing to the low catalytic activity of the ClO_4^- ion, which is due to its low polarizability. Vanyukova and Kabanov (^{4}), studying the electrochemical behavior of an Fe electrode in alkaline solutions by the charging-curve method, found that ClO_4^- ions activate iron, but more weakly than Cl^- ions, and explained this effect by adsorption displacement of passivating oxygen by the corresponding anions. Later, Kashcheev, Leikis, and Kabanov (^{5}), who studied the anodic behavior of Fe in acid solutions by the potentiostatic method, detected activation of passive iron in $1N$ $HClO_4$ at a potential near +1.3 V (on the n.h.e. scale). The almost horizontal course of the polarization curve in the activation region is analogous to the corresponding curve for zirconium in solutions containing halide ions (^{6}); however, in the latter case the activation is expressed in the development of pitting corrosion, whereas in work (^{5}) no data are given on the character of corrosion of the activated electrode.

In our study of the electrochemical behavior of iron in neutral solutions, data were obtained showing the local character of the activation of passive iron by ClO_4^- ions. The Armco-iron specimens used were, before the experiment, cleaned with corundum paper and glass powder, degreased with ethyl alcohol, and washed twice with distilled water. The experiments were carried out in a combined cell made of polyethylene and glass, with the specimen pressed by a special clamp against an opening (3 mm in diameter) in the polyethylene body of the cell, after which the cell was filled with solution. This design, in particular, made it convenient to study the character of corrosion of the metal at a small working surface. For preparing the solutions, three-times recrystallized salts Na_2SO_4 and $NaClO_4$ and twice-distilled water were used. The experiments were conducted in an atmosphere of nitrogen purified of oxygen impurity. As the measurement method, a quasi-potentiostatic method was used: the electrode was held at each specified potential for a constant time (from 30 sec to 1.5 hr). The graph gives the current-density values in the last second of the holding period. The potential was set in increments of 50 mV.

The measurement results show (Fig. 1) that, in contrast to the behavior in Na_2SO_4 solution, where at high anodic potentials on the electrode

oxygen evolution begins; in a solution of $NaClO_4$, when the potential is increased from 1.41 to 1.46 V, a sharp increase in the dissolution rate occurs (by approximately 3 orders of magnitude). After the curve was recorded, distinct large pits were visible to the naked eye on the electrode surface (for ease of comparison with the results of other experiments, the corresponding microphotograph is shown in Fig. 2a). Special experiments showed that pit formation occurred only in the indicated narrow range of potentials.

Analogous activation in the same potential range occurred during anodic polarization of iron in a solution of $1N$ $NaClO_4 + 0.01N$ KOH; however, the pits that formed were narrower and deeper (Fig. 2b). Experiments were also carried out to clarify the nature of corrosion during activation of iron in $1N$ $HClO_4$, observed by the authors (5). For technical reasons, in this case the galvanostatic method was used. On the reverse branch of the polarization curve (Fig. 3), sharp potential oscillations occur in the segment *cd* (±150 mV and more), and small potential oscillations (±20 mV) occur in the nearly horizontal segment *de*, corresponding

Fig. 1. Quasi-potentiostatic anodic polarization curves of an Fe electrode (holding time at each potential 30 sec).
a $-1N$ Na_2SO_4, b $-1N$ $NaClO_4$

Fig. 2. Microphotographs of pits formed during activation of iron in various solutions (×130),
a $-1N$ $NaClO_4$; b $-1N$ $NaClO_4 + 0.01N$ KOH;
c $-1N$ $HClO_4$

to a potential of +1.37 V. This value is in satisfactory agreement with the data of work (5) for the activation potential. In the region of active dissolution, the corrosion had a uniform character, whereas after recording the forward and reverse branches of the curve, the electrode surface contained many small pits, whose density increased from the edge toward the center of the working surface of the electrode (Fig. 2c).

The data presented show that activation of iron by ClO_4^- ions

in neutral, alkaline, and acidic solutions is associated with pitting corrosion of the metal. In developing the explanation of activation proposed by the authors of work (5), it should be assumed that displacement of the passivating oxygen by ClO_4^- ions occurs at localized areas of the surface. As in the case of activation by halide ions, this leads to the subsequent development of pitting corrosion.

Fig. 3. Galvanostatic anodic polarization curve of the Fe electrode in

1N $HClO_4$:
abc –forward run, *cdef* –reverse run

The constancy of the potential over a broad range of current densities during activation, in accordance with the conclusions of work (6), can be explained by an increase in the size or number of pits with increasing current density. As in the case of activation by halide ions (6, 7), the activation potential of iron by ClO_4^- ions depends only very weakly on the pH of the solution. However, pH has a considerable effect on the shape, dimensions, and density of the pits (Fig. 2).

As Engell and Stolica (8) showed, activation and pitting corrosion of iron by Cl^- ions are not associated with any definite critical potential. The existence of such a potential during activation by ClO_4^- ions indicates significant differences in the adsorbability of Cl^- and ClO_4^- ions on the surface of iron. Comparing the results obtained in works (6, 7) and in the present work, it may be concluded that the activation potential of the metal by ClO_4^- ions is considerably more positive than the activation potential by halide ions. This shows that the ability of ClO_4^- ions to activate the metal and cause pitting corrosion is expressed much more weakly than that of halide ions. In particular, this difference is manifested in the difference in the effectiveness of protecting the metal against corrosion by chromium additions. Under the experimental conditions, chromium steel 1Kh13, containing $\sim 12.5\%$ Cr, was not subject to activation and pitting corrosion, whereas, according to the data of work (7), such steel is activated comparatively readily by halide ions.

Note added in proof. After our work had already been submitted for publication, an article by B. N. Kabanov and V. D. Kashcheev (9) appeared, the data of which, naturally, could not be taken into account in the present work.

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