THE ANODIC ACTIVATION OF IRON

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In the anodic polarization of certain previously passivated metals it is observed that the corrosion rate begins to increase as soon as the potential takes on a sufficiently high positive value. This effect can be due to either superpassivation or anodic activation of the metal. Superpassivation involves dissolution of the metal and the oxide film with the formation of ions of higher valence, and thus leads to an increase in the rate of passage of metal into solution [1-3]. The situation is different when the metal is anodically activated. Study has been made of the activation of iron by Cl^- and ClO_4^- ions in anodic polarization, but only in alkaline media [4]. Here it has been shown that the activation proceeds only after the potential has taken on a definite, and rather high, positive value. Activation leads to the adsorption of chlorine on a portion of the electrode surface, with displacement of the adsorbed oxygen and hydroxyl groups. This reduces the passivation which has impeded the process: $Fe \rightarrow Fe^{2+} \rightarrow Fe(OH)_2$, without diminishing it so far as to result in a completely active electrode [9]. The fact that the activating action of the ClO_4^- ion is weaker than that of the Cl^- ion is to be explained in terms of the ability of the ClO_4^- to adsorb on iron and displace oxygen.

It has seemed to us that it would be of interest to explain the fact that iron will undergo anodic activation even in acidic media, the more so since an understanding of this process could aid in establishing the mechanism of passivation and the nature of the passive state. It is well known that some authors [5-7] have assumed the passivation of an iron group metal to be due to the formation of a blocking film phase on the metallic surface, while others [8, 9] consider it to be the result of the adsorption of oxygen by the metal.

The iron employed for the electrodes of these experiments had been prepared electrolytically, remelted in an atmosphere of purified hydrogen, and then drawn to wires 0.2 mm in diameter.* Each such wire was freed of traces of grease and vacuum-fused in glass. Prior to measurements, a 1-4 mm length of the electrode was freed by grinding away the glass on a small emery wheel. The surface of the electrode was then cleaned with moist glass powder, degreased in boiling 2 N alkali, and washed with doubly distilled water. Measurements were made in solutions of doubly distilled sulfuric and hydrochloric acids whose concentrations ranged from 1 to 5 N.

The anodic behavior of iron was studied by developing polarization curves and measuring capacitances. Potentials were established with an electronic potentiostat which had a coefficient of amplification ranging up to 50,000 and a time constant of 10^{-5} sec.** Potential displacement in the anodic region was carried out stepwise, usually over 100 mV intervals. An ÉNO-1 oscillograph was used to record current changes over a fixed time interval following potential alteration. Measurements of the capacitance and the ohmic component of the electrode impedance were carried out during development of the polarization curve by making use of a standard bridge circuit.

The curves of Fig. 1a show the dependence of current on potential for iron in 1 N H_2SO_4, while those of Fig. 1b show the same dependence for iron in 1 N $HClO_4$. Over the A-B segments of each of these curves, the dependence of current on time under potential displacement is similar to that observed by others [3, 5], instantaneous increase in the current (Fig. 2A, a) being followed by a rapid return to the original value as a result of an increase in the passivity of the electrode (Fig. 2 A, b). Further stepwise increase in the potential leads to different curve forms for the two acids.

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*These iron wires contained 0.005% Ni and 0.003% Cu. The amounts of other alloying materials were below the sensitivity limit of the spectral analysis.

**This potentiostat was constructed by L. L. Knots and V. N. Alekseev, to whom we express our thanks.

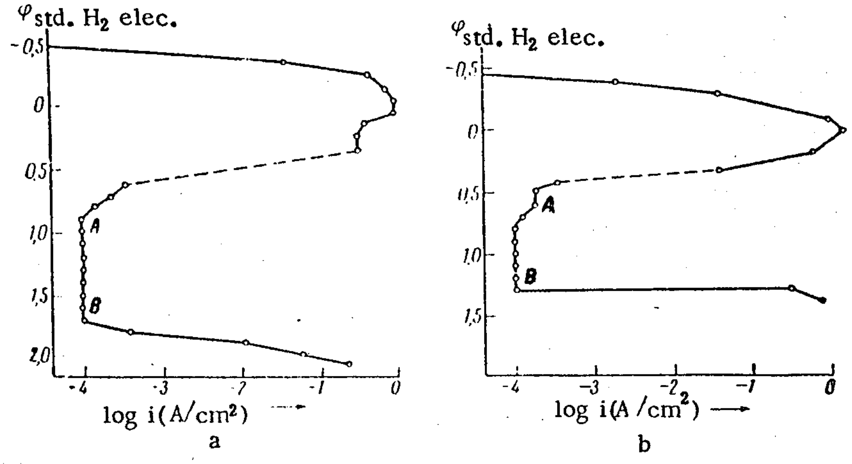

Fig. 1. Potentiostatic anodic polarization curves, developed in 1 N H_2SO_4 (a), and in 1 N $HClO_4$ (b).

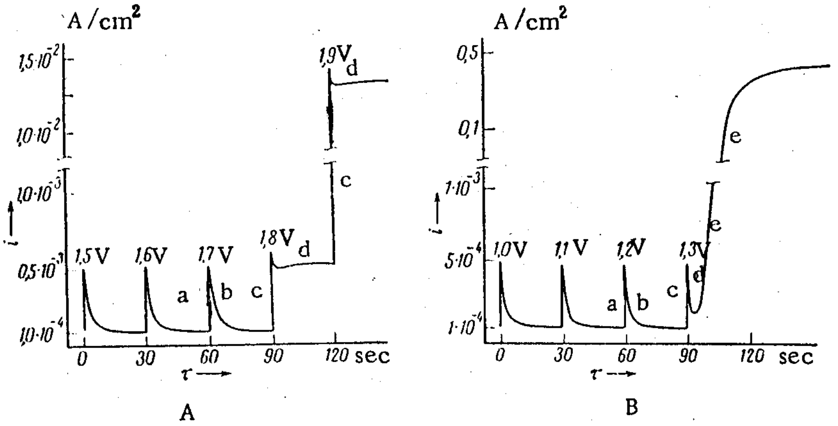

Fig. 2. Oscillographic curves showing the time alteration of anodic current density after potential displacement (at fixed potential) in 1 N H_2SO_4 (A), and in 1 N $HClO_4$ (B).

In sulfuric acid, the initial increase in the current proceeds almost instantaneously, just as before (Fig. 2A, c), but the passivational reduction of the current is diminished (superpassivation) (Fig. 2A, d). The stationary values of the current strength and potential follow the Tafel law (Fig. 1a). In the perchloric acid, it is observed that stepwise increase and rapid reduction of the current (Fig. 2B, c, d) are followed by a considerable rise in the current. The current increases by 2 or 3 orders even for a potential alteration of only 0.05-0.1 V (Fig. 2B, e). The current begins to increase from anodic activation at potentials which are less positive than those required for initiating superpassivation in sulfuric acid. The new current value is established in the course of several tens of seconds. The relatively slow change in the current strength points to a chemical alteration of the electrode surface [10] which leads, first to a slight retardation, and then to a high acceleration, of the dissolution of iron. Thus it has been shown that anodic passivation of iron in acid solution can be accompanied by anodic activation. The rate of the process Fe → Fe (II) after anodic activation in perchloric acid solution is, at fixed potential, much less than the rate of the anodic reaction Fe → Fe (II) on cathodically activated iron, the situation being the same here as in alkaline solutions [4].

It can be assumed that the anodic activation of iron in perchloric acid solution is adsorptional in character.* This is indicated by the fact that this very great increase in the reaction rate occurs over a narrow potential interval. The

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*The adsorption of ClO_4^- ions on platinum in this region of potentials is shown by the data of M. A. Gerovich and R. I. Kaganovich [11], who have studied the mechanism of the anodic evolution of hydrogen on platinum in H_2SO_4 and $HClO_4$ by a combination of electrochemical methods and methods involving labeled atoms.

small alteration in the differential capacity of iron from passivation after previous anodic activation also indicates the passivation in perchloric acid to be adsorptional. The formation and removal of an oxide film phase from the metallic surface would lead to a more pronounced alteration in the capacity [8].

The gradual change in the current which is observed during anodic activation of iron in perchloric acid is an indication of the low rate of desorption of the passivating oxygen, the latter being displaced from the surface by the ClO_4^- ion adsorption.

Thus it can be concluded that anodic activation of iron takes place in perchloric acid solutions, this being the result of the specific adsorption of ClO_4^- ions at definite potential with the reversible displacement of the adsorbed oxygen from the electrode surface. The phase film is, at the same time, irreversibly eliminated from the surface. The adsorbed ClO_4^- ions also retard the dissolution of iron, but to a much lower degree than the adsorbed passivating oxygen. The opposite effect has been observed in the ionization of hydrogen [12].

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