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Abstract

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ANODIC ACTIVATION OF IRON

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During anodic polarization of certain previously passivated metals, beginning at sufficiently positive values of the potential, an increase in the corrosion rate is observed. This may be a consequence either of transpassivation of the metal or of its anodic activation. In transpassivation both the metal and the oxide film dissolve with the formation of ions of higher valence, as a result of which the rate of dissolution of the metal also increases ([1]-[3]). A different picture is found in the anodic activation of metals. The activation of iron by Cl^- and ClO_4^- ions was studied under anodic polarization only in an alkaline medium ([4]). It was shown that activation occurs only upon attainment of definite, sufficiently positive potentials. Activation is caused by the adsorption, on part of the electrode, of chlorine, which displaces adsorbed oxygen or hydroxyl from the surface. This diminishes the passivation which had prevented the process $Fe \rightarrow Fe^{2+} \rightarrow Fe(OH)_2$ from proceeding, but does not reduce passivation to the degree corresponding to a fully active electrode ([9]). The activating action of the ClO_4^- ion, weaker than that of Cl^- ions, is also explained by the ability of the ClO_4^- ion to adsorb on iron, displacing oxygen.

We considered it of interest to clarify the question of the existence of anodic activation of iron also in an acid medium and to determine the causes of this phenomenon, especially since a correct understanding of this process may help in establishing the mechanism of passivation and the nature of the passive state. As is known, in some studies ([5]-[7]) it is assumed that the cause of passivation of metals of the iron group is the formation on the metal surface of a blocking phase film; in others ([8],[9]), that passivation is the result of adsorption of oxygen on the metal surface.

The iron used for the electrodes in our experiments was deposited electrolytically, then remelted in an atmosphere of purified hydrogen and drawn into wire 0.2 mm in diameter*. The wire, cleaned of traces of lubricant, was sealed into glass in vacuum. Before measurement, the required part of the electrode, 1-4 mm long, was freed from the glass by grinding on a fine emery wheel; the electrode surface was then cleaned with moist glass powder, degreased in boiling 2 N alkali, and washed with bidistilled water. Measurements were carried out in solutions of twice-distilled sulfuric and hydrochloric acids, with concentrations from 1 to 5 N.

Figure 1

Figure 1: Figure 1

The anodic behavior of iron was studied by recording polarization curves and by measuring capacitance. The potential was set with an electronic potentiostat with an amplification factor up to 50,000 and a time constant $T = 10^{-5}$ sec.** The potential was shifted into the anodic region by the potentiostat in steps, as a rule with an interval of 100 mV. [[unclear: continuation cut off at bottom of page]]

* The iron wire contained 0.005% Ni and 0.003% Cu. The amount of other impurities was below the sensitivity limit of spectral analysis.
** The potentiostat was designed by L. L. Knots and V. N. Alekseev, to whom we express our gratitude.

the change in current for a certain interval of time after the potential shift was recorded on an ÉNO-1 oscillograph. Measurement of the capacitive and ohmic components of the electrode impedance, carried out simultaneously with the recording of the polarization curves, was performed by the usual bridge circuit.

Figure 1a gives the curves of the dependence of current on potential for iron in 1 N H_2SO_4, and Fig. 1b for 1 N $HClO_4$. In the region (A—B) of both curves the character of the change of current with time upon a potential shift is analogous

Fig. 1. Potentiostatic anodic polarization curve recorded in 1 N H_2SO_4 (a) and in 1 N $HClO_4$ (b)

to that observed by other authors (3,5): after an instantaneous increase in current (Fig. 2 A, a) there occurs a rapid decrease of it to its former value as a consequence of an increase in the degree of passivity of the electrode (Fig. 2 A, b). With a further stepwise increase in potential, the course of the curves is different for each of the acids. In sulfuric acid the initial increase in current still occurs practically instantaneously (Fig. 2 A, c), while the passivating decrease in current is diminished (repassivation) (Fig. 2 A, d). The stationary value of the current and potential obeys the Tafel law (Fig. 1a). In perchloric acid, after a stepwise increase and rapid decrease (Fig. 2 B, c, d), a large increase in current was observed. The current increases by 2-3 orders of magnitude with a stepwise change in potential of only 0.05-0.1 V (Fig. 2 B, e). The increase in current associated with anodic activation begins at a value less positive than the potential for the onset of repassivation in a sulfuric acid solution. A new value of the current is established over tens of seconds. The relatively slow change in current indicates a chemical change of the electrode surface (10), leading at first to a slight retardation and then to a great acceleration of iron dissolution. Thus, we have established that in an acid solution, along with anodic passivation, anodic activation of iron can occur. As in alkaline solutions (4), in perchloric acid the rate of the process Fe → Fe(II) after anodic activation, referred to equal potentials, is much lower than the rate of the anodic process Fe → Fe(II) on cathodically activated iron.

It may be supposed that the anodic activation of iron in perchloric acid is of an adsorption character*. This is indicated by the small interval of potential change in which such a considerable increase in the rate of the process occurs. The small magnitude of the change in the differential capacitance of iron upon passivation after preliminary anodic activation also indicates the adsorption character of the passivation of iron in hydrochloric acid. The formation and removal from the metal surface of a phase oxide film leads to a more substantial change in capacitance (^{8}).

The slow change of the current with time, observed during the anodic activation of iron in hydrochloric acid, indicates a low rate of desorption of the passivating oxygen displaced from the surface by adsorbing ClO_4^- ions.

Fig. 2. Oscillographic curves of the change in anodic current density with time, observed after a shift of potential (at constant potential) in 1 *N* H_2SO_4 (**A**), in 1 *N* $HClO_4$ (**B**)

Thus, it may be concluded that in hydrochloric acid solutions anodic activation of iron occurs, caused by the fact that at a certain potential there is specific adsorption of the ClO_4^- ion, which reversibly displaces adsorbed oxygen from the electrode surface. At the same time a phase film is irreversibly removed from the surface. Although the adsorbing ClO_4^- ion also slows the rate of the iron-dissolution reaction, it does so to a much lesser extent than the adsorbed passivating oxygen. The opposite effect was observed in the case of the hydrogen ionization reaction (^{12}).

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* The existence of adsorption of ClO_4 ions in this region of potentials in the case of platinum is indicated by the data of M. A. Gerovich and R. I. Kaganovich (^{11}), who studied the mechanism of the anodic process of oxygen evolution on platinum in H_2SO_4 and $HClO_4$ by combining electrochemical methods with the method of labeled atoms.

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