MECHANISM OF ANODIC DISSOLUTION OF IRON AT HIGH CURRENT DENSITIES

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In determining the mechanism of the initial period involving rapid anodic dissolution of metals it is of interest to carry out tests with the pulse method. To avoid considerable variations in concentrations at the electrodes and local overheating at high current densities it is necessary to pass a stream of electrolyte at high rate through the gap between the electrodes [1]. Investigations of anodic dissolution kinetics at high current densities are usually hampered by specific electrolysis conditions—high flow rate of the electrolyte, short distance between the electrodes, and high electric field gradient in the solution. Moreover complications can also arise from variations in the true surface area of the electrode and in the distance between the electrodes on account of rapid dissolution of anode [2].

To investigate the anode dissolution process we employed a method involving the passage of short, high, direct current pulses through the electrolytic cell. In this method, even at very high currents, the layer of metal which suffers the pulse over a fairly short period of time is extremely thin, and this provides constant conditions under which the measurements can be made. The potential measurements were made oscillographically after the polarizing current had ceased, and the required electrode potential value was calculated by extrapolation to zero time with the Frumkin formula [3], which takes account of the exponential variation of the electrode process rate with potential and the capacity parameters of the whole electrode system. The pulse generator was a specially designed oscillator producing pulses between 5 and 2000 μsec in length with a current up to 50 A and a decay time of 0.5 μsec.

Owing to the unsuitability of the calomel or mercury-sulfate reference electrodes, which because of the high resistance of the electrolytic circuit have a high electric time constant [2], for the pulse measurements reference electrodes with low time constant made from wire of a metal close to composition to the investigated metal were used. The readings were reduced to a known scale by measuring the potential of the reference electrode against a supplementary calomel half cell without current.

EXPERIMENTAL

The investigations were carried out on Hilger and Armco iron electrodes in cells with separate anode and cathode compartments. In all cases except those specially mentioned a 4.5 N sodium chloride solution, buffered to the required pH with mixtures of $H_3BO_3 + Na_2B_4O_7$ or $H_3BO_3 + Na_2CO_3$, was used as electrolyte. As a rule the electrodes were polarized with 20 μsec current pulses, but longer pulses were used in some experiments. Some of the measurements were made by a potentiostatic method. The potentials are given in relation to the normal hydrogen electrode. The content and valency state of the iron in the solution were determined photocolorimetrically from the color of Fe(II) complexes with o-phenanthroline. The total Fe (II) and Fe (III) content was determined in a separate sample after reducing the Fe (III) to Fe (II) with hydroxylamine.

The results from investigation by the pulse method of the relationship between the rate of the initial stage of anodic dissolution and potential at various pH values are given in Fig. 1. The slopes of the pulsed polarization curves at potentials between 0.0 and 0.2 V (Curves 2-9) are approximately the same as that of the curve taken by the stationary potentiostatic method (Fig. 1, Curve 1, Section AB). As the current density increases the pulsed anode curves become steeper, which is evidently due to passivation of the iron. However, at a certain pH on Curves 2-5 there is an inflection and with further increase in current density the potential moves to the negative side. This anomalous shape is due to anodic activation of the iron surface similar to that observed in the anodic dissolution of iron at low current densities in alkaline sodium chloride solutions [5] or in perchlorate solutions [6]. An indication of the anodic activation state of the iron is provided by the fact that iron passes into solution in the divalent form at potentials more positive than the passivation potential and the standard potential of the Fe (II)/Fe (III) system. The anodic

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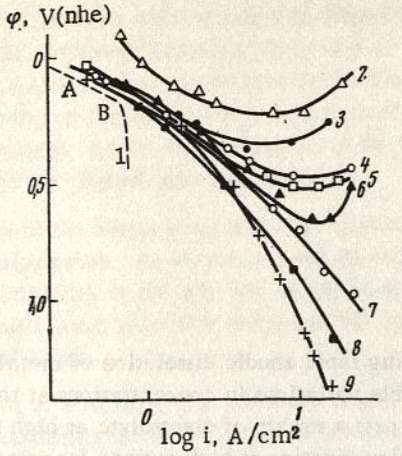

Fig. 1.

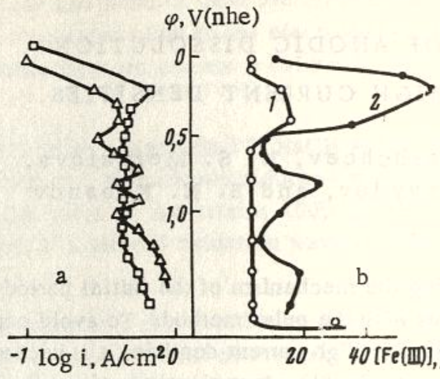

Fig. 2

Fig. 1. Polarization curves recorded by the pulse method on Armco iron electrodes in 4.5 N NaCl solutions at various pH values: 2) 0.2; 3) 2.8; 4) 4.3; 5) 7.2; 6) 7.7; 7) 7.8; 8) 8.3; 9) 9.4. Curve 1 was taken at pH 6.1 by the potentiostatic method.

Fig. 2. a) Potentiostatic polarization curves in 4.5 N NaCl solutions at pH values: 1) 0.06; 2) 6.0; b) curves for variation of relative Fe (III) content of iron passing into solution with potential in 4.5 N NaCl solutions with pH values: 1) 0.06; 2) 6.0.

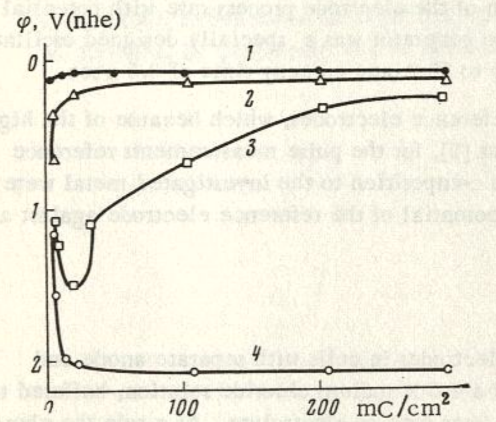

Fig. 3. Dependence of anodic potential of Hilger iron electrodes on amount of electricity passing at a current density of 10 A/cm² in 4.5 N NaCl at various pH values: 1) 2; 3) 3.7; 3) 2.08; 4) 11.7.

activation mechanism involves an adsorption regrouping process on the surface or adsorption displacement of the passivating oxygen from the metal surface by the anions [6, 7].

To verify that anodic activation of the iron does occur in our case we carried out parallel potentiostatic and analytical determinations at various potentials and pH values. The potentiostatic curves are given in Fig. 2a and the analytical curves in Fig. 2b. As seen from the analytical results, in an acid medium (pH $<$ 1) iron goes into solution as Fe^{2+} even at high positive potentials. Only in a small potential region (0.1-0.5 V) are noticeable amounts of Fe^{3+} ions found. In neutral solutions (pH 6) ferric ions are found over the whole range of measured potentials more positive than 0.05 V, but the ferrous content nevertheless predominates. Thus at these current densities and in this electrolyte iron dissolves mainly in the divalent form from the whole surface and is consequently in the anodic activation state.* This suggestion is also supported by the measurements which we made by the pulse method on the amount of electricity required to activate the electrode. From the curves in Fig. 3 it is seen that at a certain fixed current density (10 A/cm²) as the ratio of Cl^- and OH^- in the solution decreases the amount of electricity required to move the electrode potential to the negative side, i.e., for anodic activation, increases. The amount of electricity required to start the anodic activation process is of the same order of magnitude as that determined by other authors at lower current densities [5, 8].

Regarding the mechanism of the transfer of anodically activated iron atoms into solution, according to [7] it can be assumed that in neutral solution as in acid solution the process must proceed according to the equation $Fe \rightarrow Fe^{2+} + 2e$. It should be noted that if dissolution occurred solely by this reaction one could not expect a change of pH near the anode, since the H^+ and OH^- ions do not take part in the reaction. However, it was observed that acidification can occur near the anode during anodic dissolution of an iron electrode in an activating solution, and calculations

* It is interesting that at potentials more positive than 0.6 V the electrode surface becomes smooth and bright with traces of pitting, which were also "polished" away.

have shown that only tenths of a percent of the electricity passing through the cell is used on this acidification. The appearance of H^+ ions near the anode cannot be explained by formation of molecular oxygen since in our experiments the electrode potential was 0.5 V more negative than the oxygen evolution potential. This effect becomes clear if account is taken of the fact that although the iron dissolves predominantly in simple ionic form as Fe^{2+}, as shown above, it dissolves partly in the trivalent form, and hydrolysis then occurs, for example, by the reaction $Fe + H_2O + Cl^- \rightarrow FeOCl + 2H^+ + 3e^-$ or $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$, which leads to acidification of the solution.

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