CORROSION OF IRON IN AGITATED AERATED SOLUTIONS

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Dissolution of metals has been studied in a number of works by means of a rotating disk electrode [1-6]. However, this method has been inadequately used in an investigation of the corrosion of iron in solutions containing oxygen. It was stated in [7] that rotating Fe-disks corrode uniformly over the entire surface regardless of diameter. Zembura and Cohorts [8] showed that, in acidified solutions of sodium sulfate saturated with air the corrosion rate of the disk Fe-electrode is directly proportional to the square root of the rate of its rotation, i.e., this process obeys diffusion kinetics. At pH < 2-3 there is also a noticeable reduction of hydrogen ions, but when pH > 3-4 their effect is negligible. According to a calculation by Levich's formula [9], the number of electrons participating in the reactions were 3 and 4.

In this work we studied the corrosion of a rotating Fe-disk and its dissolution in the presence of cathodic polarization in aerated acid solutions.

METHOD

The method of recording the polarization curves is described in a previous work [10]. The dissolution rate of iron was determined by analyzing the solution by the orthophenanthroline method [11] with the use of a FÉK-2 photocolorimeter-nephelometer. Calibration of the photocolorimeter against a standard solution of $FeSO_4 \cdot 7H_2O$ showed the possibility of determining iron with a sensitivity of $5 \cdot 10^{-8}$ g/ml. Potentiostatic experiments on the determination of the dissolution rate lasted from 2 to 6 h depending on the prescribed potential. The dissolution rates given below were obtained by averaging the data of three or four experiments. The divergence of individual determinations was 10-20% on the average and 20-40% in the very negative region of the potentials. The potentials are given with respect to a standard calomel electrode (s.c.e.). The experiments were carried out at a temperature of 20 ± 1°.

RESULTS OF EXPERIMENTS

In aerated acid solutions the dependence of the corrosion rate of iron (i_{Fe}) on the square root of the speed of rotation of the disk (m) represents a straight line which passes through the origin of the coordinates (Fig. 1) and coincides nicely with a similar straight line for the limiting current of oxygen diffusion i_d [10]. Thus, in accord with [8] the corrosion rate i_{Fe} at different speeds of rotation of the disk is equal to the limiting current density of cathodic reduction of oxygen. This conclusion holds true for all our investigated solutions: from 0.03 to 1.0 N H_2SO_4 at $[SO_4^{2-}] = 1.0$ N. In the absence of dissolved oxygen the dissolution rate of the Fe-disk does not depend on the speed of rotation [4, 6].

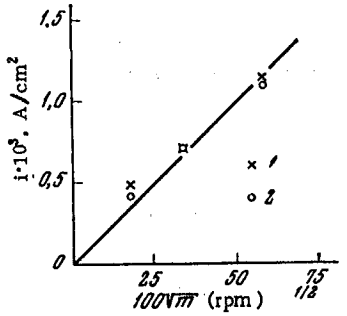

Fig. 1. Dependence of the dissolution rate of Armco iron (1) and limiting current of oxygen diffusion (2) on the square root of the speed of rotation (m) of the electrode in a solution of 0.3 N H_2SO_4 + 0.7 Na_2SO_4 saturated with air.

In the presence of cathodic polarization in the region from φ_{st} to potentials corresponding to the limiting rate of reduction of oxygen ($\varphi \simeq -0.66$), the dissolution rate of iron drops with a shift of the potential to more negative values (Fig. 2). In coordinates $\varphi - \log i_{Fe}$, for Armco iron we obtain a straight line with a slope of 110 mV in a solution of 0.3 N H_2SO_4 + 0.7 Na_2SO_4 and 90 mV in a solution of 0.03 N H_2SO_4 + 0.97 N Na_2SO_4. In this region the dissolution of iron evidently occurs by an electrochemical mechanism.

In the region of the limiting current of oxygen reduction the dissolution rate of iron increases more slowly with an increase of m than in accord with $\sqrt{m}$. For example, when $\varphi_c = -0.56$ V in a solution of 0.3 N

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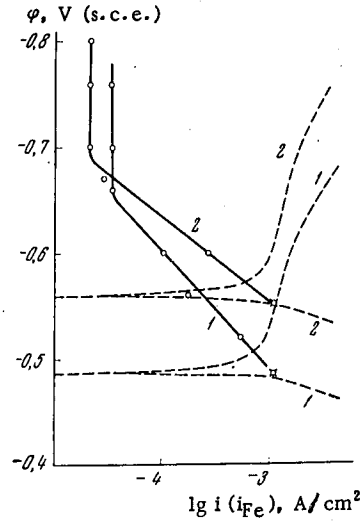

Fig. 2

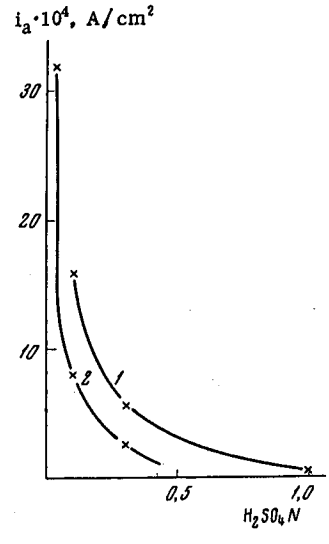

Fig. 3

Fig. 2. Dependence on potential (for m = 3550 rpm) of the logarithm of the cathode and anode current density (dashed lines) and dissolution rate of iron (solid lines) in solutions: 1) 0.3 N H_2SO_4 + 0.7 N Na_2SO_4; 2) 0.03 H_2SO_4 + 0.97 N Na_2SO_4 saturated with air.

Fig. 3. Dependence of dissolution rate of iron for m = 0 on acid content in air-saturated sulfate solutions with a constant ionic strength ($[SO_4^{2-}] = 1$ N). Potential: 1) 0.49 V; 2) −0.51 V (s.c.e.).

H_2SO_4 + 0.7 N Na_2SO_4, i_{Fe} is 0.13, 0.16, and 0.19 mA/cm², respectively, for m = 1180, 3550, and 7600 rpm.

When $\varphi_c = -0.66$ V and at more negative values we observe that the dissolution rate of iron does not depend on the potential (which indicates a chemical mechanism of dissolution) or on agitation.

For example, in a solution of 0.3 N H_2SO_4 + 0.7 N Na_2SO_4 with $\varphi_c = 0.7$ V, the dissolution rate when m = 1180 and 3550 rpm was equal, respectively, to $3.40 \cdot 10^{-5}$ and $3.38 \cdot 10^{-5}$ A/cm². Here the presence of oxygen has no effect on the dissolution rate. For instance, in the same solution i_{Fe} proved to be equal to $3.5 \cdot 10^{-5}$ A/cm² in a hydrogen atmosphere when m = 1180 rpm and $\varphi_c = -0.70$ V.

At potentials more positive than φ_{st} the dissolution rate of the Fe-disk, in conformity with [12], drops with an increase of acidity of the solution (Fig. 3). The slope of the Tafel portion of the anodic polarization curves is 20-30 mV.

In an air-saturated alkali solution (0.1 N KOH + 0.9 N Na_2SO_4) and in the absence of an external current, when m = const the ionization rate of iron is appreciably less than the limiting current of oxygen diffusion. When m = 3550 rpm it is equal to $1.7 \cdot 10^{-5}$ A/cm² for zone-melted iron, whereas $i_d = 1.06 \cdot 10^{-3}$ A/cm² (see polarization curves in [10]). This difference is obviously related with passivation of the electrode. In the presence of cathodic polarization in the region of the limiting current ($\varphi_c = -1.00$ V) the dissolution rate of iron is somewhat higher ($i_{Fe} = 3.4 \cdot 10^{-5}$ A/cm²), which indicates partial removal of the passive film.

DISCUSSION OF RESULTS

In acid solutions containing dissolved oxygen the following reactions are possible on the iron electrode:

$$Fe \rightarrow Fe^{2+} + 2e, \quad (1)$$

$$H_3O^+ + e \rightarrow H_2O + {}^1/_2H_2 \quad (2)$$

$$O_2 + 4H_3O^+ + 4e \rightarrow 6H_2O. \quad (3)$$

In the absence of an external current, reaction (1) is in electrochemical union with reactions (2) and (3) [13]:

$$i_{Fe} = i_H + i_{O_2}. \quad (4)$$

Here i_{O_2} is the rate of reaction (3), determined by the diffusion of oxygen to the electrode in conformity with Levich's equation [9], i_H is the rate of reaction (2).

The validity of Eq. (4) was confirmed by experiment. For example, in a 1 N solution of H_2SO_4 saturated with air, when m = 3550 rpm the value of i_{Fe} determined by the loss of weight of the electrode at φ_{st} was equal to $1.47 \cdot 10^{-3}$ A/cm^2. The value of i_H found by extrapolation to φ_{st} of the cathode curve recorded in a hydrogen atmosphere was equal to $0.15 \cdot 10^{-3}$ A/cm^2, * the limiting current density of oxygen reduction in an air atmosphere was $1.2 \cdot 10^{-3}$ A/cm^2. Hence $i_{Fe} + i_{O_2} = 1.35 \cdot 10^{-3}$ A/cm^2, which is close to the indicated i_{Fe}. With a decrease of acidity the value of i_H decreases and becomes quite small in comparison with i_{O_2}. Then $i_{Fe} = i_{O_2}$, as was already noted above for the solution of 0.3 N H_2SO_4 + 0.7 N Na_2SO_4. The number of electrons in reaction (3) calculated from experimental data for i_{O_2} or i_{Fe} (Fig. 1) is equal to $\simeq 3.8$.

In the region of potentials $\varphi_c < -0.66$ V the dissolution of iron probably occurs primarily by a chemical mechanism—by the direct interaction of the iron atoms with components of the solution which are capable of being reduced, for example with water molecules.

$$Fe + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \quad (5)$$

or hydrogen ions

$$Fe + 2H_3O^+ \rightarrow Fe^{2+} + H_2 + H_2O. \quad (6)$$

The increase of the rate of chemical dissolution with an increase of acidity attests on behalf of the last equation (see Fig. 2).

The independence of the dissolution rate of metal on the potential was detected earlier in experiments on the decomposition of amalgams of alkali metals by alkali solutions [14] and also in the works of Ya. M. Kolotyrkin and G. M. Florianovich in a study of the ionization rate of iron and its alloys in the region of cathodic potentials [15].

Proof of the chemical mechanism of the reaction in this region of potentials is the fact that, as shown in [15], the experimental values of the dissolution rate are appreciably higher than those obtained by extrapolation of the anode $\varphi - \log i_a$ curve to potentials more negative than −0.66 V. We must assume that, as in the case of decomposition of amalgams [14], the ionization reaction of iron occurs simultaneously by electrochemical and chemical mechanisms, the share of the electrochemical reaction being very small in the region of negative potentials.

CONCLUSIONS

1. The corrosion rate of iron in acid solution saturated with air is equal to the limiting current of oxygen reduction; with an increase of the speed of rotation of the iron disk electrode both quantities increase in accord with the same law.

2. The dependence of the dissolution rate of iron on the potential at a constant speed of rotation of the electrode has a complex character. With cathodic polarization in the region from the standard potential to $\simeq -0.66$ V with respect to a s. c. e., dissolution occurs by an electrochemical mechanism; the slope of the straight line $\varphi - \log i_{Fe}$ is close to 100 mV. At more negative potentials the dissolution rate of iron ceases to depend on the potential, which indicates the occurrence of the process by a chemical mechanism. In this case neither agitation nor the oxygen content in the solution has a substantial effect on the dissolution rate.

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