USE OF A DISK ELECTRODE WITH A RING TO STUDY THE CORROSION OF IRON IN ACID SOLUTIONS

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Corrosion of iron in acid solutions can be due either to an electrochemical or to a chemical mechanism [1-4]. To elucidate the contributions of these processes to corrosion, we performed experiments by means of a disk electrode with a ring. The amounts of dissolved iron and evolved hydrogen were determined at the ring electrode by means of the limiting currents for oxidation of Fe^{2+} ions to Fe^{3+} and H_2 to H_2O.

The iron disk electrode was polished with micron abrasive paper and glass, then washed with alcohol and double-distilled water and the test solution. The platinum ring electrode was platinized, and before each measurement was activated by means of triangular pulses in the potential range 0.05 ... 1.5 V. The solutions were prepared from double-distilled concentrated sulfuric acid and double-distilled water. Preliminary experiments revealed that the limiting oxidation currents of Fe^{2+} and H_2 lie in the potential ranges 1.2-1.4 V and 0.3-0.4 V, respectively (with respect to a hydrogen electrode in 0.1 H_2SO_4). With the aim of checking the correctness of these potentials, we performed a number of experiments on a platinum disk electrode with a ring. In an inert atmosphere, to the solution we added Fe^{3+} ions at various concentrations; these were reduced to Fe^{2+}; at the ring at ε_R = 1.4 V we observed the oxidation current of Fe^{2+}. The relation

$$I_R = NI_D \tag{1}$$

(where I_D and I_R are the currents to the disk and ring electrodes and N is the geometric factor) was satisfied, showing that we were registering the limiting current for oxidation of Fe^{2+} to Fe^{3+}. In another series of experiments, in which molecular hydrogen was evolved at the disk at low cathodic polarization and was oxidized at the ring at ε_R = 0.3 V, we also observed the satisfaction of relation (1). The value of N, calculated as in [5], was 0.4 in both cases.

In subsequent experiments the required potential was maintained at the disk for 1 min, and then the currents at the disk and ring electrodes were measured at ε_R = 0.3 and 1.4 V. To study the influence of the surface state on the rate of solution of iron, with the aid of a triangular pulse generator we programmed the potential changes at the disk, oxidizing or reducing its surface. In a study of the corrosion of iron with oxygen depolarization we determined the amount of hydrogen peroxide formed at the disk electrode. Since the half-wave potential for the oxidation of Fe^{2+} is close to that for H_2O_2, the currents corresponding to these processes cannot be distinguished at the ring. For this reason, the partial current of oxidation of hydrogen peroxide at the ring was found as the difference between the currents at the ring electrode in oxygen and in an inert atmosphere. We allowed for the possibility of reaction of Fe^{2+} with oxygen and hydrogen peroxide. Changes in rotation rate do not influence the currents at the disk electrode, showing that they are kinetic in nature.

The graph of the rate of solution of iron vs potential, when compared with the hydrogen evolution curves, enables us to distinguish the regions in which the electrochemical and chemical solutions mechanisms are superimposed ($\varepsilon \approx \varepsilon_{st}$), in which solution is predominantly chemical ($\varepsilon \leq -0.3$ V), and in which it is predominantly electrochemical ($\varepsilon \geq -0.15$ V). In the region from -0.3 to -0.5 V, the current due to oxidation of Fe^{2+} ions at the ring (Fig. 1, curve 3) is independent of potential, showing that solution is chemical, in agreement with various authors' ideas [1-4] concerning the possibility of this process. At the corrosion potential ε_{st} and a little to the positive side of it (from -0.25 to -0.15 V), the rates of chemical and electrochemical solution of iron are comparable. At potentials more positive than -0.1 V the electrochemical mechanism becomes predominant.

Assuming (1) equivalence of the quantities of molecular hydrogen and iron ions formed by the chemical reaction,

$$I_{Fe}^{chem} = I_{H_2}^{chem} \tag{2}$$

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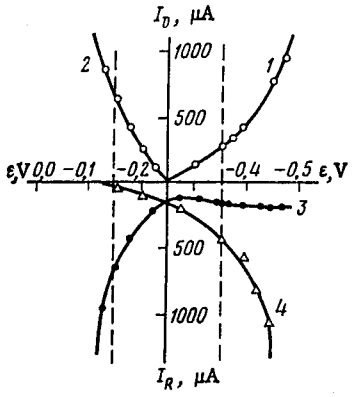

Fig. 1

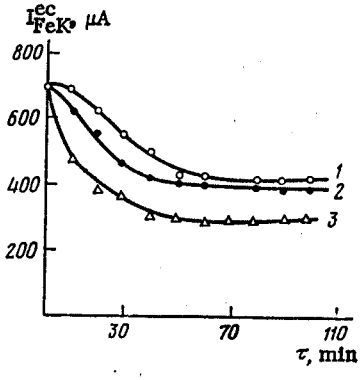

Fig. 2

Fig. 1. Polarization curves of iron disk electrode in pure solution of 0.1 N H_2SO_4 (1, 2), and graphs of corresponding currents due to oxidation of Fe^{2+} (3) and H_2 (4) at platinum ring electrode vs potential of disk electrode.

Fig. 2. Currents due to solution of iron by electrochemical mechanism at $\varepsilon_R = -0.15$ V vs residence time of electrode at oxidation potentials of −0.25 V (1), −0.1 V (2), and 0.3 V (3).

we can represent the currents at the disk and ring electrodes by means of the equations

$$I_D = I_{H_2}^T - I_{Fe}^T; \tag{3}$$

$$I_{Fe}^R = I_{Fe}^T + I_{FeK}^{ec} + I_{FeK}^c; \tag{4}$$

$$I_{H_2}^R = I_{H_2}^T + I_{H_2K}^{ec} + I_{H_2K}^c, \tag{5}$$

where the superscripts c and ec denote chemical and electrochemical mechanisms, respectively, K refers to corrosion processes, and T to processes with polarization. There are not enough equations here to determine all the independent variables. However, they can be found by means of the polarization curves, together with a knowledge of the regions in which either of the two iron solution mechanisms predominates. In fact, if $\varepsilon = \varepsilon_{st}$ the current at the disk is $I_D = 0$, and by Eq. (3) the currents due to solution of iron and evolution of hydrogen can be found by extrapolation of the partial polarization curves to ε_{st}. Then

$$I_{H_2}^T = I_{Fe}^T, \qquad I_{FeK}^{ec} = I_{H_2K}^{ec}; \tag{6}$$

$$I_{Fe}^R = I_{H_2}^R. \tag{7}$$

Further, at high negative potentials (−0.35 V), $I_{Fe}^T = 0$, and Eq. (4) becomes

$$I_{FeK} = I_{Fe}^R = I_{FeK}^c. \tag{8}$$

Finally, at potentials more positive than −0.15 V we can neglect electrochemical evolution of hydrogen,

$$I_{FeK} = I_{Fe}^R - I_{Fe}^T = I_{Fe}^R - I_D, \tag{9}$$

$$I_{FeK}^{ec} = I_{FeK} - I_{FeK}^c. \tag{10}$$

Since

$$I_{FeK}^c = I_{H_2K}^c, \tag{11}$$

and

$$I_{H_2K}^c = I_{H_2}^R, \tag{12}$$

therefore

$$I_{FeK}^{ec} = I_{Fe}^{R} - I_D - I_{H_2}^{R}.$$

On the above basis we determined the rate of solution of iron by a chemical mechanism at $\varepsilon_R = -0.4$ V and by an electrochemical mechanism at $\varepsilon_R = -0.15$ V.

From Fig. 2 it follows that oxidation of the iron electrode leads to a reduction in the electrochemical component of corrosion.

On the basis of the theory of parallel–series reactions of oxygen electroreduction (6), from the experimental data we calculated the constants of reduction of oxygen on iron with direct formation of water (k_1) and via intermediate formation of hydrogen peroxide (k_2). These constants are seen to increase as the potential of the iron electrode shifts toward the cathode side. The proportion of the oxygen reduction reaction which forms water directly is higher than the proportion which involves the intermediate formation of hydrogen peroxide.

LITERATURE CITED

1. G. M. Florianovich and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 157, 422 (1964).
2. Ya. M. Kolotyrkin and G. M. Florianovich, Itogi Nauki, Élektrokhimiya, VINITI, 7, 5 (1971).
3. M. A. Makhbuba and Z. A. Iofa, Zashch. Met., 4, 4 (1968).
4. M. A. Makhbuba and Z. A. Iofa, Zashch. Met., 3, 1027 (1967).
5. S. Bruckenstein and D. T. Napp, J. Am. Chem. Soc., 90, 6303 (1968).
6. V. S. Bagotskii, M. R. Tarasevich, and V. Yu. Filinovskii, Élektrokhimiya, 4, 1247 (1968); 5, 1218 (1969).

CORROSION AND ELECTROCHEMICAL BEHAVIOR OF COPPER IN PHOSPHATE SOLUTIONS

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The extensive use of alkali phosphate solutions as wetting agents for deslushing and cleaning metal artifacts (instead of inflammable and toxic organic solvents) is prevented by their high corrosiveness with respect to copper alloys.

We have investigated the mechanism of solution of copper alloys in a 0.5 M solution of $NaH_2PO_4 \cdot 2H_2O$ at pH 6.0-11.7.

The corrosion investigations were performed by the gravimetric method on cylindrical specimens of M-3 copper with total immersion of the specimens in the solutions for 10 h at 25-75°C.

The polarization curves were recorded potentiodynamically (12 mV/min) after establishment of a steady potential on disk electrodes of M-3 copper.

It will be seen from Fig. 1 that at all the pH values, on increase in the solution temperature the corrosion rate K is enhanced and the steady potential "denobled." The low activation energy suggests that diffusion is the governing stage of the corrosion process: At pH 6.5, 8.0, 9.5, and 11.7, E_{act} is respectively 2.049, 2.277, 7.468, and 4.0 kcal/mole.

However, the diffusion stages themselves in phosphate solutions at different pH may differ, as shown by the value of E_{act}, which is maximal at pH 9.5. It is precisely at this pH that the steady potential of copper is most positive and the corrosion rate (Fig. 1) and anodic solution rate (Fig. 2) are minimal.

A closer investigation of the anode process in phosphate solutions (Fig. 3) shows that at pH $\leq$ 9.5 the passivation potential φ_p is practically independent of the pH, and the passivation current decreases on alkalization of the solution. At pH > 9.5 the passivation potential is "denobilized" but i_p increases. Thus, the passivatability of copper in a phosphate solution remains maximal at pH 9.5.

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