INVESTIGATION OF THE PASSIVATION OF METALS BY OXYGEN BY MEASUREMENT OF THE CONTACT POTENTIAL DIFFERENCE AND BY ELECTROCHEMICAL METHODS

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For understanding the mechanism of the passivation of metals by oxygen, it seemed interesting to study the first stages of the oxidation of metals in combination with an investigation of the effect of oxygen on the kinetics of electrochemical processes. Valuable information on the mechanism of the oxidation of metals may be obtained by investigating the effect of absorbed oxygen on the electronic work function.

In work carried out together with M. D. Surova [1], N. A. Shurmovskaya [2], and T. V. Kalish [3], a study was made of the change in electronic work function during the first stages of the oxidation of iron and nickel and during the absorption of oxygen on platinum. The data obtained indicate a change in the nature of the bond in relation to the conditions under which the metal reacts with oxygen.

The change in the electronic work function of a metal produced by the absorption of oxygen was investigated by the thermoelectronic method, through the displacement of the volt-ampere characteristics. The instrument in which the experiments were carried out was a diode with a movable tungsten cathode; the anode was made of the metal investigated and had a true surface of 30-40 cm^2. By plotting the volt-ampere characteristics of the diode with a pure anode and an anode which had absorbed various amounts of oxygen, it was possible to use the displacement of the characteristics to determine the relation between the amount of oxygen absorbed and the contact potential difference.*

The first stages of iron oxidation were investigated over the temperature range of -120 to -270°. At such temperatures (-120°), the electronic work function increased as the amount of absorbed oxygen increased; at a higher temperature (+100°) an increase in the amount of oxygen absorbed to 2.10^{15} molecules per cm^2 of true surface lead to a decrease in the electronic work function (Fig. 1). Further absorption of oxygen produced an increase in the electronic work function, which became greater than the electronic work function of the pure metal at a definite absorption.

Analogous experiments were carried out at 150 and 270°. In these cases there was also a decrease in the electronic work function as oxygen was absorbed by the iron, but, as Fig. 1 shows, the maximum on the curve corresponded to larger amounts of absorbed oxygen. With an increase in the amount of absorbed oxygen, the electronic work function increased and became greater than the work function of the pure metal (150°).

According to data obtained recently by Hackerman et al. [4], small amounts of oxygen absorbed by iron at 20° also reduced the electronic work function.

Thus, from the results obtained it follows that at low temperatures the absorption of oxygen increases the electronic work function. Under these conditions the double layer has the negative envelope on the outside.

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* A contact potential difference with a plus sign (+) corresponds to a decrease, and one with a minus sign (-), an increase in the electronic work function.

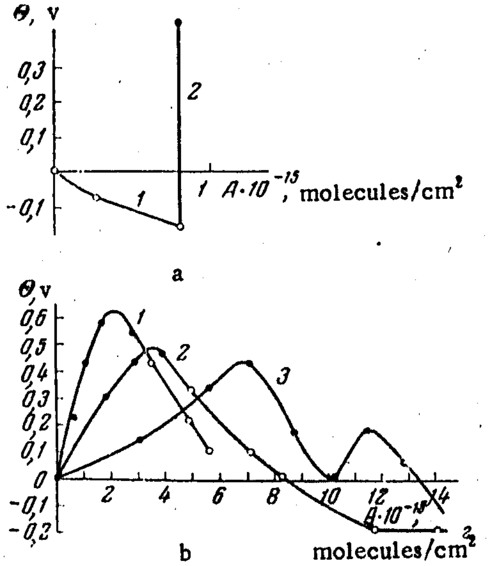

Fig. 1. Relation of contact potential difference in volts (CPD) Θ to the amount of absorbed oxygen (A) on iron. a: 1) at -120° ○ ; 2) after heating to + 95° (•); b: 1) at 100°; 2) 150°; 3) 270°. CPD measured at 95°; • — fast absorption;○— slow absorption.

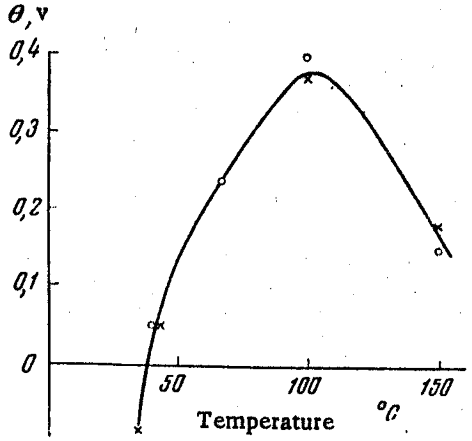

Fig. 2. Relation of CPD to temperature during the absorption of oxygen by nickel ($1.3 \cdot 10^{15}$ molecules/cm²). CPD measured at 35°.

The decrease in work function observed with an increase in temperature, which is produced by the absorption of small amounts of oxygen, is apparently connected with oxygen atoms penetrating under the upper layer of metal or metal atoms emerging on the surface covered with oxygen, as in the ideas of Mott [5]. Thereupon a double layer is formed with the positive envelope on the outside. The increase in work function with large amounts of absorbed oxygen is connected with the completion of the surface oxide, and when the surface is completely occupied by this oxide, the work function no longer changes with an increase in the amount of absorbed oxygen.

To explain the change in contact potential difference with temperature, it may be considered that oxygen atoms penetrating under the surface layer of the metal a definite distance leads to the maximum decrease in the work function. With an increase in this distance, the action of oxygen becomes less and the work function begins to increase. In this case it is necessary to assume that, as the temperature increases, the oxygen atoms penetrate more deeply; this should lead to an increase in the work function.

Results obtained recently together with N. A. Shurmovskaya [2] in an investigation of the effect of oxygen absorbed by nickel on the electronic work function are similar to the results presented above for iron (Fig. 2). From the data obtained it follows that oxygen absorbed by nickel to the extent of $1.3 \cdot 10^{15}$ molecules per cm² of true surface at 35° slightly increased the electronic work function (0.1 v); with an increase in the oxygen-absorption temperature to 45 and 100°, the work function decreased by 0.02 and 0.35 v, respectively. At a higher temperature (150°) an increase in work function was observed.

Oxygen had a different effect on the electronic work function of platinum [3]. The electronic work function of platinum which had absorbed oxygen first increased and then decreased with time and became equal to the work function of pure platinum. This phenomenon is connected with the penetration of oxygen into the platinum to a considerable depth.

The results presented on the effect of oxygen on the electronic work function of iron are in agreement with the results obtained together with V. I. Pavlova [6] in an electrochemical investigation of the properties of an iron electrode containing various amounts of oxygen. In these experiments various amounts of oxygen from the gas phase were deposited on the surface of an iron electrode (which had been reduced in hydrogen and outgassed in vacuum at a high temperature); then the iron was placed in contact with an outgassed solution of alkali, and the relation between the potential and the current density determined, and also the relation of the capacity of the iron electrode to potential investigated.

Results obtained during the investigation of the effect of absorbed oxygen on the polarization curves in 0.25 N NaOH are presented in Fig. 3. Curve 1 refers to pure iron, while curves 2, 3, 4, and 5 refer to iron which had absorbed $0.6 \cdot 10^{15}$, $0.9 \cdot 10^{15}$, $2 \cdot 10^{15}$ and $3.3 \cdot 10^{15}$ molecules of oxygen per cm² of true surface res-

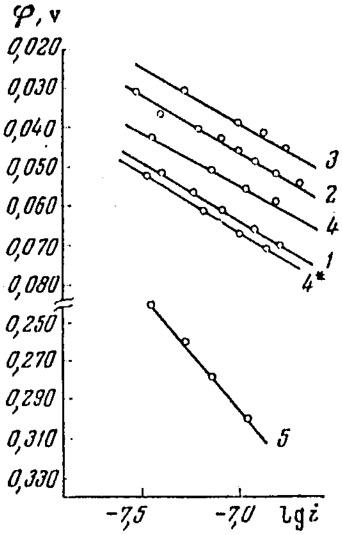

Fig. 3. Effect of oxygen absorbed by iron on the course of polarization curves. 1) Pure iron; 2, 3, 4, 5) iron that had absorbed $0.6 \cdot 10^{15}$, $0.9 \cdot 10^{15}$, $2 \cdot 10^{15}$ and $3.3 \cdot 10^{15}$ molecules of oxygen per cm^2 of surface, respectively; 4') change in curve 4 with time.

pectively. These data show that with an increase in the amount of oxygen there was first a displacement of the anode curves toward a more negative potential, which indicates activation of the electrode. With a further increase in the amount of absorbed oxygen, the anode polarization curves were displaced toward more positive potentials and the iron electrode was passivated. The maximum activation corresponded to an increase in the rate of the anode process by a factor of 7. From the data obtained it follows that the maximum displacement of the potential in a negative direction produced by oxygen corresponded to the absorption of $1.2 \cdot 10^{15}$ molecules per cm^2 of true surface. Analogous results were obtained in 0.75 N NaOH.

When the iron absorbed more oxygen than required for activation, there was a displacement of the polarization curves with time in a negative direction (Fig. 4). The self-activation of iron in alkali is analogous to the activation of iron in acid solutions, but proceeds extremely slowly. However, in the self-activation of iron in alkali after absorption of oxygen from the gas phase, there is not complete removal of the oxide film, and, as was shown for an electrode of iron powder, $2 \cdot 10^{15}$ molecules of oxygen per cm^2 remained on its surface, affecting spontaneous solution and the hydrogen overvoltage [7].

Activation of the electrode by small amounts of oxygen and passivation during the absorption of large amounts were also detected by measuring the relation between the potential and the amount of electricity passed, i.e., the yield of the electrochemical process. The results of experiments in 0.25 N NaOH are given in Fig. 5, which shows that in 0.25 N NaOH the yield of the electrochemical process first increased and then fell as the amount of absorbed oxygen increased. This is in agreement with our earlier data [8]. With $0.9 \cdot 10^{15}$ molecules of oxygen per cm^2 on the iron surface, the yield of the electrochemical process* was increased by a factor of 7.3 in comparison with that of pure iron. In a solution of higher concentration, the activating action of the oxygen has less effect on the yield of the process.

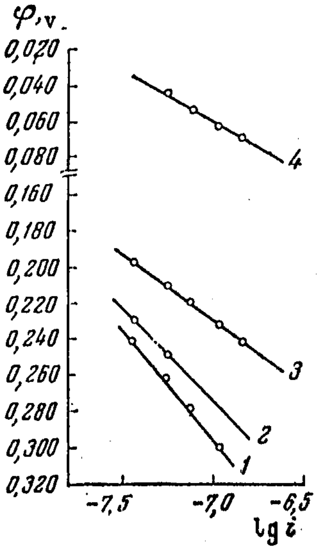

Fig. 4. Change in course of polarization curves with time. Curves 1, 2, 3, and 4 correspond to 5, 10, 130, and 280 min from the δ beginning of the experiment, respectively.

If the ratio of the yield of the electrochemical process for an electrode which has absorbed oxygen Q_1 to the yield of the process on pure iron Q_2 is taken as a measure of the activating effect, then from the data obtained it follows that Q_1/Q_2 is approximately inversely proportional to the alkali concentration.

All the data on the effect of oxygen absorbed from the gas phase on the course of electrochemical processes in alkali solutions lead to the conclusion that the action of this oxygen continues despite considerable solution of iron, up to tens of atomic layers. This indicates that during anode oxidation there is only partial removal of oxygen deposited from the gas phase. However, the activating effect of absorbed oxygen gradually decreases with an increase in the number of iron layers removed, which undergo oxidation. The difference between the action of oxygen deposited on the iron from the gas phase and the action of oxygen deposited during anode oxidation is apparently connected with the fact that in the latter case the surface oxides are hydrated, and this hampers the penetration of oxygen under the upper layer of metal.

We also investigated the effect of oxygen absorbed from the gas phase on the capacity of an iron electrode. The capacity was measured with an alternating current. The results of the experiments are presented in Fig. 6. Curve 1 corresponds to experiments with pure iron, while

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* The yield of the electrochemical process is the amount of electricity consumed during anode polarization in the formation of Fe $(OH)_2$ until this stops, due to passivation of the iron.

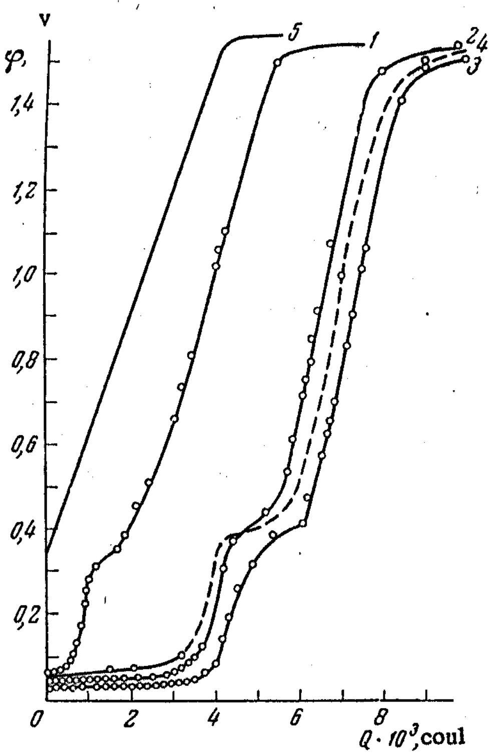

Fig. 5. Relation of the yield of the electrochemical process (Q) to the amount of oxygen absorbed. 1) Pure iron; 2, 3, 4, 5) iron which had absorbed 0.6 · 10^{15}, 0.9 · 10^{15}, 2 · 10^{15}; 3.3 · 10^{-15} molecules of oxygen per cm²; respectively.

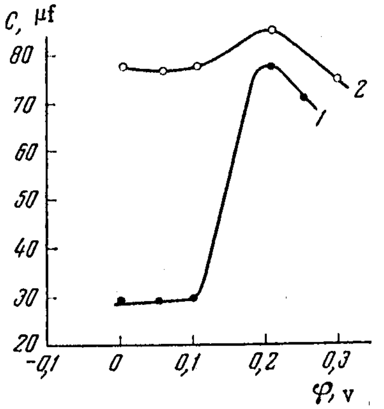

Fig. 6. Relation of capacity (C) of an iron electrode to potential φ. 1) Pure iron; 2) iron which had absorbed 2 · 10^{15} molecules of oxygen per cm². C refers to 1 cm² of true surface.

curve 2 corresponds to an experiment with iron which had absorbed oxygen (2 · 10^{15} molecules per cm²). These data show that at a potential close to the stationary value, the presence of oxygen on the iron surface leads to an increase in capacity. Figure 7 gives the relation of the capacity to frequency for both electrodes. Measurement of the capacity of the iron electrode, like the other electrochemical measurements, indicates activation of the iron electrode by small amounts of oxygen absorbed from the gas phase. Comparison of data on the effect of oxygen absorbed from the gas phase on the electronic work function of iron with the electrochemical data indicate that oxygen penetrating under the upper layer of iron atoms increases its solution rate; however, this process is retarded by oxygen which remains on the surface.

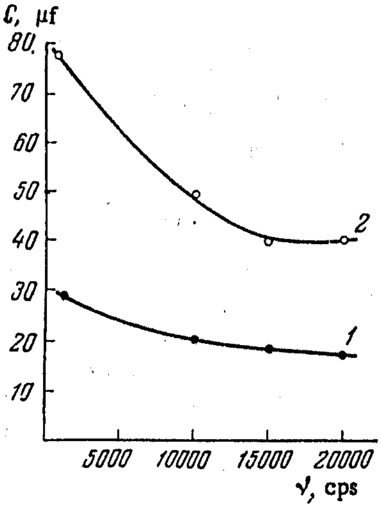

Fig. 7. Relation of the capacity of an iron electrode to frequency. 1) Pure iron; 2) iron which had absorbed 2 · 10^{15} molecules of oxygen per cm² of true surface.

It has been suggested [9] that the solution of iron in alkali proceeds through the intermediate electrochemical adsorption of oxygen:

$$\mathrm{Fe} + \mathrm{OH}^- = (\mathrm{FeOH})_{\mathrm{ads}} + e$$

$$(\mathrm{FeOH})_{\mathrm{ads}} + \mathrm{OH}^- = (\mathrm{FeO})_{\mathrm{ads}} + H_2O - e,$$

whereupon the electrochemical adsorption increases the rate of iron solution. In the light of these ideas and the data obtained on the effect of oxygen on the capacity of an iron electrode, it may be considered that the presence of a small amount of oxygen absorbed from the gas phase on the iron surface increases the electrochemical adsorption.

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