R. Kh. Burshtein, G. M. Kornacheva, N. A. Shurmovskaya

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

R. Kh. Burshtein, G. M. Kornacheva, N. A. Shurmovskaya

INVESTIGATION OF THE GAS CORROSION OF IRON BY THE CONTACT POTENTIAL DIFFERENCE METHOD

(Presented by Academician A. N. Frumkin, May 24, 1962)

In the present work an attempt has been made to approach the elucidation of the mechanism of gas corrosion of iron by studying the kinetics of oxygen uptake and investigating changes in the state of the iron surface during corrosion by the contact potential difference method. For measuring the contact potential difference we used the vibrating-capacitor method, employed by us in a number of earlier works (^{1}). A molybdenum plate sealed with glass (^{2}) served as the comparison electrode, in order to protect the metal from interaction with the surrounding medium.

Measurements of the contact potential difference were carried out at room temperature on “Hilger” iron, previously repeatedly reduced in hydrogen at 400° and then degassed to a pressure of 10^{-6} mm Hg while heated by a high-frequency current to 700°.

For adsorption measurements, iron powder obtained by reduction of iron oxides was used. Before the experiments the powder was additionally reduced in hydrogen and degassed by prolonged training to a pressure of 10^{-6} mm Hg at a temperature of 500°.

In studying the kinetics of oxygen uptake we used the method previously employed by us (^{3}). The surface under investigation was brought into contact with small portions of oxygen, and the rate of uptake of each portion was determined.

The resulting dependence of the change in the rate of oxygen uptake as the iron surface became covered with it is presented in Fig. 1a (curve 1). The rate of the process is expressed as $\lg \frac{1}{\tau}$, where τ is the time for uptake of half a portion of oxygen, in minutes. These results are in agreement with data obtained in earlier work of the laboratory (^{3}). Chemisorption of oxygen proceeds on the iron surface in two stages. The rapid stage of chemisorption is characterized by a small change in rate with coverage. This stage ends upon adsorption of $2 \cdot 10^{15}$ molecules of O_2 per 1 cm^2 of true surface, which corresponds to an oxide-film thickness of 6 Å calculated as Fe_2O_3. With further uptake of oxygen the chemisorption rate falls sharply (Fig. 1a, 1). The influence of water vapor on the process of interaction of iron with oxygen was studied by methods applied

Fig. 1

Figure 1: Fig. 1

in the case of germanium (4). After formation on the iron surface of the limiting oxide film, oxygen was pumped out of the gas phase; this, however, did not cause a decrease in the amount of oxygen taken up, since chemisorption of oxygen on iron is irreversible. The iron powder was then brought into contact with water vapor at a pressure of 16-17 mm Hg and kept under these conditions for two hours. After this the iron was degassed, and on such a surface the rate of uptake of individual portions of oxygen was again determined.

It follows from the results obtained that if, after completion of the rapid and slow stages of chemisorption (Fig. 1a, 1), the iron was brought into contact with water vapor, then after its removal by pumping the rate

the chemisorption of oxygen increases sharply, by approximately 10^3 times. By additional adsorption of oxygen, iron can again be brought into the passive state. Upon repeated contact of iron with water vapor and its subsequent removal, the iron again acquires the ability to chemisorb oxygen at a high rate (Fig. 1a, 2, 3, 4, 5). Such activation of iron with respect to oxygen by water vapor can be repeated many times, as a result of which thick oxide layers form on the surface of the iron.

Fig. 1. Dependence of the rate of O_2 absorption by a coating of its surface. $1a, 1b$—adsorption on "reduced iron" ; $2a$—$5a$—at $p_{\mathrm{H_2O}} = 16$—17 mm Hg; $2b$—$p_{\mathrm{H_2O}} = 2.53$ mm; $3b$—$p = 4.58$ mm; $4b$—$p = 8.8$ mm; $5b$—$7b$—$p = 16$—18 mm Hg.

As can be seen from Fig. 1b (curves 2, 3, 4), the activating action depends noticeably on the pressure of the water vapor; moreover, water vapor has the greatest influence at pressures above 9 mm Hg, which is apparently connected with an increase in the amount of adsorbed water.

Heating iron covered with the limiting oxide film leads to phenomena analogous to those observed under the action of water vapor. It follows from Fig. 2 that, after heating in vacuum, passivated iron acquires the ability at room temperature to absorb oxygen again at a considerable rate. As the heating temperature is raised to 200°, the rate of subsequent oxygen chemisorption increases (Fig. 2, 2, 3, 4). Such activation of iron can be repeated many times. The data obtained both under the action of water vapor and upon heating in vacuum indicate a disturbance of the protective properties of the oxide film.

As mentioned above, in order to clarify the mechanism of the disturbance of the protective properties of the oxide film, the interaction of iron with oxygen and water vapor was investigated by the contact-potential-difference method. Figure 3 gives a curve expressing the change in the contact potential difference as a function of the temperature of interaction of iron with oxygen at equal amounts of absorbed O_2. In the temperature interval studied (20—300°)), upon absorption by iron of $2 \cdot 10^{15}$ molecules of O_2 per 1 cm^2 of the true surface of the electrode, the work function is lower than the work function of pure iron. The maximum decrease was observed for a temperature of 100° and amounted to 0.57 V. This value is in complete agreement with data obtained earlier in our laboratory by the thermoelectronic method[5].* The change in the charge of the iron surface under the successive action on it of oxygen, water (at a vapor pressure of 16—17 mm Hg), and vacuum is shown in Fig. 4a. Chemisorption of oxygen at 20° in an amount corresponding to the limiting oxygen film decreases the electron work function by 0.20—0.25 V.

* The agreement of the results obtained by the indicated methods confirms the correctness of the data measured using a comparison electrode sealed with glass.

Upon subsequent exposure to water vapor, an additional decrease in the electron work function by 0.30 V is observed. Removal of the water vapor by degassing practically does not change the value of the contact potential difference. However, if after removal of the water vapor the iron is again brought into contact with oxygen, the work function increases and reaches approximately the value observed before adsorption of the water vapor. Repeated cycles of surface treatment, consisting of successive exposure to oxygen, water vapor, and vacuum, lead to similar changes in the electron work function for all cycles. As in the case of adsorption measurements, heating iron with chemisorbed oxygen at 300° produces an effect analogous to the action of water vapor. The results obtained are shown in Fig. 4b. After each heating, additional absorption of oxygen is observed, leading to an increase in the electron work function in comparison with the value for iron covered with an oxide film at 20°.

Fig. 2. Dependence of the rate of O_2 absorption on the surface coverage by it. 1—adsorption of oxygen on reduced iron; 2—the same on iron after heating at 100°; 3—on iron after heating at 200°; 4—on iron after heating at 300°.

Thus, the combined set of adsorption measurements and measurements of the contact potential difference makes it possible to draw the following conclusions. Chemisorption of oxygen on iron brings it into a passive state. On contact with water vapor, and also as a result of thermal treatment at temperatures of 200-300°, the protective properties of the oxide film are impaired, causing additional absorption of oxygen and formation of thick oxide layers on the surface.

Impairment of the protective properties of the oxide film in the presence of water vapor proves to be the result either of crystallization of the oxides with formation of larger crystals and liberation of part of the metal surface from oxides, or of an increase in the rate of migration of iron atoms to the oxide surface.

The data presented above on changes in the contact potential difference during the interaction of iron with oxygen and water vapor speak rather in favor of the second mechanism. If under the action of water only

Fig. 3

Fig. 4

Fig. 3. Dependence of the contact potential difference on the temperature of interaction of iron with oxygen.

Fig. 4. Effect on the contact potential difference of chemisorbed O_2 (1*a*), water vapor (2*a*), degassing of iron (3*a*) at constant temperature, and chemisorbed O_2 at temperatures of 20° (*Ib*) and 300° (*IIb*).

···a change in the size of the crystals and, in connection with this, a discontinuity of the film arose, then after removal of the water the electron work function should have approached its value for the reduced metal. However, as indicated above, when the oxidized surface of iron comes into contact with water vapor, a further decrease in the electron work function occurs. According to concepts previously developed in our laboratory (^5), and also recently used in other works (^6), these phenomena are associated with the penetration of metal atoms onto the surface of the oxide film and the consequent formation of a double electric layer with its positive end directed outward. The identical decrease in the electron work function, equal to 0.6 V, observed both in the presence of water vapor and upon heating iron coated with a protective oxide film obtained at 20°, also argues in favor of the view that these processes have an analogous nature, apparently associated with the penetration of iron atoms through the oxide film to the surface.

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
24 V 1962

REFERENCES

1. R. Kh. Burshtein, L. A. Larin, DAN, **130**, 565 (1960); G. M. Popova, N. A. Shurmovskaya, R. Kh. Burshtein, DAN, **137**, 904 (1961).
2. R. Kh. Burshtein, L. A. Larin, ZhFKh, **32**, 194 (1958).
3. R. Kh. Burshtein, N. A. Shumilova, K. A. Gol'bert, ZhFKh, **20**, 78 (1946).
4. R. Kh. Burshtein, L. A. Larin, G. F. Voronina, DAN, **133**, 148 (1960).
5. R. Kh. Burshtein, M. D. Surova, I. A. Zaideman, ZhFKh, **24**, 214 (1950).
6. J. S. Anderson, D. F. Klemperer, Proc. Roy. Soc., **258**, 350 (1960).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.