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## Abstract

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# ELECTROCHEMICAL STUDY OF THE KINETICS OF THE REDUCTION OF IRON FROM MOLTEN OXIDES BY GRAPHITE

*(Presented by Academician A. N. Frumkin, July 2, 1964)*

The so-called direct reduction reaction

$$\mathrm{FeO_{sol}} + \mathrm{C_{gr}} = \mathrm{CO_{gas}} + \mathrm{Fe_{met}} \tag{1}$$

is an example of a corrosion process ($^1$) with reversed electrochemical stages ($^2$). Instead of anodic dissolution of the metal, cathodic deposition of iron occurs here:

$$\mathrm{Fe^{2+}_{sol}} + 2e = \mathrm{Fe_{met}}. \tag{2}$$

The cathodic evolution of hydrogen is replaced by formation at the anode:

$$\mathrm{C_{gr}} + \mathrm{O^{2-}_{sol}} = \mathrm{CO_{gas}} + 2e. \tag{3}$$

As in corrosion processes, stage (2) is usually accompanied by concentration polarization ($^3$), and stage (3) by overvoltage.

In this connection, the kinetics of reaction (1) can be studied, like corrosion processes, with the aid of potential—current-density diagrams ($^1$). As a first approximation, for this purpose we used polarization curves obtained at 1350° separately for stages (2) and (3), by a method close to that described earlier ($^3$). A rotating disk electrode ($^4$) was used in combination with the commutator method (50 interruptions per 1 sec). To measure the part of the potential drop occurring in the time interval $10^{-4} \div 10^{-2}$ sec, an EO-7 oscillograph with a sensitivity of $3 \cdot 10^{-5}$ sec/mm was used. The reference electrode was a platinum wire immersed in melt No. 1, located in an alundum test tube. The latter was introduced into the melts under study, the compositions of which are given in Table 1. The disk anode was the end face

**Table 1**

| No. of experiment | Composition | $\varphi_{\mathrm{Fe}^{++}/\mathrm{Fe}}$, by Fe electrode | $\varphi_{\mathrm{Fe}^{++}/\mathrm{Fe}}$, according to Fig. 2 | Reduction rates, A/cm$^2$, (*) | Reduction rates, A/cm$^2$, our data $\sqrt{\omega} = 2{,}7$ |
|---|---|---|---|---|---|
| 1 | 40% CaO, 40% $SiO_2$, 20% $Al_2O_3$ | – | – | – | – |
| 2 | Melt No. 1 + 0.33% FeO + 0.33% $Fe_2O_3$ | −720 | −740 | 0,02 | 0,013 |
| 3 | Melt No. 1 + 0.94% FeO + 1.16% $Fe_2O_3$ | −605 | −670 | 0,21 | 0,02 |
| 4 | Melt No. 1 + 4.6% FeO + 2.2% $Fe_2O_3$ | −507 | −520 | – | 0,048 |

of a carbon cylinder ($d = 5$ mm), the lateral surface of which was protected by a corundum tube. Owing to poor wettability, the solidified melt at the point of contact with graphite was mirror-smooth, i.e., the macro-surface of the electrode did not differ greatly from the working one. At the same time, low wettability has little effect on the frictional force between a liquid and a solid body ($^5$), which helped to preserve similar hydrodynamic conditions.

Curve 1 in Fig. 1 was obtained for a graphite anode in melt No. 1. The weak dependence of the current density ($i$) on the angular velocity of rotation ($\omega$) of the disk indicates that the polarization ($\eta$) here is mainly chemical. This is also consistent with the considerable (30%) drop in $\eta$ during $10^{-3}$ sec after the current was switched off. The cathodic curves (2–6) for iron deposition from melts (No. 2–No. 4) were constructed using the data of work ($^3$), in which a disk electrode made of iron was used.

Fig. 1. Potential-current density diagram.

Figure 1: Fig. 1. Potential-current density diagram.

It was shown therein that in this case concentration polarization mainly occurs, obeying the equation:

$$\eta = \varphi - \varphi_{\mathrm{p}} = \frac{RT}{2F} \ln \left( 1 - \frac{i}{i_{\mathrm{p}}} \right), \tag{4}$$

in which the limiting current is equal to:

$$i_{\mathrm{p}} = i_{\mathrm{p}}^{\mathrm{Fe}^{2+}} + i_{\mathrm{p}}^{\mathrm{Fe}^{3+}} = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2} \left( 2C_{\mathrm{Fe}^{2+}} + 3C_{\mathrm{Fe}^{3+}} \right) = K \left( 2C_{\mathrm{Fe}^{2+}} + 3C_{\mathrm{Fe}^{3+}} \right), \tag{5}$$

where $D$ is the effective diffusion coefficient, $\nu$ is the kinematic viscosity of the melt, and $C_{\mathrm{Fe}^{2+}}$ and $C_{\mathrm{Fe}^{3+}}$ are the concentrations of the $\mathrm{Fe}^{2+}$ and $\mathrm{Fe}^{3+}$ ions.

**Fig. 1.** Potential-current density diagram. **1**—anodic polarization in melt no. 1; **2–8**—polarization curves for cathodic deposition of iron: **2**—melt no. 2, $\sqrt{\omega} = 8.9$; **3**—melt no. 3, $\sqrt{\omega} = 2.7$; **4**—melt no. 3, $\sqrt{\omega} = 8.9$; **5**—melt no. 4, $\sqrt{\omega} = 2.7$; **6**—melt no. 4, $\sqrt{\omega} = 8.9$; **7**—melt no. 4, $\sqrt{\omega} = 2.7$, with allowance for reaction (7); **8**—melt no. 4, $\sqrt{\omega} = 8.9$, with allowance for reaction (7); **9**—polarization curve for anodic dissolution of iron, $\sqrt{\omega} = 8.9$.

When reaction (1) proceeds, reduced iron appears, which dissolves graphite, forming an Fe—C alloy on its surface. Since in this case the activity $a_{\mathrm{Fe}}$ changes little (6), it may be assumed that the equilibrium potential

$$\varphi_{\mathrm{Fe}^{2+}/\mathrm{Fe}} = \varphi^{0}_{\mathrm{Fe}^{2+}/\mathrm{Fe}} + \frac{RT}{2F} \ln \frac{a_{\mathrm{Fe}^{2+}}}{a_{\mathrm{Fe}}} \tag{6}$$

will differ only insignificantly from that for pure iron. From these considerations the initial potentials of curves (2-6) were determined (Table 1).

With the aid of the diagram in Fig. 1 it is possible to predict the magnitude of the stationary potential ($\varphi_{\mathrm{c}}$) at the graphite boundary with melts (nos. 2-4). As is known (1), $\varphi_{\mathrm{c}}$ is found from the condition of equality of currents ($i_2 = i_3$) for stages (3) and (2). The values of $\varphi_{\mathrm{c}}$ found in this way (curves 4-6) are compared in Fig. 2 with those measured by us directly for a rotating carbon disk (curves 1-3). Taking into account the assumptions made, it must be acknowledged that the calculated values of $\varphi_{\mathrm{c}}$ are close to those found experimentally. In this connection a dependence of the stationary potential on the rate of rotation is observed. The existence of such a relation in aqueous solutions was first pointed out by Ya. M. Kolotyrkin (1, 7).

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

However, the experimental curves $\varphi - \omega^{1/2}$, in contrast to the calculated ones, have inflections. They are caused by the occurrence at the cathode of charge transfer:

$$\mathrm{Fe}^{3+}_{\mathrm{p-p}} + \mathrm{e} = \mathrm{Fe}^{2+}_{\mathrm{p-p}}, \tag{7}$$

which begins at more positive potentials than stage (2). In Fig. 1, for melt no. 4, polarization curves (7) and (8) are constructed with allowance for this circumstance. The value of $i$ for potentials to the right of $\varphi = -0.507$ V is equal to $i_1 = KC_{\mathrm{Fe}^{3+}}$, and to the left:

$$i = i_1 + i_{\mathrm{p}} \left(1 - \exp\left\{[\varphi - \varphi_{\mathrm{Fe}^{2+}/\mathrm{Fe}}] \frac{2F}{RT}\right\}\right), \tag{8}$$

where $i_{\mathrm{p}} = 2K\left(C_{\mathrm{Fe}^{3+}} + C_{\mathrm{Fe}^{2+}}\right)$. In this case the potential $\varphi_{\mathrm{c}}$ calculated from the polarization diagram may (see Fig. 1) assume more positive values than $\varphi_{\mathrm{Fe}^{2+}/\mathrm{Fe}}$, and an inflection should appear on the curve $\varphi - \omega^{1/2}$ at $\varphi_{\mathrm{c}} = \varphi_{\mathrm{Fe}^{2+}/\mathrm{Fe}}$. Fig. 2 and the data of Table 1 confirm that

the inflection potential found is indeed close to the value of $\varphi_{\mathrm{Fe}^{2+}/\mathrm{Fe}}$. Since, on the graphite surface, as a result of reaction (1), an Fe–C alloy is formed, anodic dissolution of iron at potentials more positive than $\varphi_{\mathrm{Fe}^{2+}/\mathrm{Fe}}$ is also possible. In this case the anodic current will be partly provided also by dissolution of Fe (Fig. 1, 9), and the stationary potential will decrease (to $\varphi_{\mathrm{c}3}$).

**Fig. 2.** Dependence of the stationary potential on the rotation rate of the electrode: **1, 4** –melt No. 2; **2, 5** –melt No. 3; **3, 6** –melt No. 4

**Fig. 3.** Dependence of the reduction rate on the rotation rate of the disk: **1** –melt No. 2; **2** –melt No. 3; **3** –melt No. 4

The values of $\varphi_{\mathrm{c}}$, together with the polarization curve for the graphite anode, make it possible to predict the rate of reaction (1) and of the reaction

$$\mathrm{C} + \mathrm{Fe}_2\mathrm{O}_3 = 2\mathrm{FeO} + \mathrm{CO}. \tag{9}$$

It is equal to the value of the polarizing current ($i$) at the given $\varphi_{\mathrm{c}}$. As can be seen from Fig. 3, $v_{\mathrm{c}}$ is proportional to $\omega$ not to the power 0.5, which would correspond to a purely diffusion regime.

Unfortunately, the literature contains no data on the kinetics of direct reduction close in temperature and hydrodynamic conditions, which makes it difficult to compare the rate values calculated by us with experimental ones. Only qualitative agreement may be noted with the results obtained in work (8) at 1430° and natural convection.

In conclusion, we note that the maximum possible (without diffusion limitations) reduction rates (see, for example, $i_m$ in Fig. 1) for more electropositive ions (for example, $Cu^+$, $Co^{2+}$, etc.) should be higher, since the corresponding potentials are more positive than $\varphi_{Fe^{2+}/Fe}$.

A parallelism between the rate of direct reduction and the elasticity of dissociation has also been indicated earlier for solid oxides (9).

The results obtained by us indicate the promise of using the method of corrosion diagrams for studying the regularities of the kinetics of metallurgical reactions.

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## CITED LITERATURE

1. A. N. Frumkin, V. S. Bagotskii et al., *Kinetics of Electrode Processes*, Moscow, 1952.
2. A. I. Sotnikov, O. A. Esin, Yu. P. Nikitin, *Izv. Vyssh. uchebn. zaved. Chernaya metallurgiya*, No. 8, 19 (1963).
3. V. N. Boronenkov, O. A. Esin, P. M. Shurygin, DAN, 151, No. 4, 872 (1963).
4. V. G. Levich, *Physicochemical Hydrodynamics*, 1959.
5. B. V. Deryagin, *What Is Friction?*, Publishing House of the Academy of Sciences of the USSR, 1963.
6. S. T. Rostovtsev, *Theory of Metallurgical Processes*, 1957.
7. Ya. M. Kolotyrkin, ZhFKh, 25, 1248 (1950).
8. W. O. Philbrook, L. D. Kirbride, *J. Metals*, 8, No. 3, 351 (1956).
9. P. V. Geld, *Usp. khim.*, 26, 1070 (1957).

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