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MATHEMATICAL SIMULATION OF BORATING OF IRON

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Results of a numerical study of borating of iron with allowance for the kinetics of chemical reactions are presented. It is shown that the chemical potential of the external source of boron exerts the main effect on the composition and size of the borides. The existence of an intermediate region consisting of FeB and Fe_2B is detected.

Introduction. The first work in our series of studies [1] presents results of a study of the chemicothermal process of borating iron [2] within the framework of the Stefan approximation. Here it was assumed that diffusion of "free" boron both inside iron and inside each of the borides is the limiting process in the motion of the boundaries between the borides. The boundaries between the borides were taken to be infinitely thin.

In the present paper the process of borating iron is studied within the framework of the so-called kinetic approach [3], which explicitly allows for the chemical nature of the borating process. The paper is aimed at the elucidation of the restrictions imposed simultaneously on the process of borating iron by the diffusional and chemical kinetics. The effect of rearrangement of the iron crystal lattice is disregarded, which makes it possible to compare only qualitatively the results of calculations with experimental data obtained by standard methods [2].

We consider two elementary chemical reactions that, we believe, play the main role:

$$\mathrm{Fe} + \mathrm{B} \underset{k_1^*}{\overset{k_1}{\rightleftarrows}} \mathrm{FeB}\,, \tag{1}$$

$$2\mathrm{FeB} \underset{k_1^*}{\overset{k_2}{\rightleftarrows}} \mathrm{Fe_2B} + \mathrm{B}. \tag{2}$$

As follows from the adopted kinetic scheme (1) and (2), at a microscopic level the lower boride Fe_2B can be formed only as a result of decay of the higher boride FeB. This is in agreement, to a certain extent, with data of a thermodynamic determination [4] that the chemical potential of the lower boride is always smaller than the chemical potential of the higher boride. Thus, the higher boride is thermodynamically less stable although the conditions for its formation are more favorable from the kinetic point of view. In other words, the macroscopic concentration of the higher boride is determined by both the processes of boron diffusion and the kinetics of chemical conversions. Recall that from the engineering point of view the formation of macroscopic phases of the higher boride is undesirable [1]. Preliminary results of this study are published in [4].

Mathematical Model. The nonlinear mathematical model of the process of borating iron involves a diffusion equation of "free" boron with a source, two equations describing the kinetics of chemical reactions (1) and (2) [5],

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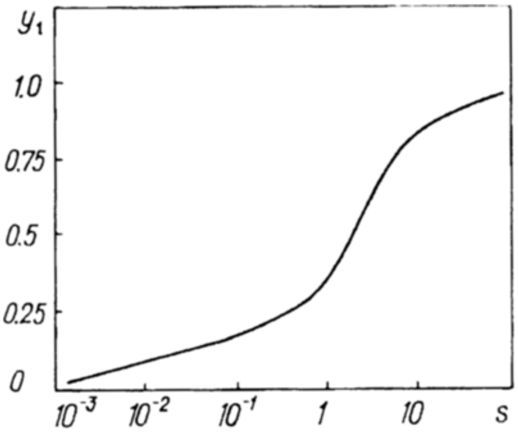

Fig. 1. Dependence of the relative concentration of the higher boride on the parameter s.

and an equation expressing the law of conservation of iron atoms [4]. In a one-dimensional approximation the mathematical model has the form

$$\frac{\partial y_B}{\partial t} = D\frac{\partial^2 y_B}{\partial x^2} - \frac{dy_1(x, t)}{dt}, \tag{3}$$

$$\frac{dy_1}{dt} = k_1 y_{Fe} y_B(x, t) - \frac{dy_2}{dt}, \tag{4}$$

$$\frac{dy_2}{dt} = k_2 y_1^2 - k_2^* y_2 y_B(x, t), \tag{5}$$

$$y_1 + 2y_2 + y_{Fe} = 1. \tag{6}$$

The dimensionless variables y_1, y_2, y_{Fe}, and $y_B(x, t)$ in Eqs. (3)-(6) are, respectively, equal to:

$$y_1 = \frac{n_1}{n_0}, \quad y_2 = \frac{n_2}{n_0}, \quad y_{Fe} = \frac{n_{Fe}}{n_0} \text{ и } y_B = \frac{n_B}{n_0},$$

where $n_0 \simeq 8 \cdot 10^{28}$ atom/m^3 is the number of iron atoms per unit volume, and n_1, n_2, n_{Fe}, and n_B are the number of atoms of the higher boride, the lower boride, iron, and "free" boron per unit volume, respectively.

The algebraic nature of Eq. (6) reflects the physically obvious fact that the mobility of "free" atoms of boron exceeds by several orders the mobility of the other elements of the studied system.

It is seen from the formulation of Eqs. (3)-(5) that the sample composition in the vicinity of the point with the coordinate x depends on the boundary conditions for free boron, the instant of time t, and the rate constants of the chemical reactions that enter into Eqs. (4) and (5). Naturally, it is more correct to describe the kinetics of chemical reactions in iron by activities [5], but we follow the traditional scheme for describing the kinetics of chemical reactions.

Spatially Uniform System. We consider the important particular case where the concentration of "free" boron is constant in space and time. Then, within the framework of the assumptions made above, after simple calculations we obtain a basic result that is needed in what follows:

$$y_1 = \frac{-k_2^*/k_2\,(0.5y_B + k_1^*/2k_1n_0) + [[k_2^*/k_2\,(0.5y_B + k_1^*/2k_1n_0)]^2 + 2y_Bk_2^*/k_2]^{0.5}}{2}.$$

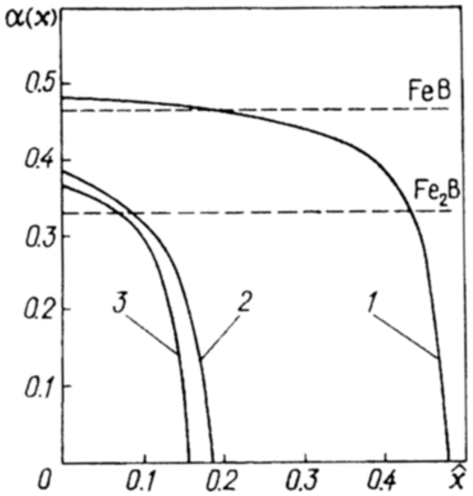

Fig. 2. Profiles of the atomic concentration of bound boron in borides in borating for 400 sec. The dimensionless length $\hat{x}$ is plotted as abscissa: 1) $c_0 = 4 \cdot 10^{-2}$; 2) $1 \cdot 10^{-3}$; 3) $4 \cdot 10^{-4}$.

The plus sign in front of the root is selected from the condition of positiveness of y_1 at any values of the parameters. Figure 1 gives the dependence of y_1 on the product of dimensionless parameters $y_B k_2^*/k_2$. It is seen that at rather large values of this parameter the higher boride is dominant in the system, and at rather small values the lower boride prevails in the system. In an intermediate state the system is a mixture of higher and lower borides. It is of interest to note that due to the large value of n_0 the dimensionless complex $k_1^*/k_1 n_0$ hardly affects the composition of the system. The dependence of y_1 on the complex $y_B k_2^*/k_2$ is described by the [1/1] Pade approximant with sufficient accuracy [6]:

$$y_1 = \frac{0.632s}{1 + 0.632s},$$

where $s = u_B k_2^*/k_2$.

Results of Numerical Calculations. Due to the fact that the characteristic times of chemical conversions in a condensed phase are much smaller than the characteristic times of a diffusion process [5], it is reasonable to solve the system of equations (3)-(6) in a quasistationary approximation. Namely, Eqs. (4)-(6) are solved in a stationary approximation, regarding, as follows from (3), the quantity $z = y_B + y_1$ to be assigned. As a result the variables y_1, y_2 depend on space-time variables only parametrically in terms of $z(x, t)$. Due to the adopted assumption of a quasistationary approximation only the ratios of the rate constants k_2^*/k_2 and $k_1^*/k_1 n_0$ are of interest.

The boundary conditions for Eq. (3) have the form

$$y_B(0, t) = c_0, \quad y_B(\infty, t) = 0. \tag{7}$$

The initial condition was selected as follows: all borides are absent and the concentration of "free" boron quickly tends to zero (at a distance of about 4 μm from the boundary). To solve Eq. (3) an explicit numerical scheme was used. Stability of the calculation was provided by the corresponding choice of space-time steps [7]. The steps depend on the value of c_0. In turn, c_0 is associated with the potential of the source of boron outside the iron [4]. We point out that boundary conditions of the third kind, which are of greatest interest for analysis of borating technologies, were used in [4].

Practically all subsequent numerical results are given for the case where $k_2^*/k_2 = 105$, $k_1^*/k_1 n_0 = 10^{-4}$, since only with this ratio of the rate constants of the reactions is qualitative agreement observed between results on the equilibrium solubility of boron in the higher boride [1] and experimental data obtained at a temperature of about 900°C [8].

TABLE 1. Correspondence of the Atomic Concentration of Boron to Data of X -Ray Structural Analysis

Atomic concentration α, %	25	33.9	39.8	45	47.9	50
Composition	Fe_2B + Fe	Fe_2B	Fe_2B + FeB	Fe_2B + FeB	FeB	FeB

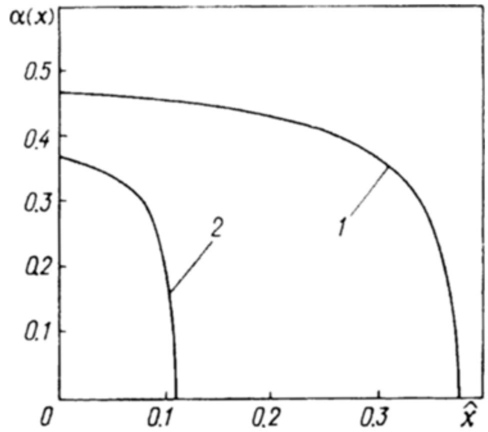

Fig. 3. Profiles of the atomic concentration of bound boron in borides in borating for 3600 sec: 1) $c_0 = 4 \cdot 10^{-2}$; 2) $4 \cdot 10^{-4}$.

Figure 2 presents profiles of the atomic concentration $\alpha(x)$ of boron "bound" in the borides [9] for $t = 400$ sec. The atomic concentration was calculated by the formula

$$\alpha(x) = (y_1 + y_2)/(2y_1 + 3y_2 + y_{Fe}) . \quad (8)$$

As follows from (8), for an ideal specimen of FeB $\alpha = 0.5$, and for a specimen of Fe_2B $\alpha = 0.33$. The thicknesses of the boride layers x are given in the dimensionless form $\hat{x}$ by the expression

$$\hat{x} = x \sqrt{Dt} .$$

It is seen that depending on the value of c_0 the formation of both one- and two-phase borides is observed. Within the framework of our model only the value of the chemical potential of the external source in terms of c_0 determines the presence of the higher boride for given ratios of the kinetic parameters, which, in turn, depend only on temperature. The value of c_0 also affects the thickness of the boride layers. The figure does not show the appearance of very small concentrations of FeB with a thickness of not more than 10 μm behind the boundary of Fe_2B and Fe.

We took Table 1 showing the correspondence of boron atomic concentrations to results of x-ray structural analysis of macroscopic phases of Fe_2B and FeB from [9]. The limits of the borides by concentration taken from Table 1 are given in Fig. 2 by the dashed horizontal lines. Thus, the presence of appreciable transition layers between the higher and lower borides follows from the kinetic description developed in the present paper. At the same time, the boundary between Fe_2B and Fe is rather sharp. In a two-front diffusion model [1] intermediate layers were absent, which makes a comparison of our numerical results with analytical one obtained by it quite difficult. In the diffusion model with a finite thicknesses for the transition layers also given in [4] the thickness of the intermediate layers was used as an adjustment parameter for comparing computational and experimental data.

Figure 3 presents profiles of the atomic concentration $\alpha(x)$ for $t = 3600$ sec. A comparison of Figs. 2 and 3 shows that the profiles are similar, although the relative thickness of the transition layers grows with the borating time. As a result the dependence of the characteristic size of the diffusion region l on time

$$l \sim \sqrt{Dt}$$

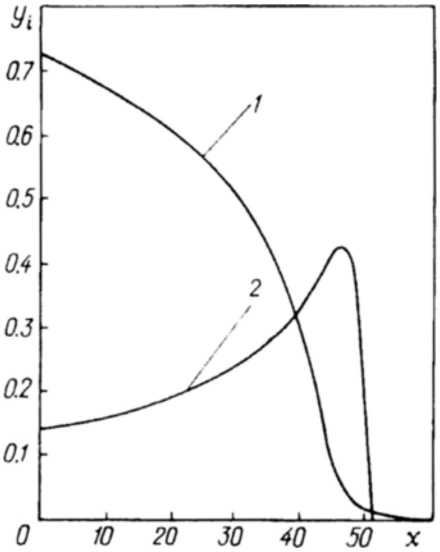

Fig. 4. Profiles of y_1 and y_2 in borating for 400 sec, $c_0 = 4 \cdot 10^{-2}$: 1) relative concentration of the higher boride; 2) relative concentration of Fe_2B.

is fulfilled only approximately: the smaller c_0 the more satisfactorily. Figure 4 gives profiles of y_1 and y_2 for $c_0 = 0.04$ and $t = 400$ sec. It is seen that a large portion of the boride layer is an intermediate phase consisting, from the macroscopic point of view, of molecules of both the higher and lower borides. We note the appearance of indications of the higher boride (FeB) in accordance with the kinetic scheme (1) and (2).

In this study the problem of the the constants of the chemical reactions occupies an important place. We had to solve it by a trial-and-error method using experimental data. In general the problem of reproducing rate constants of chemical reactions from experimental data is rather complex and requires a large amount of experimental information. We show that in our problem it is possible to estimate k_2^*/k_2 and $k_1^*/k_1 n_0$ using the kinetic equations (4)-(6) and the value of the equilibrium solubility of "free" boron obtained in [1] and also additional conditions. In fact, assuming that in the higher boride $y_1 \approx 0.7$ (then $\alpha \geq 0.43$) and in the lower boride $y_2 \approx 0.4$ ($\alpha \sim 0.35$) and imposing the condition of positiveness of k_2^*/k_2 and $k_1^*/k_1 n_0$, one can find the maximum value of the solubility of boron in the lower boride and the corresponding values of the kinetic parameters. In particular, under these conditions the solubility of boron in the lower boride does not exceed $8 \cdot 10^{-4}$. This value is about an order of magnitude smaller than that obtained in [1] on the basis of processing experimental data within the framework of a two-front model. The divergence is associated with the fact that within the framework of the two-front model one neglected, as the results given above show, the presence of an aooreciable amount of the higher boride in the sample, which, from the macroscopic point of view, is the lower boride. We note that, as our numerical experiments showed, a 10% variation of the parameter k_2^*/k_2 does not affect the basic results of our work. A decrease in the parameter $k_1^*/k_1 n_0$ hardly influences the numerical results, whereas a increase in this parameter suppresses formation of macroscopic regions of the lower boride.

Conclusions. 1. Within the framework of the kinetic approach it is found by methods of mathematical simulation that the Stefan approximation in describing borating is a rather strong idealization. An analysis of experimental data [8] based on analysis of microsections (partially presented in [4], Table 5) and the results given above shows that the boundary between the borides, which is associated with rearrangement of the crystal lattice, appears at the value of the atomic concentration $\alpha \cong 0.435-0.42$.

2. The problem of equilibrium solubilities of free boron in the borides due to the presence of large intermediate regions involving both FeB and Fe_2B becomes incorrect in many respects. Due to this, experimental data on their determination should be contradictory, as mentioned in [2].

3. The ratio of the rate constants of the chemical reactions k_2^*/k_2, which plays an important role in the kinetics of borating, depends on temperature. This ratio, as experiments on annealing the higher boride show [5, 6], decreases as the temperature increases.

4. The mathematical model developed can be used to study not only the process of borating, but also deborating and isothermal annealing. It is of interest to refine experimentally the relation between the composition of the intermediate phase and structural conversions in the crystal lattice of iron.

NOTATION

x, space coordinate inside the iron; $x = 0$, the boundary of a semi-infinite specimen of iron; t, time coordinate; n_0, number of iron atoms per unit volume; y_1, y_2, y_{Fe}, dimensionless concentrations of the higher boride, the lower boride, and iron, respectively; c_0, boundary condition on the dimensionless concentration of "free" boron y_B; D, coefficient of diffusion of boron; k_i and k_i^*, rate constants of the direct and reverse reactions (i), $i = 1, 2$.

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