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MATHEMATICAL SIMULATION OF BORATING OF IRON. DIFFUSIONAL APPROXIMATION

B. S. Kukharev, A. N. Rogozhnikov, S. P. Fisenko, and S. I. Shabunya

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The growth of ferroborides on borating and diffusional annealing is investigated within the framework of the diffusional approximation. The solubility of boron in Fe_2B, FeB is evaluated from comparison of calculated and experimental data.

Introduction. The chemicothermal boration process [1-4], in which boron is incorporated into a surface layer of iron as well as some other materials, is widely employed in industry. Boron, having diffused into a metallic sample, and the base metal form a film at the corresponding temperatures of treatment (about 1000°C for iron), consisting of one or several intermetallic phases, the so-called borides. In many cases the presence of borides in the surface zone of a metal sharply improves the service properties of articles.

An engineering approach to investigating the boration process has allowed a number of important laws of this complicated process to be revealed. However, it is natural to desire to study this process also using other approaches.

In principle, two more approaches are possible, namely, physicochemical and kinetic [5]. In the case of the physicochemical approach, all elementary processes are analyzed independently of the degree of their effect, in our case, on a boration process. Within the framework of the physicochemical approach, the main attention is paid to the limiting process, i.e., that proceeding at the lowest rate, while physicochemical aspects of the problem serve only for formulating and refining the initial and boundary conditions. The present work is mainly concerned with the kinetic approach to the boration process, with all transfer processes being investigated in a one-dimensional approximation.

In the case of the kinetic approach, the rates of the chemical reactions resulting in formation of the lower Fe_2B and higher FeB borides are assumed to be sufficiently high so that the limiting process represents diffusional boron transfer both inside iron and inside each of the borides.

Investigation of the growth of the intermetallic phases (Fe_2B and FeB) is of keen interest since experimental data on the dimensions of the boride layers are often necessary for deciding whether to use an article or a technology in practice.

Mathematical Model of Boration in the Diffusional Approximation. Figure 1 represents schematically the arrangement of the boride layers when iron is borated, with the position of boundaries ζ_1 and ζ_2 being dependent on time.

In region I we have the diffusion equation for "free" chemically unbound boron

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c}{\partial x^2}, \tag{1}$$

where c(x, t) is the number of boron atoms in the neighborhood of the point x at the moment t. The x axis runs perpendicular to the surface through which borating is carried out.

The boundary condition at infinity is of the form

$$c(\infty, t) = 0,$$

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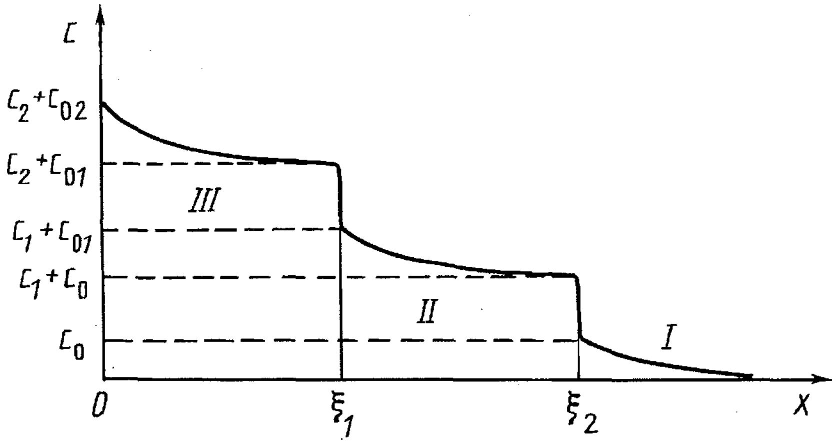

Fig. 1. Atomic concentration profile of boron (free + chemically bound) on two-phase borating. c, concentration.

and the boron density at the boundary ζ_2 is

$$c(\zeta_2,\ t) = c_0, \tag{2}$$

where c_0 is the equilibrium solubility of boron. In the case of iron, where boron is the interstitial impurity, the equilibrium solubility [2] is $c_0 = 1.4 \cdot 10^{25}$ atom/m^3.

D_1 is the diffusion coefficient of boron in the material. For diffusion of boron in iron, the diffusion coefficient depends on the temperature as follows: at T = 1000, 1100, 1200, 1300 K D = (5, 17, 28, 58) $\cdot 10^{12}$ m/sec.

In region II (Fe_2B), for $\zeta_2 < x < \zeta_1$ we also have the diffusion equation for free boron but with another diffusion coefficient:

$$\frac{\partial c}{\partial t} = D_2 \frac{\partial^2 c}{\partial x^2} \tag{3}$$

with the boundary conditions

$$c(\zeta_2,\ t) = c_0, \quad c(\zeta_1,\ t) = c_{01} \tag{4}$$

and the condition for determining the velocity of the interface between the lower boride and iron

$$-D_2 \frac{\partial c}{\partial x}\bigg|_{x=\zeta_2} = v_1 c_1 - D_1 \frac{\partial c}{\partial x}\bigg|_{x=\zeta_2}, \tag{5}$$

where D_2 is the diffusion coefficient of boron in Fe_2B; c_1 is the number of atoms of chemically "bound" boron in the boride Fe_2B [2], equal to $c_1 = 4 \cdot 10^{26}$ atom/m^3; V_1 is the velocity of motion of the Fe_2B-Fe interface; c_{01} is the solubility of boron in the lower boride; its determination from the data on the intermetallic phase dimensions is one of the goals of the present work.

In region III (FeB), for $0 < x < \zeta_1$ we have the diffusion equation for free boron

$$\frac{\partial c}{\partial t} = D_3 \frac{\partial^2 c}{\partial x^2} \tag{6}$$

with the boundary conditions

$$c(\zeta_1,\ t) = c_{01}, \quad c(0,\ t) = c_{02} \tag{7}$$

and the condition for determining the velocity of the interface between the higher and lower borides

$$-D_3 \frac{\partial c}{\partial x}\bigg|_{x=\zeta_1} = v_2 (c_2 - c_1) - D_2 \frac{\partial c}{\partial x}\bigg|_{x=\zeta_1}, \tag{8}$$

where D_3 is the diffusion coefficient of boron in FeB; c_2 is the number of atoms of "bound" boron in FeB equal to $c_2 = 8 \cdot 10^{28}$ atom/m^3; v_2 is the velocity of motion of the FeB-Fe$_2$B interface; c_{02} is the equilibrium solubility of boron in FeB.

Unfortunately, at present, the values of D_2 and D_3 are unknown. However, by virtue of the high mobility of boron atoms it is reasonable to assume that

$$D_1 \simeq D_2 \simeq D_3 \simeq D.$$

For technological purposes borating of iron is performed at a sufficiently high temperature T, when $T/T_m > 0.5$, where T_m is the melting temperature of either iron or the borides. At such temperatures an account of structural stresses, occurring near an interface, gives only a small correction for volume mass transfer by diffusion [6]. Furthermore, in cases important in practice, the dimensions of the phases attain hundreds of microns, which greatly exceeds those of the interphase region, so that contribution of structural stresses is insignificant even at not very high temperatures. Taking into consideration the above assumption about the equality of the diffusion coefficients, we shall neglect the contribution of structural stresses in order to follow the adopted accuracy of the investigation.

We consider the boration process, incorporating dimensionality theory. Within the framework of the problem formulated above, the position of the boundaries of the higher and lower borides is determined by the following parameters: D, t, c_1, c_0, c_{01}, c_{02}. Then from dimensionality theory it follows that

$$\zeta_1 = \sqrt{Dt}\, F_1\left(\frac{c_0}{c_1}, \frac{c_{01}}{c_1}, \frac{c_{02}}{c_1}\right), \quad \zeta_2 = \sqrt{Dt}\, F_2\left(\frac{c_0}{c_1}, \frac{c_{01}}{c_1}, \frac{c_{02}}{c_1}\right), \tag{9}$$

where F_1 and F_2 are dimensionless functions of dimensionless arguments, which are not determined in dimensionality theory. Hence we immediately arrive at the important result that $\zeta_1/\zeta_2 = \text{const}$. Moreover, this circumstance will be employed in searching for experimental data pertaining to first-kind boundary conditions.

In order to obtain functions F_1 and F_2 in explicit form by processing experimental data, it is necessary to preliminarily know c_{01} and c_{02}. Therefore, it is important to obtain more detailed formulas relating ζ_1 and ζ_2 within the framework of diffusional approximation (1)-(8).

Seeking to obtaining results by the simplest analytical method, we shall solve diffusion problems in the approximation that in zones I, II the density of free boron c(x) changes according to a linear law [7]. It is sufficiently easy to show that the condition of applicability of this approximation has the form

$$\frac{c_{02} - c_{01}}{c_1} \ll 1$$

and

$$\frac{c_{01} - c_0}{c_1} \ll 1.$$

In the case of borating of iron, as shown below, these inequalities are satisfied sufficiently well.

In zone I (see Fig. 1)

$$\left.\frac{\partial c}{\partial x}\right|_{x=\zeta_2} \simeq \frac{c_0}{L}, \tag{10}$$

where $L = \sqrt{2Dt}$ [6]; it is clear that the contribution of this term at large times may be neglected.

In zone II

$$\frac{\partial c}{\partial x} \simeq \frac{c_{01} - c_0}{\zeta_2(t) - \zeta_1(t)} \tag{11}$$

and in zone III

$$\frac{\partial c}{\partial x} \simeq \frac{c_{02} - c_{01}}{\zeta_1(t)}. \tag{12}$$

Substituting expressions (10)-(12) into (5) and (8), we arrive at the following system of equations for determining the velocities v_1 and v_2 of the moving fronts:

$$v_2 = \frac{d\zeta_2}{\partial t} = \frac{D}{c_1}\left(\frac{c_{01} - c_0}{\zeta_2(t) - \zeta_1(t)}\right), \tag{13}$$

$$v_1 = \frac{d\zeta_1}{\partial t} = \frac{D}{c_2 - c_1}\left[\frac{c_{02} - c_{01}}{\zeta_1(t)} - \frac{c_{01} - c_0}{\zeta_2(t) - \zeta_1(t)}\right]. \tag{14}$$

We shall seek a solution to system (13), (14) at sufficiently large times. Then with consideration of (9) the coordinates of fronts are represented as

$$\zeta_1 = \beta_1 \sqrt{t}, \quad \zeta_2 = \beta_2 \sqrt{t}. \tag{15}$$

Substituting (15) into (13), (14), we obtain an algebraic system for determining of β_1 and β_2:

$$\beta_2 = \frac{A_1}{\beta_2 - \beta_1}, \quad \beta_1 = \frac{A_2}{\beta_1} - \beta_2, \tag{16}$$

where

$$A_1 = 2D(c_{01} - c_0)/c_1, \quad A_2 = 2D(c_{02} - c_{01})/c_1$$

and it is taken into account that in borating of iron $c_2 - c_1 = c_1$.

We rewrite (16) in the form

$$\beta_2^2 - \beta_2\beta_1 = A_1, \quad \beta_1^2 + \beta_2\beta_1 = A_2. \tag{17}$$

Using (15), (17) and experimental data from [8] on boride layer thicknesses in Armco iron obtained in borating in powders at 1173 K during $t^* = 4$ h ($\zeta_1 = 106\ \mu$m, $\zeta_2 = 180\ \mu$m), we arrive at the following system of equations for determining c_{01} and c_{02}:

$$\zeta_2^2 - \zeta_1\zeta_2 = \frac{2Dt^*}{c_1}(c_{01} - c_0), \quad \zeta_1^2 + \zeta_1\zeta_2 = \frac{2Dt^*}{c_1}(c_{02} - c_{01}). \tag{18}$$

From (18) after substitution of experimental data we obtain that

$$c_{01} = 7{,}4 \cdot 10^{26}\ \text{atom/m}^3 \tag{19}$$

$$c_{02} = 24{,}2 \cdot 10^{26}\ \text{atom/m}^3 \tag{20}$$

It is of interest to note that from (17) the following approximate equalities may be written:

$$\begin{gathered} \beta_2 = \sqrt{\frac{A_2 + 3A_1}{2}} = \sqrt{\frac{D}{c_1}(c_{02} + 2c_{01} - 3c_0)}, \\ \beta_1 = \beta_2 - \sqrt{\frac{4D(c_{01} - c_0)^2}{c_1(c_{02} + 2c_{01} - 3c_0)}}. \end{gathered} \tag{21}$$

The above formulas allow evaluation of the specific (per unit area) flow rate of boron in the boration process. The specific flow rate j must not be less than j_0 ($j_0 = mc_1(v_1 + v_2) = mc_1(\beta_1 + \beta_2)t^{-1/2}$).

Simulation of Diffusional Annealing. The process of diffusional annealing [8], aimed at destruction of the higher boride formed at the first boration stage, is of importance in borating of iron articles. The system of equations (1)-(8) and, consequently, (13), (14) allows its description in the diffusional approach. During optimum diffusional annealing, conditions are provided at the external boundary of the higher boride such that

$$c(0,\ t) \simeq c_{01}. \tag{22}$$

Then the system of equations (13), (14) acquires the form

$$\frac{d\zeta_2}{dt} = \frac{A_1}{2(\zeta_2 - \zeta_1)}, \quad \frac{d\zeta_1}{dt} = -\frac{A_1}{2(\zeta_2 - \zeta_1)} \tag{23}$$

with the initial condition: at $t = 0, \zeta_1(0) = L_1$, $\zeta_2(0) = L_2$, so that $L_2 - L_1 = L$.

Subtracting the second equation from the first equation of system (23) and integrating, we obtain

$$\zeta_2(t) - \zeta_1(t) = \sqrt{2A_1t + L^2}. \tag{24}$$

The width of the region occupied by the lower boride is equal to $\zeta_2(t) - \zeta_1(t)$. The time of higher boride decomposition t_p may be found with an account of the circumstance that the left and right boundaries of the region occupied by the lower boride move with the same, in absolute value, velocity (see (23)) in annealing. As a result, we may write a relation for determining t_p when $\zeta_1(t_p) = 0$:

$$\zeta_2(t_p) - \zeta_1(t_p) = 2L_1 + L = \sqrt{2A_1t_p + L^2},$$

and having solved it, we obtain

$$t_p = \frac{2L_1L}{A_1} = \frac{L_1L_2c_1}{D(c_{01} - c_0)}. \tag{25}$$

After the lapse of time t_p the problem on diffusional annealing loses, naturally, its meaning because of higher boride decomposition. At this moment, the lower boride thickness is naturally equal to

$$\zeta_2(t_p) = 2L_1 + L.$$

If the annealing process proceeds for times exceeding t_p, then the lower boride continues to grow but at a lower rate. As follows from (13), at $\zeta_1 = 0$ its growth is characterized by the formula

$$\zeta_2(t) = \sqrt{\frac{2D(c_{01} - c_0)(t - t_p)}{c_1}} + 2L_1 + L.$$

Conclusion. Within the limits of the assumption that in borating of iron the diffusion of "free" boron is the slowest but a sufficiently intensive process, a mathematical model of the boration process is built that allows one to obtain simple analytical results. The parameters growth of the boride layers in borating and diffusional annealing are determined. As a result of processing the experimental data, boron solubility values for the higher and lower borides are obtained that are considerably higher than for iron. Also, an expression is obtained for the time of decomposition of the higher boride in diffusional annealing.

NOTATION

ζ_1, ζ_2, coordinates of the fronts of the FeB-Fe_2B and Fe_2B-Fe transitions; $c(x, t)$, number of chemically unbound boron atoms in the neighborhood of the point x at the moment t; c_0, c_{01}, c_{02}, equilibrium solubility of boron in iron and the lower and higher ferroborides, respectively; m, mass of the boron atom; t_p, time of decomposition of the higher ferroboride in diffusional annealing.

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