Simulation of the incubation time for the formation of (FeB/Fe₂B) bilayer on pure iron

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In this work, a mathematical model was used in order to study the growth kinetics of (Fe₂B/FeB) bilayer during boriding process basing on the second Fick's law and mass balance equation. The run of the numerical simulation allowed calculating the incubation time (τ) of each boronized layer (Fe₂B or FeB), and estimating the effect of this parameter on the growth of the boronized layer. The boride incubation time for forming the FeB or Fe₂B layer on the pure iron substrate was incorporated into the present mathematical model. To simulate the value of the growth rate constant and the incubation time for the bilayer configuration, the experimental data available in the literature concerning the boronizing of pure iron were considered. Based on the experimental and simulation results, it was shown that the incubation time decreases with increasing temperature in the FeB and Fe₂B phases.

It was concluded from this study that the thickness of each boride layer depended on its growth rate constant and on another parameter k_r which was the rate constant of incubation time. The obtained results confirmed the validity of the present mathematical model and gave a good estimate of the incubation time during the formation of each boride layer as well as formulated the variation of this parameter with a mathematical equation. Furthermore, the comparison of experimental data with the simulated results of boronized layer thickness allowed to validate the present model.

INTRODUCTION

The boronizing is a thermochemical treatment widely used in the industry [1-3]. By this process, a boronized layer on the metal surface was obtained which is characterized by a good resistance to abrasive and adhesive wear [4]. The boronizing treatment is based on the diffusion of boron atom in the iron matrix (Fe) with the possibility of chemical reactions required to form the borided layer [5].

According to the Iron-Boron equilibrium diagram [6], the diffusion of the boron atoms into the crystalline lattice leads to the formation of two types of iron borides Fe₂B and FeB [7-8]. The thickness and the quality of boronized layer depend on the chemical composition of boronizing medium, the chemical composition of the treated metal and the treatment duration [3, 9]. Generally,

the boronizing is carried out in the temperature range of 1023 K to 1323 K [3, 10].

The process of boronizing is realized in various mediums, in solid medium with a paste of boron, in powder, in a liquid medium with or without electrolysis and in a gas medium [3, 11-12].

In the boronizing treatment, we have two important parameters the boron concentration and the temperature [13]. Generally, if the boron potential is high, a bilayer configuration (FeB/Fe₂B) was obtained while for a low potential of boron, a single layer of Fe₂B was formed [14].

There are many studies in the literature devoted to modeling of boronizing kinetics, using a mathematical or predictive model [15-16]. Brakman et al. [17] developed a simple model to study the growth kinetics of bilayer configuration (FeB/Fe₂B) obtained after the powder-pack boronizing. Campos et al. [18] developed another model to estimate the boron diffusivity in the Fe₂B phase. In a recent work, published by Keddám et al. [19], a kinetic model has been proposed to study the growth kinetics of FeB and Fe₂B layers on AISI D2 steel where the effect of diffusion annealing process was taken into account. Keddám et al. [20] suggested another approach to investigate the boronizing kinetics of a cast iron by using a different mathematical model.

Some of these models are developed without considering the presence of incubation times of borided layer. In general, the estimation of the incubation time of the boride layer is very difficult. It is relatively easy to indicate the incubation time of borides during gas boriding [3].

The study of the kinetics of the boride layer required a mathematical model for analyzing the effect of different parameters during the growth kinetics of the boronizing layer, in this work; a diffusion model is suggested to simulate the incubation time formation of boronized layer.

The main objective of this study is to develop a mathematical model to estimate the incubation time of

each boride layer (Fe₂B or FeB) by introducing a kinetic parameter called B(T). The modeling of the growth kinetics of FeB and Fe₂B layers on pure iron with the consideration of boride incubation time was used as a simple tool to calculate the thicknesses of borided layer with a good precision compared to other models [14].

MATHEMATICAL MODEL

The knowledge of the thermodynamic properties of the Iron-Boron system is very important to understand the boronizing process [21]. In the case of the bilayer configuration, the Iron-Boron diagram shows the following phases: the alpha iron (α -Fe) for the temperature range less than 1184.6 K. For the other temperatures, the system shows the presence of gamma iron γ -Fe besides the iron borides (FeB and Fe₂B) [22].

These structural changes are accompanied by the changes in density and mechanical properties. They have particularly important consequences for the elaboration and treatment of pure-body mixtures which exhibit such allotropic transformations.

The diffusion of boron atoms in Fe crystalline lattice is formulated with the second Fick's law as follows:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i(x, t)}{\partial x^2} \quad (1)$$

with: $C_i(x, t)$ is the boron concentration in the phase i , ($i = \text{FeB}, \text{Fe}_2\text{B}$ or Fe), for a distance x after the duration of treatment t and temperature T .

Figure 2 shows a schematic representation of the boron-concentration profile through the borided layer for a given temperature. For a high boron potential, the production of two-layers (FeB+Fe₂B) is possible.

Fig. 1. Schematic representation of the boron-concentration profile through the boride layer (λ_{FeB} and $\lambda_{\text{Fe}_2\text{B}}$ represent the boride layers' thicknesses of FeB and Fe₂B)

The present diffusion model considers the following assumptions:

- The flow of boron atoms is perpendicular to the surface of the sample,
- The temperature of the sample is constant during the process,
- The surface boron concentration does not change either with time or with temperature,
- Iron borides develop parabolically over time.

The solution of Equation (1) is the boron concentration after a time t and at a distance x during the boronizing process. The solution is given by the Equation (2) that represents a general solution of the second Fick's

$$C_i(x, t) = A_i + B_i \operatorname{erf}\left(\frac{x}{2\sqrt{D_i t}}\right) \quad (2)$$

In Equation (2), erf is the error Gauss function; A_i and B_i are the constants to be determined according to the initial and boundary conditions:

$$C(x > 0, t = 0) = 0$$

$$C_{\text{FeB}}(x > 0, t = 0) = C_B^{S/\text{FeB}} \quad (\text{Boron concentration at the surface}).$$

- at the (FeB/Fe₂B) interface:

$$C_{\text{Fe}_2\text{B}}(\lambda_{\text{sim}/\text{FeB}}, t > 0) = C_B^{\text{Fe}_2\text{B}/\text{FeB}}, \quad C_{\text{Fe}_2\text{B}}(\lambda_{\text{sim}/\text{FeB}}, t > 0) = C_B^{\text{FeB}/\text{Fe}_2\text{B}}$$

- at the (Fe₂B/Fe) interface:

$$C_{\text{Fe}_2\text{B}}(\lambda_{\text{sim}/\text{FeB}}, t > 0) = C_B^{\text{Fe}/\text{Fe}_2\text{B}}, \quad C_{\text{Fe}_2\text{B}}(\lambda_{\text{sim}/\text{Fe}_2\text{B}}, t > 0) = C_B^{\text{Fe}_2\text{B}/\text{Fe}}$$

- for $x = \infty$, $C_{\text{Fe}}(x = \infty, t > 0) = 0$

The shift of the two interfaces (FeB/Fe₂B) and (Fe₂B/Fe) with a very small distance dx is resulting from the in-flux and out-flux at the concerned interfaces expressed by Equations (3) and (4):

$$\frac{d\lambda_{\text{sim}/1}}{dt} \cdot \alpha_1 = (J_1 - J_2)_{x=\lambda_{\text{sim}/1}} \quad (3)$$

$$\frac{d\lambda_{\text{sim}/2}}{dt} \cdot \alpha_2 + \frac{d\lambda_{\text{sim}/1}}{dt} \cdot \alpha = (J_2 - J_3)_{x=\lambda_{\text{sim}/2}} \quad (4)$$

with: $\alpha_1 = \frac{1}{2} (C_B^{S/\text{FeB}} - C_B^{\text{Fe}_2\text{B}/\text{FeB}}) + (C_B^{\text{Fe}_2\text{B}/\text{FeB}} - C_B^{\text{FeB}/\text{Fe}_2\text{B}})$, $\alpha_2 = \frac{1}{2} \alpha + (C_B^{\text{Fe}/\text{Fe}_2\text{B}} - C_B^{\text{Fe}_2\text{B}/\text{Fe}})$, $\alpha = \frac{1}{2} (C_B^{\text{FeB}/\text{Fe}_2\text{B}} - C_B^{\text{Fe}/\text{Fe}_2\text{B}})$, J_i – flux of boron atoms in the phase i , $i = (1 = \text{FeB}, 2 = \text{Fe}_2\text{B}, 3 = \text{Fe})$.

$$\lambda_{\text{sim}/1} = k_{\text{FeB}} \sqrt{t} \quad \text{and} \quad \lambda_{\text{sim}/2} = k_{\text{Fe}_2\text{B}} \sqrt{t} \quad (5)$$

where $\lambda_{\text{sim}/1}$ and $\lambda_{\text{sim}/2}$ are the simulated thicknesses of FeB and Fe₂B layers, k_{FeB} and $k_{\text{Fe}_2\text{B}}$ represent the growth rate constants for the Fe₂B and FeB phases.

The growth rate constants can be determined from solving the two equations (3) and (4). These two equations allow simplifying the calculation of the growth rate constant. After simplifying the two equations (3) and (4), the two equations (6) and (7) are derived:

$$\alpha_1 \frac{k_{\text{FeB}}}{2} - \frac{1}{\sqrt{\pi t}} \left(-\theta_1 \sqrt{D_1} e^{\frac{-x^2}{4D_1 t}} - \theta_2 \sqrt{D_2} e^{\frac{-x^2}{4D_2 t}} \right)_{x=\lambda_{\text{sim}/1}} = 0 \quad (6)$$

$$\alpha_2 \frac{k_{\text{Fe}_2\text{B}}}{2} + \alpha \frac{k_{\text{FeB}}}{2} - \frac{1}{\sqrt{\pi t}} \left(-\theta_2 \sqrt{D_2} e^{\frac{-x^2}{4D_2 t}} - \theta_3 \sqrt{D_3} e^{\frac{-x^2}{4D_3 t}} \right)_{x=\lambda_{\text{sim}/2}} = 0 \quad (7)$$

with: $\theta_1 = C_B^{\text{S/FeB}}$ and $\theta_2 = C_B^{\text{FeB/Fe}_2\text{B}}/\text{erfc}(\lambda_{\text{sim}/1}/\sqrt{2} \sqrt{D_2})$ and $\theta_3 = C_B^{\text{Fe}_2\text{B/Fe}}/\text{erfc}(\lambda_{\text{sim}/2}/\sqrt{2} \sqrt{D_3})$

To solve the two Equations (6) and (7), the Newton-Raphson numerical method was used for this purpose.

Calculation of incubation time with a simple mathematical model

For the formation of boride layers, Casadesus et al. [23] proposed a description concerning the transformation allowing the formation of the iron borides at the surface of the treated steel via a diffusion mechanism of boron atoms.

According to this mechanism, the boron atoms liberated by the boronizing medium are adsorbed at the substrate surface.

After exceeding the solubility limit of boron in the matrix, at first, there is the formation of Fe₂B phase after a certain incubation time (τ) which depends on the temperature of the treatment. The first Fe₂B needles appear on the most reactive points of the substrate surface (scratches, grain boundaries, dislocations). So the incubation time corresponds to the appearance of the first crystals of Fe₂B at the substrate surface of steel or pure iron [24]. However, some publications indicated that the first phase, formed on the steel surface, was FeB boride [25, 26] because of the lower values of the Gibbs free energy of the reaction during the FeB formation.

To calculate the incubation time necessary for the formation of each boride layer (FeB or Fe₂B) and the corresponding thicknesses of Fe₂B and FeB layers, the simulated values of the growth rate constants given by a precedent mathematical model [14] are used. The thickness is estimated without considering the boride incubation time.

The incubation time is the result of the difference between the experimental data of boride layer thickness and the simulated layer thickness.

To estimate the value of the incubation time, which represents the delay time to form the boronized layer, the variation of this parameter is calculated with a simple equation.

In this study, we have used the two new parameters called k_τ and k'_τ that represent the growth rate constants of each boride layer (FeB and Fe₂B).

The differences ($\lambda_{\text{sim}} - \lambda_{\text{exp}}$) which are given by Equations (8) and (9) allow determining the values of growth rate constants

$$\lambda_{\tau/\text{FeB}}(t, T) = (\lambda_{\text{sim}/\text{FeB}} - \lambda_{\text{exp}/\text{FeB}}) = k_\tau \sqrt{t} \quad (8)$$

$$\lambda_{\tau'/\text{Fe}_2\text{B}}(t, T) = (\lambda_{\text{sim}/\text{Fe}_2\text{B}} - \lambda_{\text{exp}/\text{Fe}_2\text{B}}) = k'_\tau \sqrt{t} \quad (9)$$

with $k_{\text{Fe}_2\text{B}}$ and k_{FeB} are the growth rate constant of each boride layer (FeB or Fe₂B). $\lambda_{\tau/\text{FeB}}(t, T)$ and $\lambda_{\tau'/\text{Fe}_2\text{B}}(t, T)$ represent the lost thicknesses corresponding to the incubation times necessary to get the two layers Fe₂B and FeB. $\lambda_{\text{sim}/\text{Fe}_2\text{B}}$ and $\lambda_{\text{sim}/\text{FeB}}$ are the simulated thickness of each boride layer (FeB or Fe₂B) by using a mathematical model [14]. $\lambda_{\text{exp}/\text{FeB}}$ and $\lambda_{\text{exp}/\text{Fe}_2\text{B}}$ are the experimental thickness for each boride layer (FeB or Fe₂B). k_τ and k'_τ are the growth rate constants during the formation of FeB and Fe₂B layers with the respective boride incubation times τ and τ' .

With the relation proposed by Keddad et al. [24]:

$$\lambda_{\text{sim}/i} = k_i \sqrt{t - \tau} \quad (10)$$

where $i = (\text{FeB}, \text{Fe}_2\text{B})$.

In this study, the boride layers' thicknesses are depending on the two growth rate constants k_i and k'_τ according to the Equation (11):

$$\lambda_{\text{sim}/i} = (k_i - k'_\tau) \sqrt{t} \quad (11)$$

From the equations (10) and (11), Equation (12) was deduced:

$$\tau = -\frac{t}{k_i^2} k_\tau^2 + 2 \frac{t}{k_i} k_\tau \quad (12)$$

Equation (12) can be re-written in the following form:

$$\frac{\tau}{t} = \frac{k_\tau}{k_i} \left(2 - \frac{k_\tau}{k_i} \right) \quad (13)$$

where τ and τ' are the boride incubations times of the Fe₂B and FeB layers, respectively, or the effective times for the formation of such layers.

RESULTS AND DISCUSSIONS

The results of the simulation are validated by using the experimental data that have been given by Brakman et al [17].

The kinetic data and the boron activation energy in the pure iron were found in the reference [16-13], the diffusion coefficients of boron in the α -Fe and γ -Fe phases are taken from the reference [14-24, 27].

In this study, the diffusion coefficient of boron in FeB is as follows:

$$D_{\text{FeB}} = 1.28 \times 10^{-5} \exp \left(-\frac{175 \times 10^3}{RT} \right) \quad (14)$$

The expression of boron diffusion coefficient in Fe₂B is given by Equation (15):

$$D_{\text{Fe}_2\text{B}} = 6.3 \times 10^{-6} \exp \left(-\frac{157 \times 10^3}{RT} \right) \quad (15)$$

with $R = 8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$ is the perfect gas constant.

The boron concentration at the surface is 27.26 wt% taken from the work of Keddad et al. [14]. For the boron concentrations at the (FeB/Fe₂B) and (Fe₂B/Fe) interfaces, we used the data taken from the work of Campos et al. and Keddad et al. [28, 29]. The boron concentrations are the following: $C_B^{\text{Fe}_2\text{B/FeB}} \simeq C_B^{\text{FeB/Fe}_2\text{B}} \simeq 16.23$ wt% at the (FeB/Fe₂B) interface while the boron concentrations at the (Fe₂B/Fe) interface are $C_B^{\text{Fe/Fe}_2\text{B}} = 8.83$ wt% and $C_B^{\text{Fe}_2\text{B/Fe}} = 35 \times 10^{-4}$ wt%, respectively.

To validate the computer simulation program, the experimental data provided by Brakman et al. [17] are used when pack-boriding the pure iron to produce the (FeB/Fe₂B) bilayer.

Tab. 1. The chemical composition of pure iron used in the experimental work of Brakman et al. [17]

Fe	C	Mn	Ni
Balance	0.005	0.0013	0.004

The boronizing times are in the range of 0.25 to 8.5 h for a temperature treatment between 1023 and 1273 K. The determined values of boride layer thickness are the average of ten measurements taken from different points of the treated material.

To simulate the boronizing kinetics and calculate the incubation time for each boride layer, a computer simulation program written in C++ language was developed.

Fig. 2. Temperature dependence of the simulated growth rate constants for the FeB and Fe₂B phases for two cases: ($\tau = 0$ and $\tau \neq 0$)

The boride layer thickness can also be estimated by using this program.

Figure 2 represents the temperature dependence of simulated values of the growth rate constants for the Fe₂B and FeB phases by considering two cases for the boride incubation time ($\tau = 0$ and $\tau \neq 0$). From the Figure 2, the growth rate constant for each phase increases with an increase in the boriding temperature, it is noticed that the value of simulated growth rate constant for $\tau \neq 0$ is less than the value obtained for $\tau = 0$.

Fig. 3. Temperature dependence of the growth rate constant K_τ for the FeB phase

Fig. 4. Temperature dependence of the growth rate constant k'_τ by considering the incubation time for the Fe₂B phase

Tab. 2. Simulated values of the growth rate constants for the FeB and Fe₂B phases with ($\tau = 0$)

Temperature (K)	1023	1073	1123	1173	1223	1273
$k_{\text{FeB}} (\mu\text{m s}^{-1/2})$	0.0607	0.1012	0.1611	0.2462	0.3632	0.5193
$k_{\text{Fe}_2\text{B}} (\mu\text{m s}^{-1/2})$	0.2818	0.4356	0.6479	0.9319	1.3020	1.7710

The temperature dependence of the simulated values of growth rate constants (K_r and K'_r) of each phase (FeB or Fe₂B) is shown in the Figures 3 and 4.

For the FeB phase, the variation in temperature of K_r parameter is not linear whereas the evolution of k' parameter as a function of the process temperature is linear for the Fe₂B phase.

The incubation time in FeB and Fe₂B phase is reported in Figures 3 and 4, the incubation time is a function of temperature and time.

From the simulation data, we observe that growth incubation time constant for the formation of the Fe₂B layer increase when the temperature increases.

Figures 5 and 6 depicted the simulated values of (τ/t) ratio as a function of boriding temperature for each phase. It is noticed that the boride incubation time for each boride layer is decreased when the temperature increases.

Fig. 5. The (τ/t) ratio as a function of boriding temperature for the FeB phase

To demonstrate the effect of boride incubation time for each boride layer, the $B(T)$ parameter was incorporated into the simulation program and can be described by Equation (16):

This parameter [30] was used to estimate the boride layer thickness at a given temperature.

$$B(T) = \sqrt{1 - (\tau/t)} \quad (16)$$

The $B(T)$ parameter given in the Equation (16) depends on the process temperature. It was used in many studies [26, 30], it can be re-written in the following form:

$$B(T) = \left[1 - \frac{k_r}{k} \left(2 - \frac{k_r}{k} \right) \right]^{1/2} \quad (17)$$

The simulated values of the $B(T)$ parameter relative to each boride layer (FeB or Fe₂B) as a function of the process temperature are plotted in Figures 7 and 8

Fig. 7. The temperature dependence of $B(T)$ parameter for 2 h for the FeB phase

Fig. 6. The (τ/t) ratio as a function of boriding temperature for the Fe₂B phase

Fig. 8. The temperature dependence of $B'(T)$ parameter for 2 h for the Fe₂B phase

for a treatment time of 2 h. The evolution of the two parameters follows a linear relationship with the process temperature.

The change of boride incubation time with the growth rate constant of each boride layer is shown in Figure 9 for a treatment time of 2 h. The boride layer thickness is given by Equation (18), which is used in the majority of research works [31, 32] as follows:

$$\lambda_i = k_i B(T) \sqrt{t} \quad (18)$$

The comparison of Equations (11) and (18) led to the comparison of the values of $k_i B(T)$ and $(k_i - k_r)$. In the Figure 10, we depicted the simulated values of the new growth rate constant taken from our model ($k_i - k_r$) and the growth rate constant normalized by the $B(T)$ parameter represented in Equation (18) for each boride layer (FeB or Fe₂B).

We found a good agreement between the two simulated results. The expression regarding the growth rate constant ($k_i - k_r$), proposed in this study, provides good results by considering the values of boride incubation times. With this constant we can calculate the thickness of the boronized layer.

Figure 11 describes the evolution of the boronized layer thickness with the presence of boride incubation time based on Equation (11), this equation is simulated based on the rate constant of the incubation time (k_r) of the FeB and Fe₂B layers.

It is seen that the growth kinetics of each boride layer follows a parabolic law with respect to the treatment time for increasing boriding temperatures.

The simulated curves coincide with the experimental ones. So a good agreement was observed between the experiments and the simulated results.

Fig. 9. The boride incubation time as a function of the growth rate constant of each boride layer for 2 h of treatment: a) FeB and b) Fe₂B

Fig. 10. Temperature dependence of the new value of the growth rate constant of each boride layer, obtained with our model by using the equation (11)

Fig. 11. Comparison between the simulated and experimental values of boride layer thickness obtained for different temperatures by means of Equation (11) proposed in this study [17]: a) FeB and b) Fe₂B

Therefore, the simulation provides a good result compared to another simulation [14] which is justified by the importance of the boride incubation time.

The present mathematical model used in this study represents an alternative approach to simulate the boronizing kinetics of pure iron. It can be used as a tool for estimating the effect of incubation time on the kinetics of formation of each boride layer (FeB or Fe₂B).

CONCLUSION

In the present work, a kinetic diffusion model has been proposed to estimate the boride incubation time of each boride layer (FeB or Fe₂B) by incorporating into the computer program the $B(T)$ parameter.

This simulation program is capable of predicting the growth kinetic constants at each temperature and simulates the incubation time relative to each boride layer (FeB or Fe₂B).

This kinetic approach can be used to calculate the boronized layer thickness as a function time and with taking into account the effect of boride incubation times. These simulations give a good result consistent with the experimental data.

Simulating the incubation times during the formation of boride layers gives an idea on the importance of $B(T)$ parameter. This last parameter was related to the growth rate constant of each phase (FeB or Fe₂B).

From this study, it was shown that the incubation time τ decreased with increasing temperature. The simulation gives an estimate of the boride incubation time by using the $B(T)$ parameter based on the experimental data available in the literature on the powder-pack boriding of pure iron.

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