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Prediction models for the kinetics of iron boride layers on AISI 316L steel

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The boronizing kinetics of AISI 316L steel has been analyzed by employing five prediction models. The boron diffusion coefficients as well as the growth rate constants in the FeB and Fe_2B phases were firstly evaluated in the range of 1123-1223 K. Afterwards, the values of boron activation energies in FeB and Fe_2B were secondly deduced by adopting the Arrhenius relationships.In addition, the prediction models have been validated experimentally for two boronizing conditions (1170 K for 1.6 h and 1210 K for 1.1 h). The predicted results were deemed very concordant with the experiments. Furthermore, advantages and limitations about the applicability of these models were also discussed.

INTRODUCTION

The boronizing process is a surface hardening technique applied to steels. It consists in diffusing at atomic level the boron atoms at the steel surface to produce iron borides between 800 and 1050 °C during 0.5 to 10 h [1]. This thermochemical treatment enhances the surface characteristics of treated steels resulting in a high surface hardness and resistance against wear and corrosion. As per the Iron-Boron phase diagram, two stable phases (iron monoboride and diiron boride) can be formed at the surfaces of steels. Therefore, either a monophase layer (Fe_2B) [2, 3] or a double–phase layer (FeB + Fe_2B) [4-6] can be generated.

In the literature data, various boronizing techniques are used in the industry and the laboratories to surface harden the workpieces made of steels. However, the widely used process is the pack-boriding due to its technical advantages and low investment in comparison with other boronizing processes [5].

In terms of kinetic modelling of boriding process, a certain number of mathematical models was implemented and dedicated to the growth of FeB and Fe_2B layers on some steels [7-13]. In the following mathematical models [7-10, 12], the boride incubation periods were considered during the growth of both phases. Thus, all these models can be used as tools for searching for the optimized values of boride layers' thicknesses for the practical utilization of treated steels during the extreme working conditions. In the kinetic model applied by Delai et al. [7] to the low-alloy steel of type 4Cr5MoSiV1, the non linearity of boron concentration profiles in the iron borides was assumed. The mass balance equations associated with the Second Fick's law in each phase were numerically solved by introducing two dimensionless parameters for predicting the growth kinetics of both layers (FeB and Fe_2B) by overlooking the presence of incubation periods. Campos-Silva et al.[8] suggested a kinetic model for the boronizing kinetics of AISI M2 steel by assuming a linear distribution of boron concentration inside each iron boride layer (FeB and Fe_2B) with the consideration of boride incubation times. Keddam and Kuka [9] implemented a new recent approach named the alternative diffusion model (ADM) that was applied to the AISI 316 steel for the bilayer growth (FeB/Fe_2B). The mathematical formulation of this approach is independent on the shape of boron concentration profile in each iron boride layer. As a consequence, the diffusivities of boron in both phases were a function of natural logarithms of two dimensionless parameters. For predicting the boriding kinetics of AIS 316 steel, the mean values of these two parameters were then considered to solve this diffusion problem. Keddam and Jurci [10] proposed two different approaches (the integral diffusion model and a modified version of the Dybkov model [13] with the inclusion of boride incubation periods) for the bilayer growth (FeB/Fe_2B) onto the AISI M2 steel. Finally, Nait Abdelah et al.[11] suggested a numerical treatment regarding the boriding kinetics of AISI H13 steel by employing the mean diffusion coefficient (MDC) method and ignoring the incubation periods for the formation of iron boride layers.

The objective of the undertaken work was to simulate the growth kinetics of FeB and Fe_2B layers generated at the surface of AISI 316L steel by the pulsed direct-current pack boriding (PDCPB) process.

The originality of the present work was to demonstrate the potential applications of five different approaches for describing the boriding kinetics of this type of steel. During the application of these mathematical models, the boron diffusivities in iron borides have been firstly assessed. Afterwards, the values of boron activation energies were deduced by fitting the obtained results with Arrhenius relationships. Finally, the five models have been validated experimentally for the two additional boriding conditions (1170 K for 1.6 h and 1210 K for 1.1 h). Furthermore, advantages and limitations about the applicability of these models were also discussed.

PREDICTION MODELS

Five different models were used to kinetically model the growth of iron boride layers on AISI 316L steel. The boron concentration–profiles within the FeB and Fe_2B layers are schematically depicted in Figure 1.

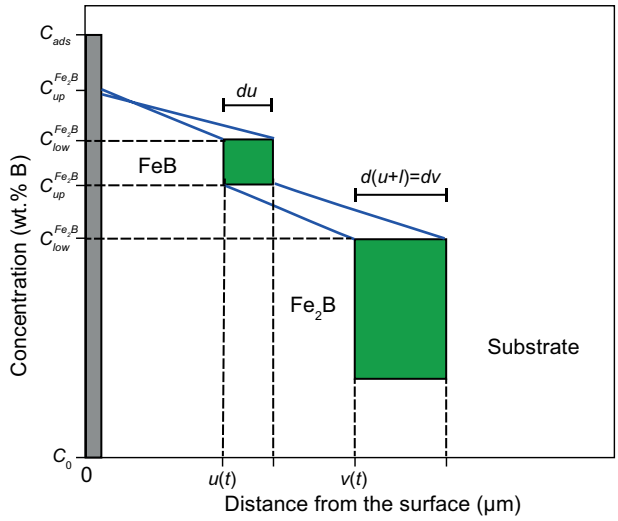


Fig. 1. Schematic depiction of boron-concentration profiles in the FeB and Fe_2B layers

The constant C_{up}^{FeB} is the maximum content of boron in FeB (=16.40 wt.%) while C_{low}^{FeB} denotes the minimum content of boron in the same phase (=16.23 wt.%) [10]. $C_{up}^{Fe_2B}$ is the maximum boron concentraton Fe_2B (=9.00 wt.%) whilst $C_{low}^{Fe_2B}$ is the minimum boron concentration in Fe_2B (8.83 wt.%) [10]. The variable $v(t)$ denotes the position of (FeB/Fe_2B) interface while v is the position of (Fe_2B/substrate) interface. The term C_{ads} is the adsorbed content of active boron over the material's surface[14]. C_0 represents the boron concentration within the substrate which can be ignored (≈0.00 wt.%) [15]. The thickness of FeB layer $u(t)$ is descibed by Equation (1):

$$u(t) = k_u \sqrt{t - t_0^{FeB}} \tag{1}$$

where k_u is the parabolic growth constant at the first interface for an incubation time t_0^{FeB}. The (FeB + Fe_2B) layer thickness $v(t)$ is expressed by Equation (2) :

$$v(t) = k\sqrt{t - t_0} \tag{2}$$

where k denotes the parabolic growth constant at the second interface for an incubation time $t_0\,(T)$. Equation (1) can be converted into Equation (3) by considering an incubation time $t_0\,(T)$.

$$u(t) = k'\sqrt{t - t_0} \tag{3}$$

where k' is the corresponding parabolic growth constant at the first interface for an incubation time t_0. Equations (1) and (2) can alternatively be rewritten in the following manner :

$$u(t) = k_1\sqrt{t} \tag{4}$$

and

$$v(t) = k_2\sqrt{t} \tag{5}$$

where k_1 and k_2 are the new corresponding parabolic growth constants. The difference $l(t) = v(t) - u(t)$ is the Fe_2B layer thickness.

The alternative diffusion model (ADM)

This kinetic model [9] considered the mass balance equations for the two interfaces (FeB/Fe_2B) and (Fe_2B/substrate) regardless the shape of boron concentration profiles along the FeB and Fe_2B layers. Following this approach, the boron diffusion coefficients in FeB and Fe_2B are expressed by Equations (6) and (7):

$$D_{FeB} = \frac{[w_{FeB}k_1^2 \ln(\frac{t}{t_0^{Fe\,B}}) + (w_{Fe_2B}k_2^2 + w'k_1k_2)\ln(\frac{t}{t_0})]}{2(C_{up}^{FeB} - C_{low}^{FeB})} \tag{6}$$

and

$$D_{Fe_2B} = \frac{(w_{Fe_2B}k_2^2 + w'k_1k_2)\ln(\frac{t}{t_0})}{2(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})} \tag{7}$$

with $w_{FeB} = [\frac{(C_{up}^{FeB} + C_{low}^{FeB})}{2} - C_{up}^{Fe_2B}]$,

$$w_{Fe_2B} = [\frac{(C_{up}^{Fe_2B} + C_{low}^{Fe_2B})}{2} - C_0]\,,$$

$$w' = \frac{(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})}{2}\,.$$

The two temperature-dependent parameters Φ_1 and Φ_2 are given by Equations (8) and (9):

$$\Phi_1 = \sqrt{1 - \frac{t_0^{FeB}}{t}} = \frac{k_1}{k_u} \tag{8}$$

and

$$\Phi_2 = \sqrt{1-\frac{t_0}{t}} = \frac{k_2}{k} = \frac{k_1}{k'} \tag{9}$$

By using the alternative diffusion model (ADM), the layers' thicknesses can be determined by solving numerically the following set of differential Equations (10) and (11) with the Runge-Kutta method [16]:

$$\beta_{11}u(t)\frac{du(t)}{dt} + \beta_{12}\frac{d(u(t)l(t))}{dt} + \beta_{13}l(t)\frac{dl(t)}{dt} = \\ = 2D_{FeB}(C_{up}^{FeB} - C_{low}^{FeB}) \tag{10}$$

and

$$\beta_{21}u(t)\frac{du(t)}{dt} + \beta_{22}\frac{d(u(t)l(t))}{dt} + \beta_{23}l(t)\frac{dl(t)}{dt} = \\ = 2D_{Fe_2B}(C_{up}^{Fe_2B} - C_{low}^{Fe_2B}) \tag{11}$$

with $\beta_{11} = 2w_{FeB}\ln(\frac{1}{1-\Phi_1^2}) + 2(w' + w_{Fe_2B})\ln(\frac{1}{1-\Phi_2^2})$,

$\beta_{12} = \beta_{22} = (w' + 2w_{Fe_2B})\ln(\frac{1}{1-\Phi_2^2})$,

$\beta_{13} = \beta_{23} = 2w_{Fe_2B}\ln(\frac{1}{1-\Phi_2^2})$,

$\beta_{21} = 2(w_{Fe_2B} + w')\ln(\frac{1}{1-\Phi_2^2})$,

once the boron diffusion coefficients in FeB and Fe_2B are known and by taking the mean values of Φ_1 and Φ_2 parameters in the considered temperature range.

The integral diffusion model

The integral diffusion model [10] is based on the numerical solutions of the resulting set of differential algebraic equations (DAE):

$$a_1(t)u(t) + b_1(t)u(t)^2 = (C_{up}^{FeB} - C_{low}^{FeB}) \tag{12}$$

$$a_2(t)l(t) + b_2(t)l(t)^2 = (C_{up}^{Fe_2B} - C_{low}^{Fe_2B}) \tag{13}$$

$$\frac{d}{dt}[\frac{u(t)^2}{2}a_1(t) + \frac{u(t)^3}{3}b_1(t)] = 2D_{FeB}b_1(t)u(t) \tag{14}$$

$$2w'\frac{du(t)}{dt} + 2w'\frac{dl(t)}{dt} + \frac{l(t)^2}{2}\frac{da_2(t)}{dt} + \\ + \frac{l(t)^3}{3}\frac{db_2(t)}{dt} = 2D_{Fe_2B}b_2(t)l(t) \tag{15}$$

$$[a_1^2(t) - 2w_{FeB}b_1(t)]D_{FeB} = a_1(t)[a_2(t) + 2b_2(t)l(t)]D_{Fe_2B} \tag{16}$$

$$a_1(t)[a_2^2(t) - 2w_{Fe_2B}b_2(t)]D_{Fe_2B} = 2w'a_2(t)b_1(t)D_{FeB} \tag{17}$$

After using a peculiar and feasible solution of DAE system [10]. The boron diffusion coefficients in FeB and Fe_2B, depending on the experimental parabolic growth constants as well as on the two dimensionless parameters ε_1 and ε_2, are expressed by Equations (18) and (19):

$$D_{FeB} = (\frac{k'}{2\varepsilon_1})^2 \tag{18}$$

and

$$D_{Fe_2B} = (\frac{k-k'}{2\varepsilon_2})^2 \tag{19}$$

with $\varepsilon_1 = 0.076$ and $\varepsilon_2 = 0.053$

The expressions of layers'thicknesses of FeB and Fe_2B can be determined from Equations (20) and (21):

$$u(t) = 2\varepsilon_1\sqrt{D_{FeB}(t-t_0)} \tag{20}$$

and

$$l(t) = 2\varepsilon_2\sqrt{D_{Fe_2B}(t-t_0)} \tag{21}$$

The mean diffusion coefficient (MDC) method

In this kinetic model [11], a linear boron concentration profile through each boride layer (FeB or Fe_2B) has been considered. Based on the MDC method, the expressions of boron diffusion coefficients in FeB and Fe_2B are given by Equations (22) and (23):

$$D_{FeB} = \frac{k'[\gamma_{11}k' + \gamma_{12}(k-k')]}{2(C_{up}^{FeB} - C_{low}^{FeB})} \tag{22}$$

$$D_{Fe_2B} = \frac{(k-k')[\gamma_{21}k' + \gamma_{22}(k-k')]}{2(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})} \tag{23}$$

with $\overline{c}_{FeB} = 0.5(C_{up}^{FeB} + c_{low}^{FeB})$, $\overline{c}_{Fe_2B} = 0.5(C_{up}^{Fe_2B} + c_{low}^{Fe_2B})$,

$\gamma_{11} = \frac{(3\overline{c}_{FeB} + c_{low}^{FeB})}{4}$, $\gamma_{22} = \frac{(3\overline{c}_{Fe_2B} + c_{low}^{Fe_2B})}{4}$,

$\gamma_{12} = \gamma_{21} = \overline{c}_{Fe_2B}$.

The layers' thicknessess of FeB and Fe_2B can be estimated numerically [16] based on the following set of first order differential equations for the boride incubation period t_0:

$$[2\gamma_{11}u(t) + \gamma_{12}l(t)]\frac{du(t)}{dt} + \gamma_{12}u(t)\frac{dl(t)}{dt} = 2D_{FeB}(C_{up}^{FeB} - C_{low}^{FeB}) \tag{24}$$

and

$$\gamma_{21}l(t)\frac{du(t)}{dt} + [2\gamma_{22}l(t) + \gamma_{21}u(t)]\frac{dl(t)}{dt} = 2D_{Fe_2B}(C_{up}^{Fe_2B} - C_{low}^{Fe_2B}) \tag{25}$$

The bilayer growth model

The bilayer growth model suggested is a modified form of that proposed by Campos-Silva [8] with the in-

clusion of boride incubation periods unlike to reference [7]. It is relying on the solutions of the two mass balance equations at the interfaces (FeB/Fe_2B) and (Fe_2B/substrate) by considering a non linear boron concentration profile in each phase:

$$w_{FeB}\frac{dx(t)}{dt}\bigg|_{x=u} = -D_{FeB}\frac{\partial C_{FeB}(x,t)}{\partial x}\bigg|_{x=u} + D_{Fe_2B}\frac{\partial C_{Fe_2B}(x,t)}{\partial x}\bigg|_{x=u} \tag{26}$$

$$w_{Fe_2B}\frac{dx(t)}{dt}\bigg|_{x=v} + w'\frac{dx(t)}{dt}\bigg|_{x=u} = -D_{Fe_2B}\frac{\partial C_{Fe_2B}(x,t)}{\partial x}\bigg|_{x=v} \tag{27}$$

In this case, the expressions of boron concentration inside the FeB and Fe_2B layers are given by Equations (28) and (29) as follows:

$$C_{FeB}(x,t) = \frac{(C_{low}^{FeB} - C_{up}^{FeB})}{erf(\frac{u}{2\sqrt{D_{FeB}t}})} erf(\frac{x}{2\sqrt{D_{FeB}t}}) + C_{up}^{FeB} \tag{28}$$

for $0 \le x \le u$

$$C_{Fe_2B}(x,t) = \frac{(C_{low}^{Fe_2B} - C_{up}^{Fe_2B})}{[erf(\frac{v}{2\sqrt{D_{Fe_2B}t}}) - erf(\frac{u}{2\sqrt{D_{Fe_2B}t}})]} [erf(\frac{x}{2\sqrt{D_{Fe_2B}t}}) - erf(\frac{v}{2\sqrt{D_{Fe_2B}t}})] + C_{low}^{Fe_2B} \tag{29}$$

for $u \le x \le v$

By derivating Equations (2) and (3) with respect to the time and considering the expression of Φ_2 parameter, the set of differential Equations (26) and (27) can be rewriten as the set of non linear Equations (30) and (31) to get the values of boron diffusion coefficicnts in FeB and Fe_2B:

$$\frac{w_{FeB}k'}{2\Phi_2} = \sqrt{\frac{D_{FeB}}{\pi}} \frac{(C_{up}^{FeB} - C_{low}^{FeB})e^{-\frac{k'^2\Phi_2^2}{4D_{FeB}}}}{erf(\frac{k'\Phi_2}{2\sqrt{D_{FeB}}})} - \sqrt{\frac{D_{Fe_2B}}{\pi}} \frac{(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})e^{-\frac{k'^2\Phi_2^2}{4D_{Fe_2B}}}}{[erf(\frac{k\Phi_2}{2\sqrt{D_{Fe_2B}}}) - erf(\frac{k'\Phi_2}{2\sqrt{D_{Fe_2B}}})]} \tag{30}$$

$$\frac{(w_{Fe_2B}k + w'k')}{2\Phi_2} = \sqrt{\frac{D_{Fe_2B}}{\pi}} \frac{(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})e^{-\frac{k^2\Phi_2^2}{4D_{Fe_2B}}}}{[erf(\frac{k\Phi_2}{2\sqrt{D_{Fe_2B}}}) - erf(\frac{k'\Phi_2}{2\sqrt{D_{Fe_2B}}})]} \tag{31}$$

The Dybkov model

The Dybkov model [10] can be employed to deal with the formation kinetics of FeB and Fe_2B layers on the AISI 316L steel. The time dependencies in terms of layers' thicknesses $u(t)$ and $l(t)$ can be formulated by using the following set of ordinary differential equations (ODE):

$$\frac{du(t)}{dt} = \frac{k_{FeB}}{u(t)} - \frac{rg}{p}\frac{k_{Fe_2B}}{l(t)} \tag{32}$$

$$\frac{dl(t)}{dt} = \frac{k_{Fe_2B}}{l(t)} - \frac{q}{sg}\frac{k_{FeB}}{u(t)} \tag{33}$$

with $k_{FeB} = \frac{0.5k'}{(p - \frac{rq}{s})}[(p - rg)k' + rgk)]$

and $k_{Fe_2B} = \frac{0.5(k - k')}{(1 - \frac{rq}{sp})}[k + (\frac{q}{sg} - 1)k']$

The two experimental fitting parameters (k_{FeB} and k_{Fe_2B}) are the respective values of growth rate constants of FeB and Fe_2B phases. The expressions of these two fitting parameters were found by substituting Equations (2) and (3) as well as their time derivatives into Equations (32) and (33). The constant $g = 0.60$ denotes the molar volume ratio of the FeB and Fe_2B phases. The constants $p = q = r = 1$ and $s = 2$ designate the stoichiometric coefficients of FeB and Fe_2B [13]. Therefore, the layers'thicknesses of FeB and Fe_2B can be estimated by using the Runge-Kutta method [16] for the given boriding parameters.

EXPERIMENTAL INFORMATION FOR THE VALIDATION OF PREDICTION MODELS

A new process named the pulsed-DC powder pack boriding process [17] has been developed to produce the bilayer (FeB/Fe_2B) onto the surface of AISI 316L steel. In the equipment used, the thermoelectric system allows a Direct Current (CD) supply so that the samples could be connected to the positive and negative output terminals of the DC power supply during the electromigration process. The samples were introduced into the container made of AISI 304 steel and filled up with the powders mixture composed of 70 wt.% B_4C, 20 wt.% SiC and 10 wt.% KBF_4. The sealed container containing the samples was put inside the conventional muffle furnace. Afterward, the specimens were heat treated at 1123, 1173 and 1273 K for 0.5, 1, 1.5 and 2 h by selecting a current flow of 5 A under polarity inversion cycles of 10 s.

For the kinetic study, the mean values of layers' thicknessess of FeB and (FeB+Fe_2B) were considered based on one hundred measurements.

SIMULATION RESULTS AND DISCUSSIONS

The experimental data about the growth kinetics of FeB and (FeB+Fe_2B) layers [17] have been exploited to assess the boron diffusion coefficients in FeB and Fe_2B in the interval of 1123 to 1223 K. In Table 1 are grouped the experimental kinetics constants at the two interfaces (FeB/Fe_2B) and (Fe_2B/substrate) with the occurrence of incubation times. The k_u and k values were obtained by fitting the kinetics curves with Equations (1) and (2) where the boride incubation times corresponded to the intercept points with time axis. The k' values in Table 1 were deduced by fitting the dependencies on time of experimental FeB layers' thicknesses with Equation (3). The slopes of the plotted straight lines represented the numerical values of experimental parabolic growth constants at the two interfaces.

It is obvious that the boride incubation times are diminished with increasing temperature due to the activation of the diffusion phenomenon of boron atoms [8,12]. The growth kinetics of boride layers are also influenced by the electromigration phenomenon during the boron diffusion [17].

Table 2 contains the new values of parabolic growth constants for the two interfaces fitted with Equations (4) and (5). These values are needed for estimating the boron difusion coefficients in FeB and Fe_2B by using the alternative diffusion model [9].

Tab. 1. Experimental parabolic growth constants at the (FeB/Fe_2B) and (Fe_2B/substrate) interfaces within the temperature range 1123-1223 K

T (K)	k_u (μm $s^{-0.5}$)	t_0^{FeB} (s)	k (μm $s^{-0.5}$)	k' (μm $s^{-0.5}$)	t_0 (s)
1123	0.19	1532	0.25	0.1843	1351
1173	0.26	1291	0.37	0.2582	1248
1223	0.40	987	0.51	0.3858	728

Tab. 2. Experimental parabolic growth constants k_1 and k_2 fitted with Equations (4) and (5)

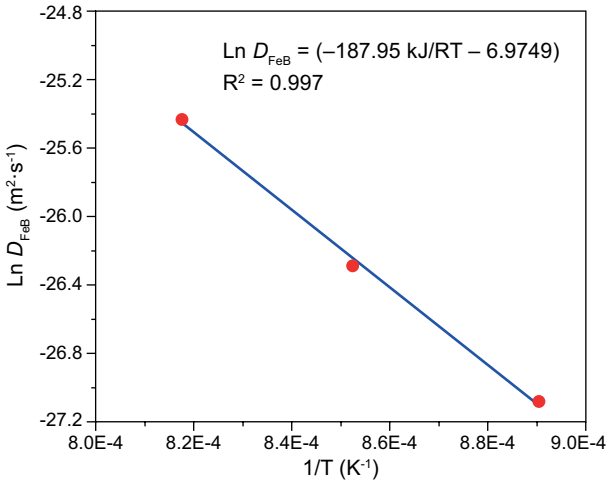
T (K)	k_1 (μm $s^{-0.5}$)	k_2 (μm $s^{-0.5}$)
1123	0.1518	0.2070
1173	0.2177	0.3122
1223	0.3521	0.4661

Assessment of boron diffusivities in iron mono-boride (FeB) and diiron boride (Fe_2B)

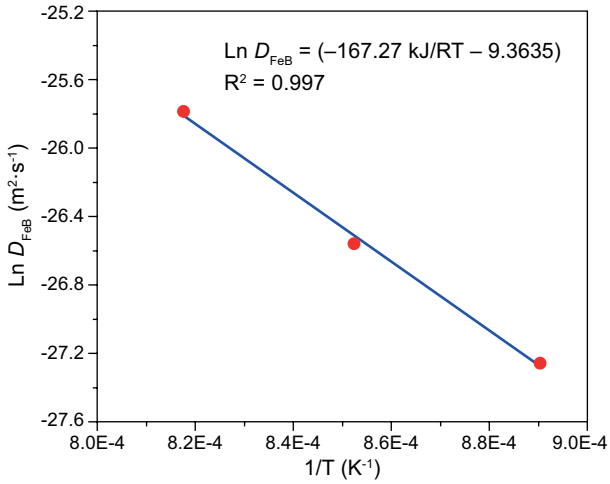
The boron diffusiivities in FeB and Fe_2B were estimated by employing the alternative diffusion model, the integral diffusion model, the mean diffusion coefficient method, the bilayer model and the Dybkov model for a maximum boron content of 16.40 wt.% in FeB.

For the alternative diffusion model, the mean values of the two dimensionless parameters Φ_1 and Φ_2 were considered [9] in the range of 1123-1223 K to get the values of boron diffusivities in iron borides.

For the bilayer diffusion model, the numerical resolution of the two non linear Equations (30) and (31), requires the determination of the temperature dependence of Φ_2 parameter which is expressed by the empirical formula: $\Phi_2 = (9.13\times10^{-4}\ T - 0.20728)$ where the boriding temperature T is given in Kelvin.' Finally, the obtained results were fitted with Arrhenius relationships and plotted in Figures 2 and 3. The growth rate constants for FeB and Fe_2B were also evaluated by using the Dybkov model and the results are displayed in Figure 4.

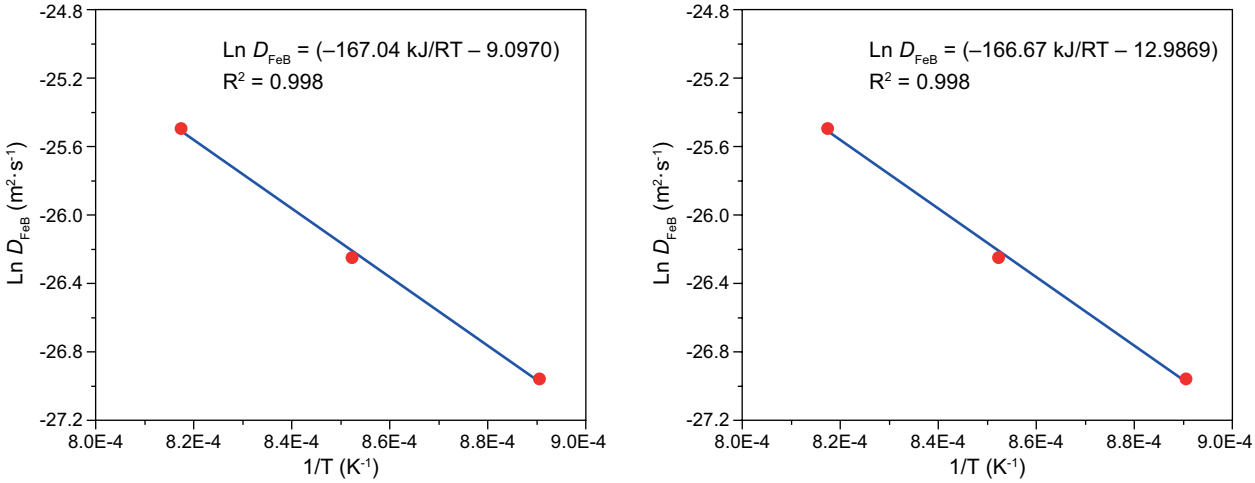


a) alternative diffusion model



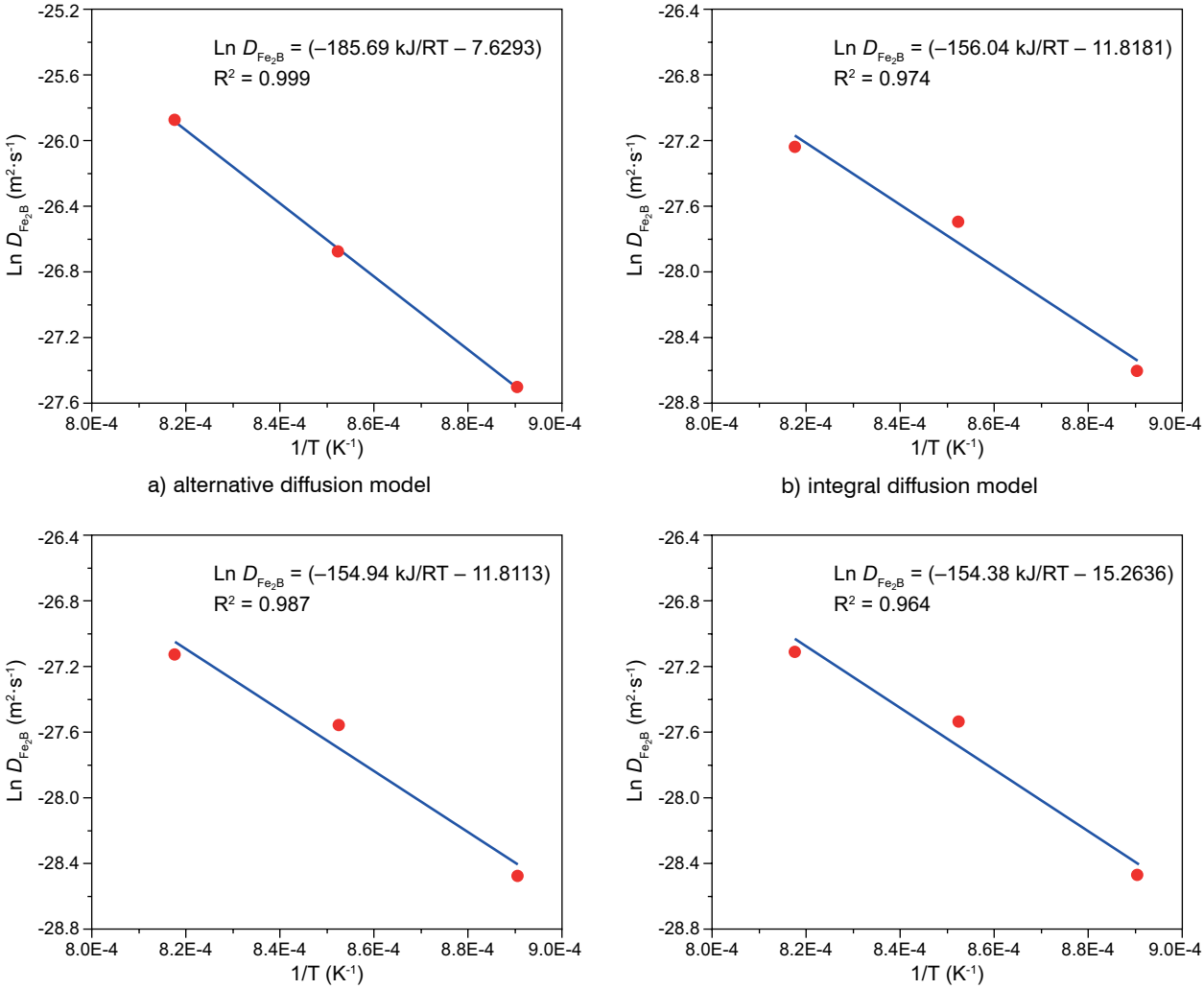
b) integral diffusion model

Fig. 2. Arrhenius behaviours of estimated boron diffusivities in FeB using different models *(Continue on next page)*



c) mean diffuson coefficient method d) bilayer diffusion model

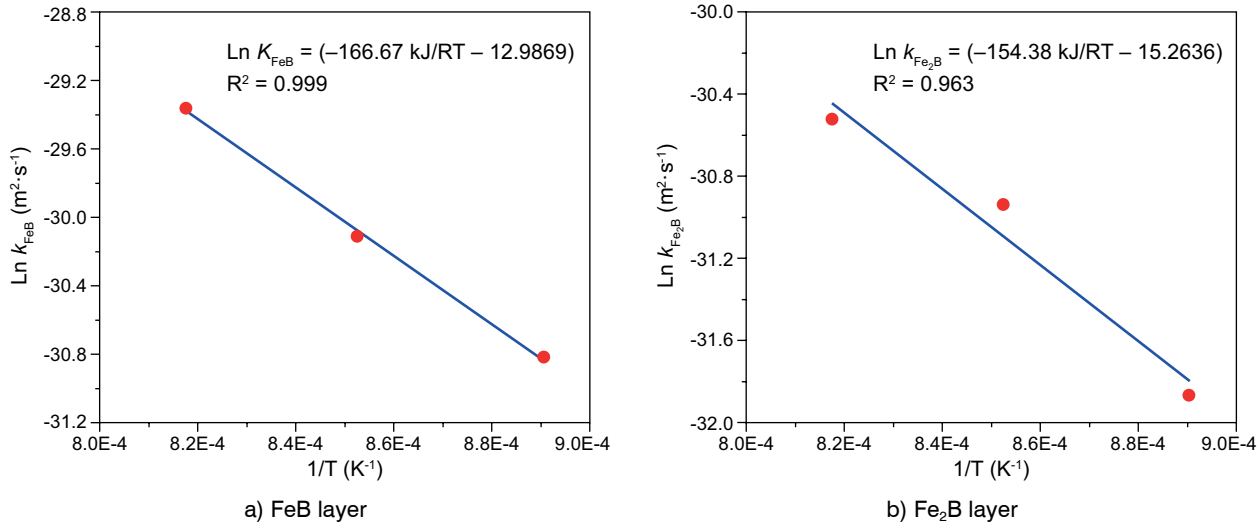
Fig. 2. Arrhenius behaviours of estimated boron diffusivities in FeB using different models



a) alternative diffusion model b) integral diffusion model

c) mean diffuson coefficient method d) bilayer diffusion model

Fig. 3. Arrhenius behaviours of estimated boron diffusivities in Fe_2B using different models



a) FeB layer b) Fe_2B layer

Fig. 4. Dependencies on temperature of assessed growth rate constants for FeB and Fe_2B using the Dybkov model

Table 3 contains the estimated boron activation energies in FeB and Fe_2B along with the respective pre-exponential factors (D_0^{FeB}, $D_0^{Fe_2B}$, k_0^{FeB} and $k_0^{Fe_2B}$) for C_{up}^{FeB} = 16.40 wt.%. By analyzing the calculated values of boron diffusion coefficients (D_{FeB} and D_{Fe_2B}) in iron borides deduced from the Arrhenius relationships at 1123, 1173 and 1223 K, it is seen the calculation results vary with the diffusion models used. For instance, the results provided for the boron diffusion coefficients in iron borides by the alternative diffusion model [9] differ by a factor of 1.1 to 1.4 for FeB and between 2.8 and 3.2 for Fe_2B in comparison to the two models [10,11] and the bilayer diffusion model. With the assumption that the k^{FeB} and k^{Fe_2B} parameters of the Dybkov model are the measures of boron mobilities in FeB and Fe_2B, the comparison between the models is feasible. Therefore, by comparing the calculated values of boron diffusion coefficients in FeB and Fe_2B [9] with k^{FeB} and k^{Fe_2B} values based on the Dybkov model, one finds that the assessed values by the alternative diffusion model differ from those of Dybkov model by a factor of 42.5 to 50.4 for FeB and between 22.4 and 94.8 for Fe_2B in the temperature range 1123-1223 K. It is also noted that the values of boron activation energies in both phases are nearly the same for other models except for the alternative diffusion model. However, the results from the alternative diffusion model are still acceptable due to the difference in its mathematical formulation.

Assessment of boron activation energies

Table 4 shows a comparison between the found values of boron activation energies in FeB and Fe_2B during the present work and the data published about the borided AISI 316L and AISI 316 steels [6, 9, 17-21]. From Table 4, it is seen that the listed values of activation energies are directly dependent on the boriding method and also on the mathematical formulation of different approaches [9,17, 19] employed to extract the values of boron activation energies from the calculations of boron diffusivities in iron borides. In the present work, the use of alternative diffusion model allowed us to get higher values of activation energies compared to other diffusion models [10, 11,13] and the bilayer diffusion model. In fact, the expressions used to assess the boron diffusivities in FeB and Fe_2B in the alternative diffusion model [9] contained two terms which are the natural logarithms of the two dimensionless parameters (Φ_1 and Φ_2) compared to other mathemtical models [10,11,13] and the bilayer diffusion model. In this work, the calculated activation

Tab. 3. Estimated values of boron diffusivities in FeB and Fe_2B by using the prediction models

D_0^{FeB} or k_0^{FeB} ($m^2\ s^{-1}$)	Q_{FeB} (kJ mol^{-1})	$D_0^{Fe_2B}$ or $k_0^{Fe_2B}$ ($m^2\ s^{-1}$)	Q_{Fe_2B} (kJ mol^{-1})	Models used
9.35×10^{-4}	187.95	4.86×10^{-4}	185.69	Alternative diffusion model
8.58×10^{-5}	167.27	7.37×10^{-6}	156.04	Integral diffusion model
1.12×10^{-4}	167.04	7.42×10^{-6}	154.94	Mean diffusion coefficient method
1.15×10^{-4}	167.21	8.61×10^{-6}	156.32	Bilayer growth model
2.29×10^{-6}	166.67	2.35×10^{-7}	154.38	Dybkov model

Tab. 4. Comparison of the present boron activation energies with other results obtained on borided AISI 316 and 316L steels

Boriding method	Activaton energies (Kj mol^{-1})	Method of calculation	Refs.
Pack	244.15 (FeB +Fe_2B)	Parabolic growth law	[6]
Pack	224.11 (FeB), 221.56 (Fe_2B)	Alternative diffusion model	[9]
	205.88 (FeB), 188.64 (Fe_2B)	Integral diffusion model	
Pack	199.0 (FeB + Fe_2B)	Parabolic growth law	[18]
Pack	204 (FeB), 198 (Fe_2B)	Diffusion Model	[19]
Pack	191.0 (FeB + Fe_2B)	Parabolic growth law	[20]
Plasma paste boriding	118.12 (FeB + Fe_2B)	Parabolic growth law	[21]
Pulsed-DC pack	162 ±7 (FeB), 171 ±5 (Fe_2B)	Diffusion model	[17]
Pulsed-DC pack	187.95 (FeB), 185.69 (Fe_2B)	Alternative diffusion model	This study
	167.27 (FeB),156.04 (Fe_2B)	Integral diffusion model	
	167.04 (FeB),154.94 (Fe_2B)	Mean diffusion coefficient method	
	167.21 (FeB),156.32 (Fe_2B)	Bilayer growth model	
	166.67 (FeB),154.38 (Fe_2B)	Dybkov model	

energies in FeB and Fe_2B were found to be comparable when using the following diffusion models [10,11, 13] and the present bilayer diffusion model. It is remarkable that the assessed values of activation energies in FeB and Fe_2B for the treated AISI 316L steel by the pulsed-DC pack boriding [17] are quite lower compared to those obtained by using the conventional pack-boriding [9, 19]. The reason of such a situation is that the pulsed-DC pack boriding imposes a uniform flux of boron atoms induced by the presence of electromigration phenomenon established in between the anode and the cathode in the electrosystem used [17]. Therefore, the electromigration effect would impact on the mobiliity of boron diffusion by accelerating its diffusion rate. The obtained boron activation energy in AISI 316 steel by the plasma-paste boriding [21] was quite lower in comparison with the determined values of activation energies for the conventional pack-boriding [6,18,20] and the pulsed-DC pack boriding process [17]. Indeed, the use of activated plasma medium allows the enhancement of the mobilities of diffusing species during the plasma-paste boriding process [22,23].

Experimental validation of prediction models

In Table 5 are listed the predicted and the experimental thicknesses of FeB and Fe_2B layers obtained at 1170 K for 1.6 h and 1210 K during 1.1 h, respectively. From Table 5, it is noticed that the predicted thicknesses agreed with the experimental values for C_{up}^{FeB} = 16.40 wt.%. For the bilayer diffusion model and the MDC method, the Runge-Kutta method [16] was used to search for the numerical solutions by taking the following initial conditions: $u(t_0)$ = 0.1 μm and $l(t_0)$ = 0.1 μm at t_0 = 1250*s* for 1170 K and t_0 = 850*s* for 1210 K. For the integral diffusion model, Equations (20) and (21) were used to get the predicted results. In the alternative diffusion model, the initial conditions employed are the same as in the two approaches (MDC method and the bilayer model) but the initial computation time was set to zero (i.e. t_0 = 0*s*). Furthermore, the following values of the two dimensionless parameters Φ_1 = 0.8786 and Φ_2 = 0.8319 were taken into account in order to reproduce the experimental layers' thicknesses at 1170 and 1210 K.

All the mathematical approaches used here were intended to simulate the boron diffusion when generating the bilayer (FeB/Fe_2B) onto the surface of AISI 316L steel. They constituted an efficient tool to predict the layers' thicknesses versus the boriding parameters (the treatment time and the process temperature). This study also demonstrated the capability of such approaches to analyze the boronizing kinetics of AISI 316L steel. The diffusivities of boron in iron borides were shown to be sensitive to the values of dimensionless parameters Φ_1 and Φ_2 in the alternative diffusion model. The bilayer diffusion model assumed a non linear boron concentration distribution in each iron boride layer. Nevertheless, this assumption did not practically affect the simulation results compared to those obtained from the same model with linear boron concentration profiles in the FeB and Fe_2B layers. In the Dybkov model, the two fitting parametres k_{FeB} and k_{Fe_2B} were introduced in order to experimentally reproduce the layers'thicknesses in a two-phase system. After getting compact iron boride layers, the subsequent growth of such layers is based on the two following partial chemical reactions [13]: B + + Fe_2B = 2FeB and Fe + FeB = Fe_2B. Furthermore, in the current work, the original version of Dybkov model [13] was modified with the purpose of introducing the boride incubation times.

Tab. 5. Predicted layers'thicknesses of FeB and Fe_2B versus the experimental values obtained at 1170 K for 1.6 h and 1210 K for 1.1 h

Boriding conditions	Experimental thicknesses (µm)		Predicted thicknesses (µm)		Models used
	FeB	Fe_2B	FeB	Fe_2B	
1170 K, 1.6 h	17 ± 1	7 ± 0.6	15.38	6.09	Alternative diffusion model
1210 K, 1.1 h	18 ± 1.5	7 ± 0.4	17.68	6.72	
1170 K, 1.6 h	17 ± 1	7 ± 0.6	17.44	6.35	Integral diffusion model
1210 K, 1.1 h	18 ± 1.5	7 ± 0.4	19.25	6.87	
1170 K, 1.6 h	17 ± 1	7 ± 0.6	17.48	6.45	Mean diffusion coefficient method
1210 K, 1.1 h	18 ± 1.5	7 ± 0.4	19.34	6.87	
1170 K, 1.6 h	17 ± 1	7 ± 0.6	17.40	6.43	Bilayer diffusion model
1210 K, 1.1 h	18 ± 1.5	7 ± 0.4	19.25	6.86	
1170 K, 1.6 h	17 ± 1	7 ± 0.6	17.49	6.45	Dybkov model
1210 K, 1.1 h	18 ± 1.5	7 ± 0.4	19.35	6.87	

In the mean diffusion coefficient method, the concept of averaged values of boron diffusion coefficients in iron borides was adopted and led to satisfactory simulation results. To sum up, all these mathematical models did not consider the influence of carbon on the boriding kinetics of AISI 316L steel and ignored the presence of CrB precipitates [17] inside the bilayer (FeB/Fe_2B).

CONCLUSIONS

In this work, five prediction models was applied to the boronizing kinetics of AISI 316L steel treated by the pulsed-DC pack boriding process between 1123 and 1223 K. The incubation periods needed for the generation of the bilayer (FeB/Fe_2B) onto the surface of AISI 316L steel were considered. The diffusion coefficients of boron in FeB and Fe_2B were then assessed.

Except for the alternative diffusion model, the deduced values of boron activation energies in FeB and Fe_2B were nearly the same about 167 kJ mol^{-1} for FeB and 155 kJ mol^{-1} for Fe_2B. For the alternative diffusion model, the corresponding values of activation energies were higher and respectively equal to 187.95 kJ mol^{-1} for FeB and 185.69 kJ mol^{-1} for Fe_2B due to the difference in its mathematical formulation. Despite this point, the calculated boron activation energies in FeB and Fe_2B were still concordant with the literature results. In addition, the predicted thicknesses were consistent with the experimental values for all diffusion models.

As limitations, these five predction models did not account for the effect of carbon on the diffusion process of boron atoms and the presence of CrB precipitates inside the bilayer (FeB/Fe_2B) that could impact on the diffusion rate of boron atoms. Furthermore, these approaches can be applied for the diffusion kinetic of any interstitial element in muti-phase compact layers.

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