Growth kinetics of diiron boride (Fe_2B) layer on a carbon steel by four approaches

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The pack-boriding kinetics of SAE 1020 steel has been addressed through utilizing four mathematical approaches in case of the formation of diiron boride layers. The values of boron diffusivities and activation energies in Fe_2B were assessed in the interval of 1123 to 1223 K by using four models. Finally, the four models were experimentally verified by comparing the predicted results to the experimental value of Fe_2B layer thickness determined at 1198 K for 6 hours. Finally, the simulated layers' thicknesses agreed with the experimental result. In addition, similarities and differences observed in the models were also discussed.

INTRODUCTION

Boronizing is a surface hardening technique that involves diffusing boron atoms into a material substrate to create a coating made up of hard borides [1]. The boriding treatment necessitates a high temperature of 1073 to 1273 K and a processing duration of 0.5 to 8 hours. The boronized layers in Armco iron [2] and steels [3-6] can be either a one phase layer (Fe_2B) or a two-phase layer (with Fe_2B and FeB) based on the following parameters: the chemical composition of boriding agent, the process temperature and the holding time.

These boron-rich compounds (iron borides) have a number of beneficial features, including high surface hardness, abrasion resistance, corrosion resistance, and oxidation resistance at temperatures up to 1123 K. However, a single phase (Fe_2B) over the treated steel 's surface is much desired from a practical point of view because the resulting boronized layer is tougher and less susceptible to cracking when applying mechanical loads. In terms of modelling, several mathematical models have been focused on the kinetics of Fe_2B layers on some steels [7-10] and Armco iron [2, 11]. The kinetics approaches [7-10] took into account the influence of boride incubation times and can be employed to assess the optimum values of layers' thicknesses that match the practical utilization of treated steels for the extreme working conditions.

The aim of this work was to simulate the kinetics of Fe_2B layers generated at the surface of SAE 1020 steel by including the influence of boride incubation periods. Four different approaches have been applied for this purpose. The boron diffusivities in diiron boride have been firstly assessed. Afterwards, the values of boron activation energies have been deduced by fitting the obtained results with Arrhenius relationship. All models have been validated experimentally for the extra boriding condition (1198 K during 6 h). Furthermore, advantages and limitations about the applicability of these models were also discussed.

DIFFUSION MODELS

Four approaches were employed to follow the growth kinetics of diiron boride layer produced by the solid boriding. A graphical illustration of boron concentration – profile along the Fe_2B layer is represented in Figure 1.

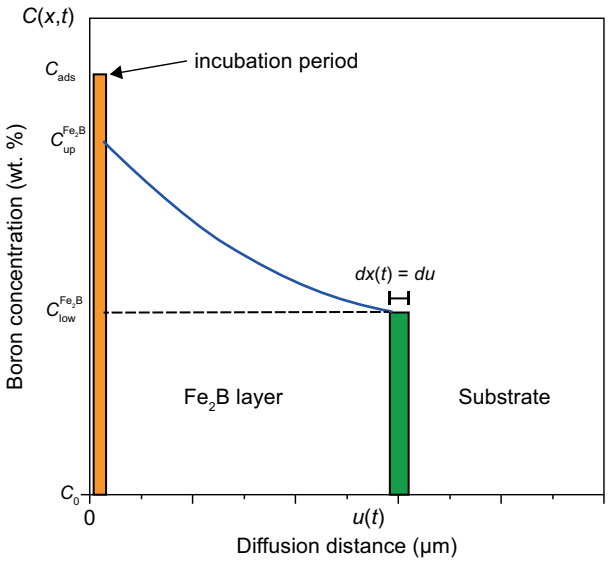


Fig. 1. Graphical illustration of boron-concentration profile in the Fe_2B layer

$C_{up}^{Fe_2B}$ is the maximum content of boron in Fe_2B (= 9 wt.%) whilst $C_{low}^{Fe_2B}$ represents the minimum content of boron in Fe_2B (=8.83 wt.%) [11]. The variable $x(t) = u$ denotes the position of (Fe_2B/substrate) interface.

The term C_{ads} is the adsorbed content of active boron over the surface of substrate [12]. C_{low} is the solubility of boron atoms in the substrate with a very low concentration (≈0 wt.%) [13].

Model 1: The alternative diffusion model

This approach [10] used the conservation equation of mass at the growing (Fe_2B/substrate) interface without assuming a priori the shape of distribution profile of boron element across the Fe_2B layer. As a result, the expression of boron diffusivity in Fe_2B is given by Equation (1):

$$D_{Fe_2B} = \frac{w\Phi^2 \ln(\frac{1}{1-\Phi^2})}{2(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})} k^2 \quad (1)$$

with $\Phi = \sqrt{1 - \frac{t_0(T)}{t}}$ and $w = [\frac{(C_{up}^{Fe_2B} + C_{low}^{Fe_2B})}{2} - C_0]$

where Φ is a dimensionless parameter related to the incubation time of Fe_2B layer. The constant k in Equation (2) is the slope of the straight line relating the thickness of boronized layer $u(t)$ to the square root of effective exposure time $(t - t_0(T)$:

$$u(t) = k[t - t_0(T)]^{1/2} \quad (2)$$

The thickness of Fe_2B layer can be predicted in this case by employing Equation (3):

$$u(t) = \frac{1}{\Phi}\sqrt{\frac{2D_{Fe_2B}(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})(t - t_0(T))}{w\Phi \ln(\frac{1}{1-\Phi^2})}} \quad (3)$$

and assuming a mean value of Φ parameter.

Model 2: The integral diffusion model

The integral diffusion model [14] is relying on the numerical resolution of the following system of differential algebraic equations (DAE):

$$a(t)u(t) + b(t)u(t)^2 = (C_{up}^{Fe_2B} - C_{low}^{Fe_2B}) \quad (4)$$

$$\frac{d}{dt}[\frac{u(t)^2}{2}a(t) + \frac{u(t)^3}{3}b(t)] = 2D_{Fe_2B}b(t)u(t) \quad (5)$$

$$2wb(t) = a(t)^2 \quad (6)$$

After using a particular solution of DAE system [14], The boron diffusion coefficient in Fe_2B was found and expressed by Equation (7):

$$D_{Fe_2B} = (\frac{k}{2\varepsilon})^2 \quad (7)$$

with

$$\varepsilon = \sqrt{\frac{3[-1 + \sqrt{1 + 2\frac{(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})}{w}}]}{2 + \sqrt{1 + 2\frac{(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})}{w}}}}$$

The thickness of Fe_2B layer can be assessed theoretically with the help of Equation (8):

$$u(t) = 2\varepsilon\sqrt{D_{Fe_2B}(t - t_0(T))} \quad (8)$$

Model 3: The mean diffusion coefficient method

In this kinetic model [11], the mean value of diffusion coefficient in Fe_2B was taken into account by assuming a linear profile for boron distribution in the Fe_2B layer with the presence of incubation times. Accordingly, the expression of boron diffusivity in Fe_2B is given by Equation (9) for an incubation period of Fe_2B:

$$D_{Fe_2B} = \frac{\gamma_{11}k^2}{2(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})} = \beta k^2 \quad (9)$$

with $\beta = \frac{\gamma_{11}}{2(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})} = \frac{(3C_{up}^{Fe_2B} + 5C_{low}^{Fe_2B})}{16(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})}$

By using the MDC method, the Fe_2B layer thickness can be assessed by using Equation (10):

$$u(t) = \sqrt{\frac{D_{Fe_2B}(t - t_0(T))}{\beta}} \quad (10)$$

Model 4: The monolayer growth model

The monolayer growth model [15] is based on the solution of the following mass conservation equation at the (Fe_2B/substrate) interface with a linear profile for boron concentration within the Fe_2B layer.

$$w\frac{dx(t)}{dt}\bigg|_{x=u} = D_{Fe_2B}(\frac{C_{up}^{Fe_2B} - C_{low}^{Fe_2B}}{u(t)}) \quad (11)$$

By substituting Equation (2) into Equation (11) and after time derivation, the boron diffusivity in Fe_2B can be determined :

$$D_{Fe_2B} = \frac{wk^2}{2(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})} \quad (12)$$

Finally, the expression of Fe_2B layer's thickness is formulated as follows:

$$u = \sqrt{\frac{2D_{Fe_2B}(C_{up}^{Fe_2B} - C_{low}^{Fe_2B})(t - t_0(T))}{w}} \quad (13)$$

EXPERIMENTAL DATA USED FOR THE CALCULATIONS

The experimental data about the growth kinetics of Fe_2B layers formed over the substrate made of SAE 1020 steel were used to perform the calculations. In the reported research paper [9], the boriding treatment has been carried out by using the powder method. Therefore, a monophase layer has been obtained by employing the

following powders mixture: (22.5 wt.% H_3BO_3, 5 wt.% KBF_4 and 72.5 wt. % SiC) given in weight percent. The boriding experiments were conducted at 1123, 1173 and 1223 K during 4, 8 and 12 h. An additional boriding condition (corresponding at 1198 K for 6 h) was also used to validate the diffusion models. In addition, more than twenty layers' measurements were made on various locations of the cross-sections of boronized samples to get statistically reliable results.

CALCULATION RESULTS AND DISCUSSIONS

The kinetic data obtained on the pack-boronized SAE 1020 steel [9] were exploited by plotting graphically the square of layer thickness against exposure time at each boriding temperature. The obtained straight lines were fitted with Equation (2) to deduce the results illustrated in Table 1. It is worth noting that the incubation period for the development of Fe_2B layer depends upon the boriding temperature as observed in other reference works [7, 16]. The incubation period is consequently reduced with the temperature rise because the diffusion rate of boron atoms is enhanced.

Tab. 1. Experimental kinetics constants at the considered interface with the presence of incubation times [9]

T (K)	Experimental kinetic constant k (μm·s$^{-0.5}$)	Incubation period $t_0(T)$ (s)
1123	0.4729	8571.4
1173	0.7026	3457.01
1223	1.0553	3037.6

Determination of boron activation energies

The boron diffusion coefficients in Fe_2B were evaluated by using the four models for a maximum boron content of 9 wt.% in Fe_2B. The obtained results were fitted with Arrhenius relation [6] as illustrated in Figure 2.

In Table 2 are grouped the deduced values of boron activation energies in Fe_2B and their pre-exponential factors for SAE 1020 steel based on four models. These values of energies were taken from the slopes of $\ln D_{Fe_2B} = f(1/T)$ as per the Arrhenius relationship [6]. For the alternative diffusion model [10], a mean arithmetic value for the Φ parameter was set to 0.905 to estimate the diffusion coefficients of boron in Fe_2B at 1123, 1173 and 1223 K. For the integral diffusion model [14], the ε parameter was determined as 0.1370 by taking the maximum and lower values of boron contents in Fe_2B. It is noted that the boron activation energies are quite similar regardless of the applied diffusion models with pre-exponential factor value that may differ by a factor of 1 to 2.79.

Tab. 2. Assessed values of boron diffusivities in Fe_2B by using four diffusion models

D_0 (m^2 s^{-1})	Q (kJ mol^{-1})	Models used
2.69×10^{-3}	183.18	Alternative diffusion model [10]
9.64×10^{-4}	183.09	Integral dffusion model [14]
1.90×10^{-3}	183.16	Mean diffusion coefficient method [11]
1.93×10^{-3}	183.24	Monolayer growth model [15]

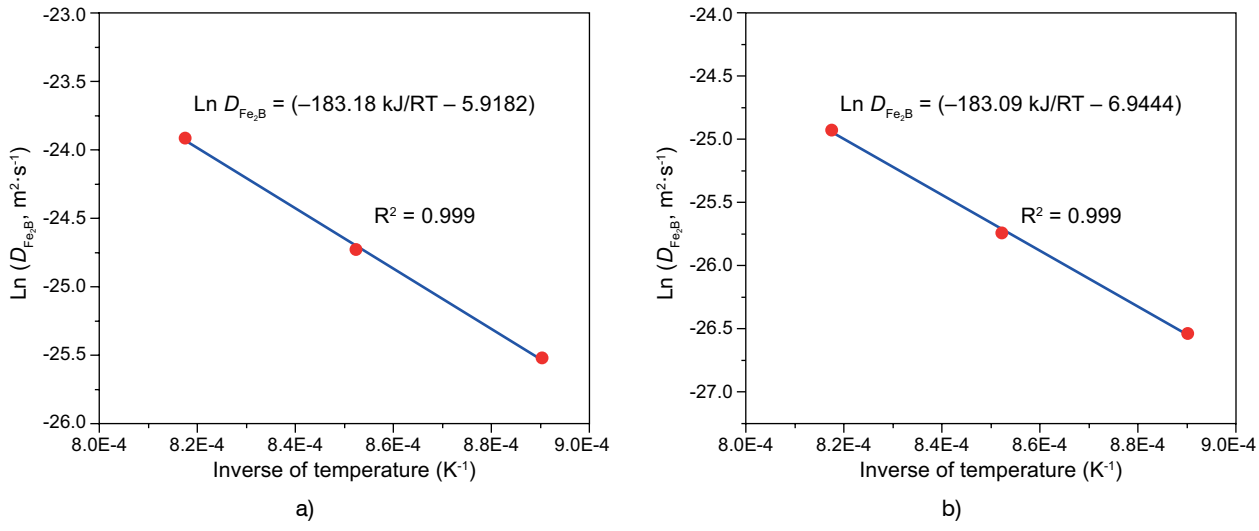


Fig. 2. Temperature dependency of assessed values of boron diffusivities in Fe_2B based on four models: a) the alternative diffusion model, b) the integral diffusion model *(Continue on next page)*

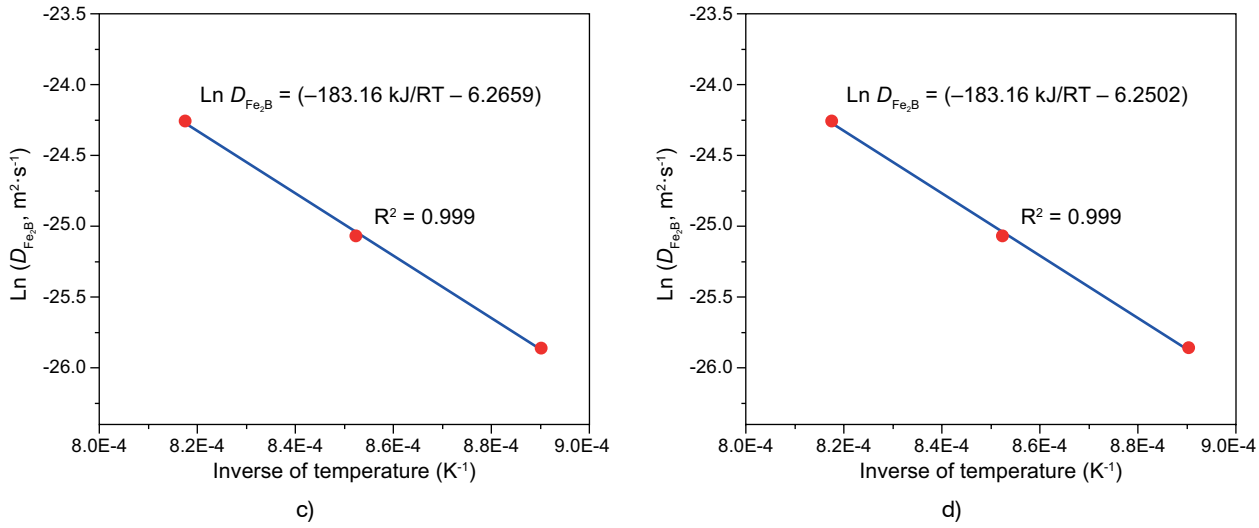


Fig. 2. Temperature dependency of assessed values of boron diffusivities in Fe_2B based on four models: c) the mean diffusion coefficient method and d) the monolayer diffusion model

Table 3 compares the values of boron activation energies found in the present work with the reported ones on some boronized steels [6, 8, 17-21]. The obtained values of activation energies for SAE 1020 steel are concordant with the literature [6,8, 20, 21]. Unlike the estimated values of activation energies in AISI 1018 steel [18] are very different and related to the dimensions of cylindrical shape of boronized samples (varying with the diameter of samples). Particularly, for a diameter of 12.7 mm, the calculated value of energy (= 155.22 kJ mol^{-1}) [18] complies with other values [6, 8, 20, 21]. However, the calculated boron activation energy in the AISI 1018 steel (= 91.20 kJ mol^{-1}) [18] was the lowest one for the cylindrical samples with a diameter of 1.85 mm and therefore incompatible with the literature data [6, 8, 20, 21]. Such a result may be related to the lowest value of boron mass flux during the diffusion process. In another investigation, Hernández-Sánchez et al.[17] also found a value of 61.37 kJmol^{-1} for the boron activation energy in AISI 1018 steel which is also inconsistent with the literature results [6, 8, 20, 21].

Experimental verification of the four models

An additional boronizing condition (at 1198 K during 6 hours) was utilized to experimentally verifiy the validitiy of the four models. The boride incubation period for generating the Fe_2B layer on SAE 1020 steel was taken as equal to 3426.5 s according to the fitting of experimental data reflected by the temperature-dependent parameter Φ. Equations (3), (8), (10) and (13) besides the numerical solution of DAE system for the integral diffusion model were employed to get the estimated values of Fe_2B layer thickness at 1198 K during 6 h. For the integral method [14], the Interactive Thermodynamics Software, running under (Version 3.2), was used by setting: (a_0 = 0.90, b_0 = 0.0453 and u_0 = = 0.18 μm) as the initial conditions for assuring the convergence of iterative computation. The analytic solution for the integral method with Equation (8) also yields the same results. Figure 3 describes the time evolution of simulated Fe_2B layers'thicknesses at 1123, 1173 and 1223 K by using the integral diffusion model [14] along with the experimental thicknesses [9]. The predicted thicknesses are in line with the experimental values highlighting a parabolic trend for the growth of Fe_2B layers with incubation times which are dependent on the process temperature.

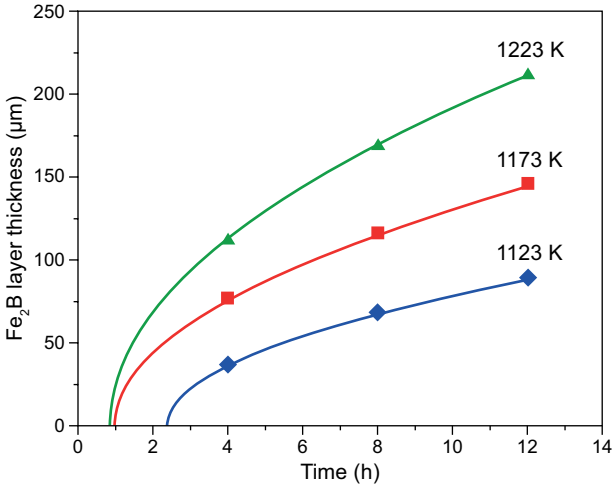


Fig. 3. Evolution of diiron boride layer thickness with the treatment time for different process temperatures. The continuous curves are from the numerical solution of the integral diffusion model [14] and the symbols denote the experimental data [9]

Tab. 3. Comparing the values of boron activation energies of this work with the literature data

Steel	Q (kJ mol^{-1})	Method of calculation	References
Hardox-450	157.99	Empirical growth law	[6]
ASTM A36	161.0	Diffusion model	[8]
AISI 1018	61.37	Diffusion model	[17]
AISI 1018	91.20-155.22	Empirical growth law	[18]
SAE 1005	133.8	Diffusion model	[19]
AISI P20	200.0	Empirical growth law	[20]
SAE 1020	183.15	Empirical growth law	[21]
SAE 1020	183.18	Alternative diffusion model	Present study
	183.09	Integral diffusion model	
	183.16	Mean diffusion coefficient method	
	183.24	Monaloyer growth model	

It is evidenced that the boride incubation time was lowered with the temperature rise because of activation of thermal energy during the diffusion of boron atoms at the steel's surface [6, 16]. Table 4 gives the simulated values of kinetics constants relative to the (Fe_2B/substrate) interface and compared to the experimental values [9] listed in Table 1. For the four models, the simulated kinetics constants are all dependent on the values of boron diffusivities in Fe_2B. The simulated kinetics constants listed in Table 4 were deduced from the linear fitting of Fe_2B layer thickness versus the square root of effective exposure time $t - t_0\,(T)$ based on the plotted curves in Figure 3. From Table 4, the predicted values of kinetics constants agreed satisfactory with the experimental values shown in Table 1.

Table 5 gathers the simulated values of layer's thickness with the experimental thickness obtained at 1198 K during 6 h. The predicted results by the four models are quite the same and concordant with the experimental thickness of Fe_2B layer.

A comparative study of the applied models showed the possibility of studying the formation kinetics of diiron boride layers on SAE 1020 steel regardless the shape of boron-concentration profile (either linear or parabolic) within a saturated or non saturated matrix with boron atoms. In the four models, the boron diffusion occurs within a semi-infinite medium.

As limitations, all the proposed models did not consider the effect of carbon present in the SAE 1020 steel on its boriding kinetics.

Tab. 4. Simulated values of kinetics constants by the four models

T (K)	Simulated kinetics constants (μm s$^{-0.5}$)			
	Alternative diffusion model [10]	Integral diffusion model [14]	Mean diffusion coefficient method [11]	Monolayer diffusion model [15]
1123	0.4941	0.4694	0.4685	0.4696
1173	0.7506	0.7129	0.7117	0.7135
1223	1.1020	1.0465	1.0447	1.0476

Tab. 5. Comparing the predicted values of diiron boride layer thickness with the obtained experimental value at 1198 K during 6 hours

Boriding conditions	Experimental Fe_2B layer thickness (μm)	Simulated Fe_2B layer thickness (μm)	Models used
1198 K for 6 h	120.66 ± 9.51	117.11	Alternative diffusion model [10]
		116.92	Integral diffusion model [14]
		116.71	Mean diffusion coefficient method [11]
		116.71	Monolayer diffusion model [15]

CONCLUSIONS

In the present study, the boriding kinetics of SAE 1020 with the Fe_2B layer formation has been considered by utilizing four mathematical models in order to simulate the boron diffusion. In this simulation work, the boride incubation period for Fe_2B layer was considered. The boron diffusion coefficients in Fe_2B have been evaluated by four models. The assessed boron activation energies in SAE 1020 steel were quite the same and roughly equal to 183 kJ mol^{-1}. Furthermore, the four models were successfully verified experimentally by considering an additional boronizing condition (at 1198 K for 6 h). A good coincidence was achieved between the experimental thickness and the predicted values. For future studies, all these models can be extended to be applied to a multiphase system (with or without the presence of boride incubation times) for simulating the boriding process.

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