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A Diffusion Model for the Fe_2B Layers Formed on a Ductile Cast Iron

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In this work, a diffusion model was applied to estimate the boron diffusion coefficients in the Fe_2B layers on the ASTM A-536 ductile iron in the temperature range 1173–1273 K by the powder-pack boriding. The mass balance equation at the (Fe_2B/substrate) interface was formulated considering the effect of boride incubation times. As a result, the value of activation energy for boron diffusion in the ductile iron was estimated and compared with the literature. To verify the validity of the present model, the experimental Fe_2B layer thickness obtained at 1173 K for 10 h was compared to the predicted value. A good concordance was observed between the predicted value of Fe_2B layer thickness and the experimental data.

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1. Introduction

Ductile iron is widely used in the automotive industry and in manufacturing of machine parts because of its excellent mechanical properties, castability, machinability, and low production costs [1, 4]. However, it has a disadvantage of a low abrasive wear resistance. Hence the boriding process is highly recommended for enhancing the wear performance of ductile iron and increasing its surface hardness. The boriding process can be carried out in solid, liquid, and gaseous medium. Among the boriding methods, the pack-boriding has many advantages that make it potentially the most industrially efficient [5].

The boriding process is a thermochemical treatment in which the boron atoms diffuse into the surface of ferrous alloys to produce hard boride layers improving their resistance against wear and corrosion [6]. From a kinetic point of view, a few diffusion models were reported for modeling the growth kinetics of Fe_2B layers on the surfaces of gray cast irons [7–9]. However, there is only one reference work regarding the simulation of the growth kinetics of Fe_2B layers in case of ductile iron ASTM A-536) [10].

The aim of the present work was to investigate the growth kinetics of Fe_2B layers grown on the ductile cast iron including the effect of boride incubation times. The model was able to estimate the diffusion coefficient of boron through the Fe_2B layers at each boriding temperature by using the continuity equation. The present model can also be used to predict the boride layer thickness according to the practical utilization of this kind of ductile cast iron in the industry for the wear resistance requirement. For this purpose, an alternative diffusion model [11] was applied for estimating the value of activation energy for boron diffusion in the ductile iron (ASTM A-536) valid in the temperature range 1173–1273 K. During the formulation of diffusion model [11], a boron concentration profile through the Fe_2B layers was assumed to be nonlinear with the presence of boride incubation times during the formation of these layers with a single phase. In this kinetic model [11], a non-dimensional parameter that depends on the values of upper and lower boron concentrations in the Fe_2B phase was introduced in order to estimate the boron diffusivity in the Fe_2B layers for the considered temperature range.

However, in the diffusion model applied by Lopez-Perrusquia [10], a linear profile for the boron distribution along the Fe_2B layer was taken with an expression of the time dependence of boride layer thickness different from that used in the present diffusion model.

Moreover, to verify the validity of this diffusion model, the experimental Fe_2B layer thickness obtained at 1173 K for 10 h was compared to the predicted value.

2. The diffusion model

2.1. The mass balance equation

The model considers the formation of Fe_2B layer on a saturated substrate with boron atoms as shown in Fig. 1. $C_{up}^{Fe_2B}$ ($= 59.8 \times 10^3$ mol m^{-3}) defines the upper limit of boron content in Fe_2B , whereas $C_{low}^{Fe_2B}$ ($= 59.2\times10^3$ mol m^{-3}) represents the lower limit of boron content in Fe_2B [12]. The term $\mathrm{d}u$ is an infinitesimal increase in the Fe_2B layer thickness during the time step $\mathrm{d}t$. The term C_{ads} is the effective boron concentration during the boriding process [13]. The activation energy associated with the adsorption phenomenon depends on the surface coverage of adsorbed species. When the adsorbed boron concentration is sufficient on the sample surface, the Fe_2B layer is formed and proceeds to grow. The term C_0 represents the boron solubility in the matrix which is very low and can be neglected [14, 15].

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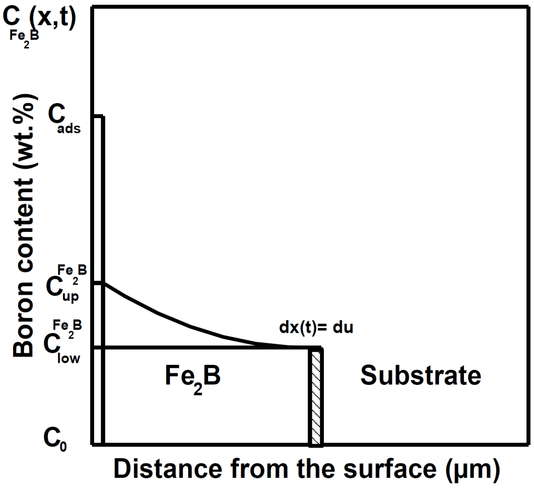

Fig. 1. Schematic boron-concentration profile through the Fe_2B layer.

The assumptions taken into account during the formulation of diffusion model are the following:

— The growth kinetics is controlled by the boron diffusion in the Fe_2B layer.

— The Fe_2B phase nucleates after a specific incubation time.

— The Fe_2B layer grows because of the boron diffusion perpendicular to the specimen surface.

— Boron concentrations remain constant in the boride layer during the treatment.

— The boride layer is thin compared to the sample thickness.

— A uniform temperature is assumed throughout the sample.

— Planar morphology is assumed for the phase interface.

The boundary conditions are given by Eqs. (1) and (2):

$$C_{Fe_2B}\left\{x\left[t=t_0(T)\right]=0,t_0(T)\right\}=C_{up}^{\mathrm{Fe_2B}}$$
$$\text{for } C_{ads} \succ 59.2\times10^3 \text{mol m}^{-3}, \tag{1}$$

$$C_{Fe_2B}\left\{x(t=t)=u,t\right\}=C_{low}^{\mathrm{Fe_2B}}$$
$$\text{for } C_{ads} \prec 59.2\times10^3 \text{mol m}^{-3} \tag{2}$$

for $0\le x\le u$.

The mass balance equation (or the continuity equation) at the (Fe_2B/substrate) interface can be formulated by Eq. (3) as follows:

$$\frac{1}{2}\left(C_{up}^{\mathrm{Fe_2B}}+C_{low}^{\mathrm{Fe_2B}}-2C_0\right)\frac{\mathrm{d}u}{\mathrm{d}t}= -D_{\mathrm{B}}^{\mathrm{Fe_2B}}\left.\frac{\partial C_{Fe_2B}(x,t)}{\partial x}\right|_{x=u}. \tag{3}$$

The boron concentration along the Fe_2B layer is given by the Fick second law

$$\frac{\partial C_{Fe_2B}(x,t)}{\partial t}=D_{\mathrm{B}}^{\mathrm{Fe_2B}}\frac{\partial^2 C_{Fe_2B}(x,t)}{\partial x^2}. \tag{4}$$

Its solution is expressed by Eq. (5), if the boron diffusion coefficient in the Fe_2B layer is constant

$$C_{Fe_2B}(x,t)=C_{up}^{\mathrm{Fe_2B}} -(C_{up}^{\mathrm{Fe_2B}}-C_{low}^{\mathrm{Fe_2B}})\frac{\operatorname{erf}\left(\frac{x}{2\sqrt{D_{\mathrm{B}}^{\mathrm{Fe_2B}}t}}\right)}{\operatorname{erf}\left(\frac{u}{2\sqrt{D_{\mathrm{B}}^{\mathrm{Fe_2B}}t}}\right)}. \tag{5}$$

Equation (5) was obtained from the boundary conditions given by Eqs. (1) and (2).

After derivation of Eq. (5) with respect to the distance $x(t)$ and substitution into Eq. (3), Eq. (6) is deduced

$$\frac{1}{2}\left(C_{up}^{\mathrm{Fe_2B}}+C_{low}^{\mathrm{Fe_2B}}-2C_0\right)\frac{\mathrm{d}u}{\mathrm{d}t}= \sqrt{\frac{D_{\mathrm{B}}^{\mathrm{Fe_2B}}}{\pi t}}\left(C_{up}^{\mathrm{Fe_2B}}-C_{low}^{\mathrm{Fe_2B}}\right)\frac{\exp\left(-\frac{u^2}{4D_{\mathrm{B}}^{\mathrm{Fe_2B}}t}\right)}{\operatorname{erf}\left(\frac{u}{2\sqrt{D_{Fe_2B}t}}\right)} \tag{6}$$

for $0\le x\le u$.

The expression of Fe_2B layer thickness (μm) can be expressed by Eq. (7):

$$u=2\varepsilon\sqrt{D_{\mathrm{B}}^{\mathrm{Fe_2B}}t}=2\varepsilon\sqrt{D_{\mathrm{B}}^{\mathrm{Fe_2B}}\ [t_{eff}+t_0(T)]}, \tag{7}$$

where t_{eff} represents the effective growth time of the Fe_2B layer [11, 16], $t_0(T)$ is the boride incubation time depending on the boriding temperature for the Fe_2B layer and t is the treatment time.

The use of Eq. (7) is acceptable from a practical point of view since it has been observed in many experiments.

After derivation of Eq. (7) with respect to the time t and substitution into Eq. (6), Eq. (8) was derived [11]:

$$\frac{1}{2}\left(C_{up}^{\mathrm{Fe_2B}}+C_{low}^{\mathrm{Fe_2B}}-2C_0\right)\varepsilon= \sqrt{\frac{1}{\pi}}\frac{\exp(-\varepsilon^2)}{\operatorname{erf}(\varepsilon)}\left(C_{up}^{\mathrm{Fe_2B}}-C_{low}^{\mathrm{Fe_2B}}\right). \tag{8}$$

The ε growth parameter depends on the values of boron concentration at the (Fe_2B/ substrate) interface. It can be estimated numerically by the Newton–Raphson method [17].

3. Simulation results and discussions

To determine the values of boron diffusion coefficients in the Fe_2B layers formed on the ductile cast iron (ASTM A-536), the experimental data found in the reference work [10] on the borided ductile cast iron were used to validate the diffusion model. In this reference work, the powder-pack boriding was carried out at the three temperatures (1173, 1223, and 1273 K) for 6, 7, and 8 h using B_4C Durborid as a boriding medium. Additional experiment was made at 1173 K for 10 h to verify the validity of the present diffusion model.

Figure 2 describes the evolution of the square of Fe_2B layer thickness as a function of time.

The experimental values of parabolic growth constants [10] at the Fe_2B/substrate interface were obtained from the slopes of the curves relating the square of the boride layer thickness against the treatment time according to Eq. (9):

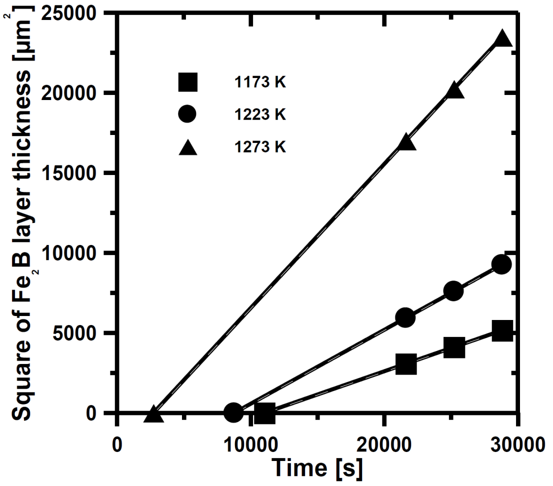

Fig. 2. Evolution of the square of Fe_2B layer thickness as a function of time.

$$u^2 = k^2[t - t_0(T)]. \tag{9}$$

Table I summarizes the experimental values of parabolic growth constants at the Fe_2B/substrate interface in the temperature range 1173–1273 K along with the corresponding incubation times [10]. From Table I it is seen the boride incubation time is decreased as the boriding temperature increases as reported in other studies [12, 18, 19].

TABLE I

Experimental values of parabolic growth constants at the Fe_2B/substrate interface along with the corresponding boride incubation times.

T [K]	Parabolic growth constants k [μms$^{-0.5}$]	Boride incubation time $t_0(T)$ [s]
1173	0.5386	11012
1223	0.6796	8743.9
1273	0.9486	2705.8

3.1. Estimation of the boron activation energy

To estimate the value of boron diffusion coefficient in the Fe_2B layers at each boriding temperature, it is necessary to plot the variation of the Fe_2B layer thickness as a function of the square root of time according to Eq. (7). The slope of the straight line at each temperature represents the value of the growth constant ($= 2\varepsilon\sqrt{D_B^{Fe_2B}}$).

Table II provides the estimated value of boron diffusion coefficient in the Fe_2B layer at each boriding temperature together with the value of ε growth parameter estimated from Eq. (8) and the corresponding values of parabolic growth constants.

The temperature dependence of the boron diffusion coefficient in the Fe_2B layer is expressed by Eq. (10):

$$D_B^{Fe_2B} = D_0 \exp(-\frac{Q}{RT}), \tag{10}$$

where D_0 is the diffusion coefficient of boron extrapolated at a value of $\frac{1}{T} = 0$. The Q parameter is the activation energy which indicates the amount of energy (kJ mol^{-1}) required for the reaction to occur, and R is the ideal gas constant ($R = 8.314$ J/(mol K)).

TABLE II

The estimated values of boron diffusion coefficients in the Fe_2B layers in the temperature range of 1173–1273 K.

T [K]	The ε growth parameter	$2\varepsilon\sqrt{D_B^{Fe_2B}}$ [μms$^{-0.5}$]	$D_B^{Fe_2B}$ [μm^{2}s^{-1}]
1173	0.070954644	0.403718	8.0935
1223		0.548893	14.9608
1273		0.896249	39.8874

The value of activation energy for boron diffusion Q can be readily obtained from the slope of the curve relating $\ln(D_B^{Fe_2B})$ to the inverse of temperature. Figure 3 describes the temperature dependence of boron diffusion coefficient in the Fe_2B layer.

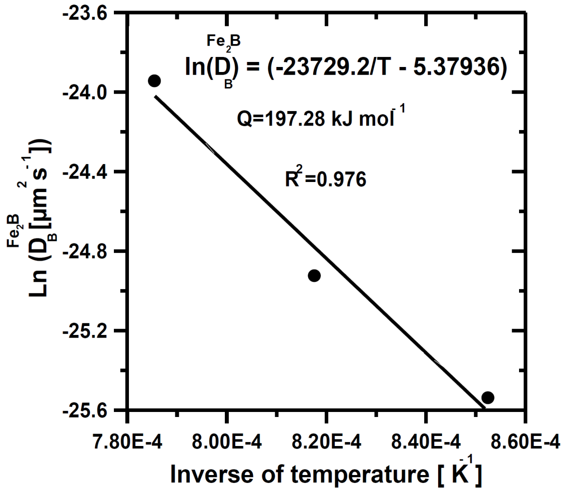

Fig. 3. Arrhenius relationship between the boron diffusion coefficients and the boriding temperature.

As a result, Eq. (11) was obtained according to the Arrhenius relationship as follows:

$$D_B^{Fe_2B} = 4.6 \times 10^{-3} \exp(\frac{-197.28\text{kJ/mol}}{RT})\ \text{m}^2\text{s}^{-1}. \tag{11}$$

Table III lists the values of activation energies for boron diffusion in some borided cast irons [7–10, 20–22] together with the value of activation energy (197.28 kJ/mol) estimated from this work. It is noticed that the reported values of activation energies for boron diffusion in the cast irons depend on various factors such as: the boriding method, the chemical composition of the substrate, the nature of boriding agent and the mechanism of boron diffusion. It is seen also that the reported values of activation energies in Table III depend on the method of calculation.

3.2. Experimental validation of the diffusion model

To check the validity of the present model, additional boriding condition was considered. Table IV shows a

TABLE III

Values of activation energies for boron diffusion obtained in borided cast irons by the pack-boriding process.

Cast iron type	Q [kJ/mol]	Method of calculation	Refs.
gray	177.4	diffusion model	[7]
gray	209.0	empirical approach	[20]
gray	134.21	empirical approach	[21]
gray	184.2	diffusion model	[8]
gray	175	diffusion model	[9]
nodular	212.28	empirical approach	[22]
ductile	155.7	diffusion model	[10]
ductile	197.28	diffusion model	present work

comparison between the experimental values of Fe_2B layers thickness [10] with the values predicted by Eq. (12) at the temperature of 1173 K for 10 h. A good agreement was observed between the predicted value and the experimental result

$$u = \frac{4}{\sqrt{\pi}} \frac{C_{up}^{\mathrm{Fe_2B}} - C_{low}^{\mathrm{Fe_2B}}}{C_{up}^{\mathrm{Fe_2B}} + C_{low}^{\mathrm{Fe_2B}}} \frac{\exp(-\varepsilon^2)}{erf(\varepsilon)} \sqrt{D_{\mathrm{B}}^{\mathrm{Fe_2B}} t}. \tag{12}$$

TABLE IV

Comparison between the simulated value of Fe_2B layer thickness and the experimental Fe_2B layer thickness.

T [K]	Fe_2B layer thickness [μm]	
	Predicted using Eq. (12)	Experimental
1173	73.73	72.04

4. Conclusion

An alternative diffusion model was used to estimate the boron diffusion coefficients in the Fe_2B layers on the ASTM A-536 ductile iron in the temperature range 1173-1273 K by the powder-pack boriding. The principle of mass balance equation was considered at the (Fe_2B/substrate) interface taking into account the occurrence of boride incubation times during the formation of Fe_2B layers. As a consequence, the value of activation energy for boron diffusion in the ductile iron was equal to 197.28 kJ/mol and compared with the literature data.

To verify the validity of the present model, a comparison was made between the experimental Fe_2B layer thickness and the predicted value for the sample pack-borided at 1173 K for 10 h. A good agreement was obtained between the experimental value and that of predicted by the present model.

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