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The effective diffusion coefficient of boron in the Fe_2B layers formed on the iron substrate

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Abstract. In this current work, the boron diffusion coefficient in Fe_2B was firstly evaluated using a diffusion model. It considers the effect of the incubation times required to form the Fe_2B layers by the paste-boriding process on the iron substrate.
This model solves the mass balance equation at the (Fe_2B/substrate) interface under certain assumptions. Afterwards, the effective boron diffusion coefficient in Fe_2B was evaluated through an application of a simple equation. As a result, the estimated value of boron activation energy in the presence of chemical stresses was found to be equal to 146.5 kJ mol^{-1} on the basis of experimental data taken from the literature.

1 Introduction

The boriding is a diffusion-related surface treatment with the purpose of improving the tribological properties, the fatigue endurance and the corrosion resistance of ferrous and non-ferrous alloys. This thermochemical treatment can be carried out between 1123 and 1323 K with the exposure times varying from 0.5 to 10 h [1]. The diffused boron atoms react with the substrate surface to form two types of borides FeB and Fe_2B. The suggested model takes into the effect of chemical stresses through the determination of effective diffusion coefficient of boron in Fe_2B grown on the iron substrate. The objective of this work was to evaluate the diffusivity of boron in Fe_2B (with and without the presence of chemical stresses) in the temperature range of 1223-1323 K by applying a recent diffusion model [2, 3] for the Fe_2B layer development.

2 Diffusion model

The diffusion model considers the growth of Fe_2B layer on a saturated substrate with boron atoms. A schematic non-linear concentration profile of boron through the Fe_2B layer is illustrated in Figure 1.

The constant $C_{up}^{Fe_2B}$ $(= 59.64\times10^3$ mol.m$^{-3})$ is the upper boron concentration in Fe_2B.

$C_{low}^{Fe_2B}$ $(= 59.2\times10^3$ mol m$^{-3})$ represents the lower boron concentration in Fe_2B and $t_0(T)$ is the boride incubation time depending upon the boriding temperature. C_{ads} is defined as the effective boron concentration [4]. The distance u is the layer depth at the (Fe_2B /substrate) interface as a function of the treatment time t.

C_0 is the boron solubility in the matrix. The assumptions taken during the formulation of the diffusion model can be found elsewhere [2].

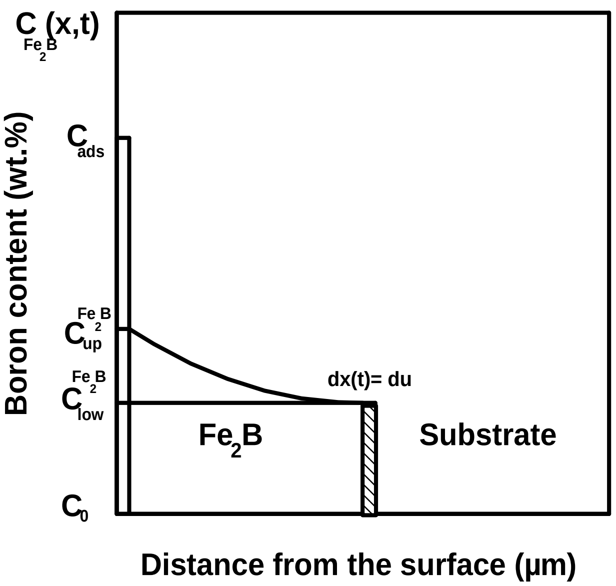

Figure 1. A schematic non-linear concentration profile of boron through the Fe_2B layer.

The initial condition of the diffusion problem is expressed by Equation (1):

$$C_{Fe_2B}(x,0) = C_0 \tag{1}$$

The boundary conditions of the diffusion problem are given by Equations (2) and (3):

$$C_{Fe_2B}\{x[t=t_0(T)]=0, t_0(T)\}=C_{up}^{Fe_2B} \text{ for}$$
$$C_{ads} \succ 59.2\times10^3 \text{ mol. m}^{-3} \quad (2)$$

$$C_{Fe_2B}\{x(t=t)=u, t\ \}=C_{low}^{Fe_2B} \text{ for}$$
$$C_{ads} \prec 59.2\times10^3 \text{ mol.m}^{-3} \quad (3)$$

for $0 \le x \le u$.
The Fick's second law of diffusion [5], relating the change in boron concentration through the Fe_2B layer with time t and location $x(t)$ is:

$$\frac{\partial C_{Fe_2B}(x,t)}{\partial t} = D_B^{Fe_2B}\frac{\partial^2 C_{Fe_2B}(x,t)}{\partial x^2} \quad (4)$$

where $D_B^{Fe_2B}$ is the diffusion coefficient of boron in Fe_2B free of chemical stresses and $C_{Fe_2B}(x,t)$ is the boron concentration through the Fe_2B layer. The distribution of boron concentration as a function of the depth satisfies Equation (5):

$$C_{Fe_2B}(x,t) = C_{up}^{Fe_2B} +$$
$$\left(\frac{C_{low}^{Fe_2B}-C_{up}^{Fe_2B}}{erf\left(u \big/ 2\sqrt{D_B^{Fe_2B}t}\right)}\right) erf\left(x \big/ 2\sqrt{D_B^{Fe_2B}t}\right) \quad (5)$$

for $0 \le x \le u$.
The continuity equation at the (Fe_2B/substrate) interface is expressed by Equation (6):

$$[0.5(C_{up}^{Fe_2B}+C_{low}^{Fe_2B})-C_0]k =$$
$$2\sqrt{\frac{D_B^{Fe_2B}}{\pi}}.\frac{(C_{up}^{Fe_2B}-C_{low}^{Fe_2B})}{erf\left(\frac{k\beta(T)}{2\sqrt{D_B^{Fe_2B}}}\right)}\exp(-\beta^2(T)k^2/4D_B^{Fe_2B})\beta(T)$$

with $\beta(T)=[1-(t_0(T)/t)]^{0.5}$ (6)

The Fe_2B layer thickness u can be expressed by Equation (7):

$$u = k[t-t_0(T)]^{1/2} \quad (7)$$

where k represents the parabolic growth constant at the (Fe_2B/substrate) interface. As stated by Brakman et al. [6], the boride incubation time is decreased with an increase of the boriding temperature.

The $\beta(T)$ parameter can be approached by a linear relationship [2] (Equation (8)) on the basis of experimental data taken from [7]:

$$\beta(T) = (5\cdot15\times10^{-4}T + 0.306637) \quad (8)$$

It is possible to numerically evaluate the diffusion coefficient of boron in Fe_2B $D_B^{Fe_2B}$ using the Newton-Raphson method [8]. For this purpose, a computer program was written in Matlab (version 6.5) to find the roots of Equation (6). By ignoring the pressure effect on the diffusion, the effective diffusion coefficient of boron in Fe_2B can be evaluated from Equation (9) as follows [3]:

$$D_B^{eff} = D_B^{Fe_2B}[1+\frac{\bar{V}^2(C_{up}^{Fe_2B}+C_{low}^{Fe_2B})E}{9RT(1-\nu)}] \quad (9)$$

where D_B^{eff} and $D_B^{Fe_2B}$ are the diffusion coefficients of boron in Fe_2B with and without the presence of chemical stresses, respectively.

The partial molar volume $\bar{V}$ is taken equal to (1.01×10^{-5} $m^3\,mol^{-1}$) [9]. E (=290 GPa) and ν (=0.3) are the Young's modulus and Poisson's ratio of the Fe_2B layer, respectively [10, 11].

3 Simulation results

The experimental results available in reference [7] were firstly used to evaluate the diffusion coefficient of boron in Fe_2B using Equation (6), and secondly to determine the effective diffusion coefficient of boron in Fe_2B based on Equation (9). The past-boriding process was carried out on the iron substrate under an argon atmosphere in a conventional furnace at 4 temperatures (1223, 1253, 1273 and 1323 K) and for variable times (2, 4, 6 and 8 h). Due to the saw-tooth morphology of the (boride layer/substrate) interface, twenty five measurements were done on different cross-sections of the borided samples to estimate the Fe_2B layer thickness. In Figure 2 is plotted the variation of the squared value of experimental boride layer thickness [7] as a function of the treatment time.

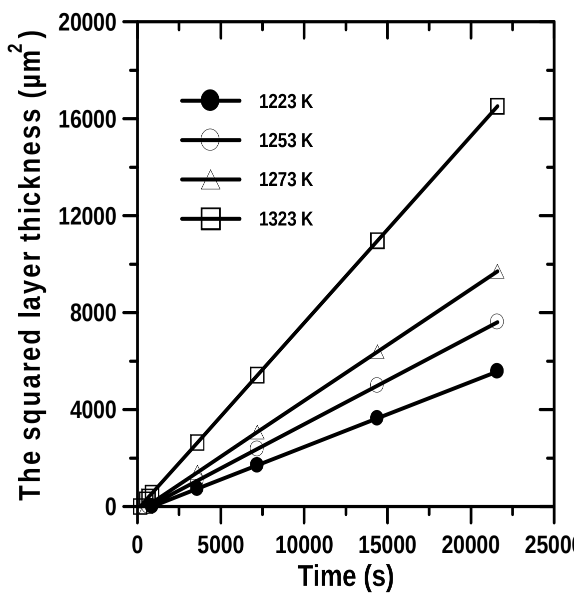

Figure 2. Variation of the squared value of the experimental boride layer thickness [7] versus the boriding time at increasing temperatures.

The model uses as input data the following parameters: the time, the temperature, the upper and lower boron concentrations in the Fe_2B iron boride and the experimental values of the parabolic growth constants at the (Fe_2B/substrate) interface. Table 1 provides the experimental value of parabolic growth constant $k_{\exp}$ at each boriding temperature with the corresponding incubation boride time.

Table 1. Experimental parabolic growth constants $k_{\exp}$ at the (Fe2B/substrate) interface with the corresponding boride incubation times $t_0(T)$.

T (K)	$k_{\exp}$ ($\mu m s^{-1/2}$)	$t_0(T)$ (s)
1223	0.518	884.3
1253	0.603	675
1273	0.678	533
1323	0.878	172

In Table 2, are gathered the computed values of $D_B^{Fe_2B}$ and D_B^{eff} obtained at each boriding temperature using Equations (6) and (9) for $C_{up}^{Fe_2B}$ = 59.64×10^3 mol m-3.

Table 2. Determination of the diffusion coefficient of boron in Fe2B and the effective diffusion coefficient for each boriding temperature for $C_{up}^{Fe_2B}$ = 59.64×10^3 mol m-3.

T(K)	$D_B^{Fe_2B}$ ($m^2 s^{-1}$)	D_B^{eff} ($m^2 s^{-1}$)
1223	1.66×10^{-11}	9.30×10^{-10}
1253	2.38×10^{-11}	1.30×10^{-9}
1273	3.02×10^{-11}	1.62×10^{-9}
1323	5.34×10^{-11}	2.76×10^{-9}

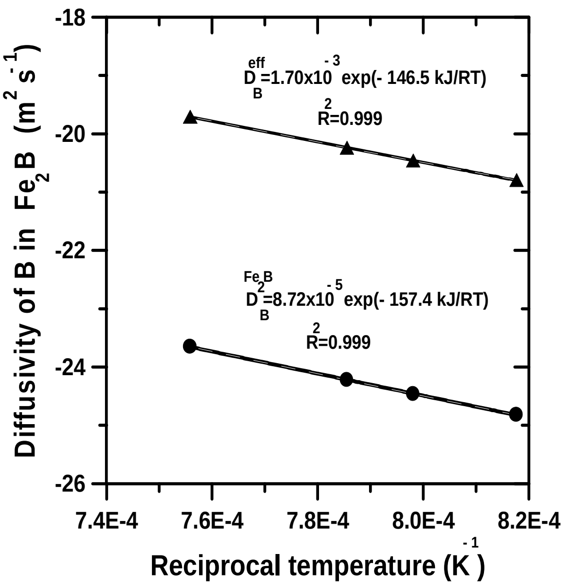

Figure 3. Temperature dependence of the diffusivity of boron in Fe_2B.

It is noticed that the presence of chemical stresses enhances the diffusion coefficient of boron in Fe_2B by a factor of 52 to 56. The dependence between the diffusivity of boron in Fe_2B and the boriding temperature is expressed by the Arrhenius equation. The activation energy of boron (with and without the presence of chemical stresses) can be obtained from the corresponding curves displayed in Figure 3.

As a result, the diffusion coefficient of boron in Fe_2B ($m^2.s^{-1}$) in the temperature range of 1223-1323 K was found to be equal to:

$$D_B^{Fe_2B} = 8.72\times10^{-5}\exp\left(\frac{-157.4kJ/mol}{RT}\right) \quad (10)$$

The effective diffusion coefficient of boron in Fe_2B ($m^2.s^{-1}$) was also determined as:

$$D_B^{eff} = 1.7\times10^{-3}\exp\left(\frac{-146.5kJ/mol}{RT}\right) \quad (11)$$

where R is the universal gas constant (= 8.314 $J.mol^{-1}.K^{-1}$), and T represents the boriding temperature in Kelvin.

The obtained value of boron activation energy (=157.4 $kJ.mol^{-1}$), without the chemical stresses, is close to that determined by Campos et al. [12] (i.e. 151 kJ mol^{-1}). This value represents the required energy to stimulate the boron diffusion in the preferential crystallographic direction [001] (i.e. in the direction perpendicular to the sample substrate). In this direction, it is reported that the boron element diffuses more speedily with a minimum resistance during the preferential growth of boride crystals.

In the direction parallel to the growth direction, the active flux of boron atoms accelerates the diffusion rate leading to a decrease in activation energy due to the chemical stresses effect. The deduced value of activation energy of boron (= 146.5 $kJ.mol^{-1}$) under the chemical stresses is lower than that of 157.4 $kJ.mol^{-1}$ due to enhancement of the boron diffusion.

4 Conclusion

In the present work, the diffusivity of boron in the Fe_2B layers grown on the iron substrate was firstly evaluated without the presence of chemical stresses through an application of a kinetic approach. This approach was based on solving the mass balance equation at the (Fe_2B/substrate) interface under certain assumptions. For the case of incorporating chemical stress effects, the boron effective diffusion coefficient in Fe_2B was secondly evaluated by applying a simple equation.

A lower value of activation energy for the effective diffusivity (= 146.5 $kJ.mol^{-1}$) was obtained for an upper boron content in Fe_2B equal to 59.64×10^3 $mol.m^{-3}$. This result is a consequence of the chemical stresses enhancing the boron diffusion through the Fe_2B layer.

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