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A model for studying the kinetics of the formation of Fe_2B boride layers at the surface of a gray cast iron

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ABSTRACT

The present work estimates, using a kinetic model, the growth kinetics of Fe_2B boride layers generated at the surface of a gray cast iron via the powder-pack boriding considering three different temperatures (1173, 1223 and 1273 K) and four treatment times (2, 4, 6 and 8 h). By the use of the mass balance equation at the (Fe_2B/substrate) interface under certain assumptions and considering the effect of the boride incubation time, it was possible to estimate the corresponding parabolic growth constant in terms of two parameters $\alpha\left(C_{\mathrm{up}}^{\mathrm{Fe_2B}}\right)$ and $\beta(T)$ depending on the boron content in the Fe_2B phase and on the process temperature, respectively. The mass gain at the material surface and the instantaneous velocity of the (Fe_2B/substrate) interface were also estimated. A fairly good agreement was observed between the experimental parabolic growth constants taken from a reference work (Campos-Silva et al., Characterization of boride layers formed at the surface of gray cast irons, Kovove Mater. 47 (2009) 1–7.) and the simulated values of the parabolic growth constants. Furthermore, the boride layer thicknesses were predicted and experimentally verified for three process temperatures and four treatment times.
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1. Introduction

One of the coating techniques widely used is boriding. The boriding treatment enables to produce the boride layers on various metallic materials by a thermodiffusion of boron atoms into their substrates in the temperature range from 973 to 1273 K for a time duration of 1–10 h. These generated hard borides with interesting properties improve the friction and wear characteristics of the boride layers [1].

The boride layers can either have a flat or saw-toothed interface with the substrate. In high-alloy steels the alloying elements contribute to flatten the interface but in low-alloy steels the interface has a saw-tooth morphology [2].

The boriding can be carried out in solid, liquid or gaseous media. Powder-pack boriding has the advantages of simplicity, the flexibility with respect to the composition of the powder, minimal equipment and cost-effectiveness [3–5].

In ferrous materials (steels and cast irons), a monolayer Fe_2B layer with a saw-tooth shaped is preferred for industrial applications in comparison with a bilayer configuration consisting of ($FeB + Fe_2B$) due to the brittleness of the highly stressed (FeB/Fe_2B) interface where crack formation is often observed [6].

It is known that the automotive industry is the major user of gray cast irons. The gray cast irons exhibit excellent damping characteristics and a good resistance to corrosion [7].

In order to optimize the parameters of the boriding treatment, the modeling is considered as a suitable tool to reduce a great number of experiments on various substrates to be treated.

So, the modeling of the growth kinetics of boride layers has received much attention to simulate the kinetics of the boride layers during these last decades. For this purpose, many models [8–17] were developed in the literature. Most of these models do not consider the influence of the boride incubation time on the kinetics of the boride layers. And recently, a few published models [18–23] have incorporated this effect.

In the present work, a diffusion model, taking into account the effect of the incubation time on the boride growth kinetics, was proposed. This model is a modified version of a model recently published and applied to the borided pure iron [18].

By considering the mass balance equation at the (Fe_2B/susbtrate) interface under certain assumptions, it was possible to estimate the corresponding parabolic growth constant in terms of two parameters $\alpha\left(C_{\mathrm{up}}^{\mathrm{Fe_2B}}\right)$ and $\beta(T)$ depending on the boron content in the Fe_2B phase and on the process temperature, respectively. The mass gain at the material surface and the instantaneous velocity of the (Fe_2B/susbtrate) interface were also estimated. The fitting parameter of the model, reflected by the value of the upper boron content in the Fe_2B phase, was obtained in order to reproduce the experimental parabolic growth constants in the range of

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1173–1273 K taken from a reference work by Campos-Silva et al. [22].

2. The mathematical model

The used kinetic approach is based on a model which considers a semi-infinite medium in a substrate to be saturated with boron atoms. The microstructural nature of the boride layers is controlled by the boron potential. This kinetic parameter is correlated to the upper boron concentration in the Fe_2B phase. From a thermodynamic point of view, the upper limit of boron content in the Fe_2B phase which is equal to 9 wt.% was indicated in Refs. [24–26]. This reported value is very consistent with the thermodynamics of the FeB phase diagram. In fact, Massalski [27] has shown that the Fe_2B phase exhibits a narrow composition range of about 1 at.%. By adjusting the boron potential, it is then possible to get a monolayer configuration composed only of Fe_2B, after exceeding a maximal value of the boron solubility in the matrix in accordance with the Fe-B binary system.

The formulation of this diffusion problem was based on the following assumptions:

(1) The growth of the borided layer occurs in a moving flat front parallel to the sample surface.
(2) A linear concentration-profile is assumed through the Fe_2B boride layer due to its narrow composition range (see Fig. 1).
(3) The Fe_2B iron boride nucleates on the material substrate after a certain incubation time.
(4) Local equilibrium is attained at the moving interface.
(5) The flux of the Fe atoms is neglected as a contributing factor of the layer growth.
(6) The borided layer is thin as compared to the thickness of the sample.
(7) The diffusion coefficient of boron in Fe_2B phase is independent of concentration and follows an Arrhenius relationship.
(8) The temperature in the treated sample is identical during the whole process.
(9) No effect of the alloying elements on the boron diffusion.

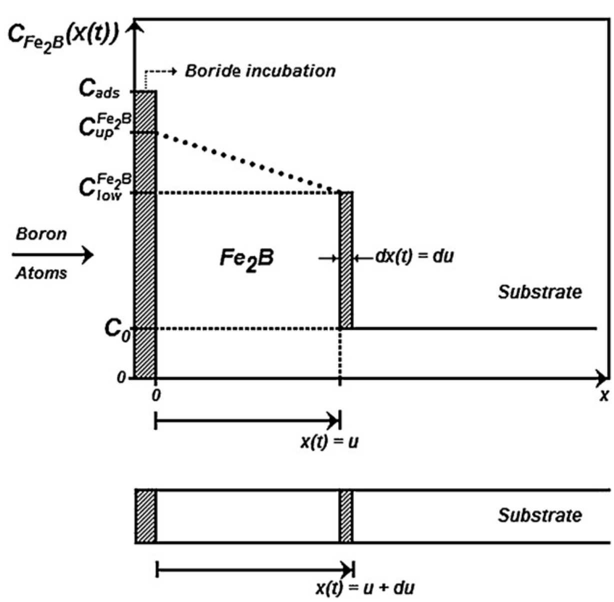

Fig. 1. A schematic concentration profile of boron through the Fe_2B layer. The hashed area is relative to the amount required to advance the Fe_2B phase by an infinitesimal distance, *du*.

The initial condition was established as:

$$C_{Fe_2B}[x(t>0)=0]=0$$

The boundary conditions were set as:

$$C_{Fe_2B}[x(t=t_0)=0]=C_{up}^{Fe_2B} \quad \text{for } C_{ads}^{B}>8.83\,\text{wt.\% B}$$

$$C_{Fe_2B}[x(t=t)=u]=C_{low}^{Fe_2B} \quad \text{for } C_{ads}^{B}<8.83\,\text{wt.\% B}$$

where $C_{up}^{Fe_2B}$ denotes the upper limit of boron concentration in the Fe_2B phase, $C_{low}^{Fe_2B}$ is the lower limit of boron content in the Fe_2B phase and equals to 8.83 wt.% B. C_{ads}^{B} is defined as the absorbed boron concentration [12] at the boride layer.

The conservation of the mass balance [28] at the (Fe_2B/susbtrate), given by the first Fick's law, can be expressed by Eq. (1):

$$\left[\frac{\left(C_{up}^{Fe_2B}+C_{low}^{Fe_2B}\right)}{2}-C_0\right]\frac{du}{dt}=D_B^{Fe_2B}\frac{\left(C_{up}^{Fe_2B}-C_{low}^{Fe_2B}\right)}{u} \tag{1}$$

where C_0 represents the boron solubility in the substrate and equals to 35×10^{-4} wt.% B [10]. du/dt is the velocity of the (Fe_2B/susbtrate) interface and u is the Fe_2B layer thickness. The diffusion coefficient of boron in the Fe_2B iron boride, expressed in ($m^2\,s^{-1}$), was taken from Ref. [21] and it is given by Eq. (2):

$$D_B^{Fe_2B}=3.34\times10^{-4}\exp\left(-\frac{175\,\text{kJ}\,\text{mol}^{-1}}{RT}\right) \tag{2}$$

where R is the universal gas constant (= 8.314 J/mol K), and T represents the absolute temperature in Kelvin.

Eq. (1) can be rewritten as:

$$\left[\frac{\left(C_{up}^{Fe_2B}+C_{low}^{Fe_2B}\right)/2-C_0}{C_{up}^{Fe_2B}-C_{low}^{Fe_2B}}\right]\int_0^u u\,du=D_B^{Fe_2B}\int_{t_0(T)}^{t}dt \tag{3}$$

The Fe_2B layer thickness is expressed by Eq. (4):

$$u=k\left[t^{1/2}-t_0^{1/2}(T)\right] \tag{4}$$

where $t_0(T)$ is the boride incubation period which is a temperature-dependent parameter and it is a time to reach saturation in the substrate. k represents the parabolic growth constant at the (Fe_2B/substrate) interface.

By substituting Eq. (4) in Eq. (3) and after rearrangement, the expression of the squared parabolic growth constant was obtained as:

$$k^2=2D_B^{Fe_2B}\left[\frac{C_{up}^{Fe_2B}-C_{low}^{Fe_2B}}{\left(C_{up}^{Fe_2B}+C_{low}^{Fe_2B}\right)/2-C_0}\right]\left[\frac{1+(t_0(T)/t)^{1/2}}{1-(t_0(T)/t)^{1/2}}\right] \tag{5}$$

By setting $C_0=0$, due to the very low boron solubility in the matrix, Eq. (5) can be rewritten as follows:

$$k^2=4\alpha\left(C_{up}^{Fe_2B}\right)\beta(T)D_B^{Fe_2B} \tag{6}$$

with $\alpha\left(C_{up}^{Fe_2B}\right)=\frac{C_{up}^{Fe_2B}-C_{low}^{Fe_2B}}{C_{up}^{Fe_2B}+C_{low}^{Fe_2B}}$ and $\beta(T)=\frac{1+(t_0(T)/t)^{1/2}}{1-(t_0(T)/t)^{1/2}}$

The $\alpha\left(C_{up}^{Fe_2B}\right)$ parameter is correlated to the boron concentration in the Fe_2B phase. It is seen from Fig. 2 that this parameter varies linearly with the boron content in the Fe_2B phase. This linear relationship is described by Eq. (7) employing a linear regression with a correlation factor equals to 0.999:

$$\alpha=5.6\times10^{-2}C_{up}^{Fe_2B}-0.4945 \tag{7}$$

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