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Applied Surface Science 252 (2006) 8662–8667

applied surface science

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Growth kinetics of iron boride layers: Dimensional analysis

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Received 18 July 2005; received in revised form 1 December 2005; accepted 2 December 2005
Available online 9 January 2006

Abstract

Dimensional analysis is presented as a powerful tool in the study of the paste boriding process. In particular, a dimensional method is used to study the growth kinetics of the boride layers FeB and Fe_2B. Experiments were performed in AISI 1045 steel and AISI M2 steel, to test the suggested model. Samples of 1045 steel were prepared and treated using boron paste thickness of 3–5 mm, at temperatures of 1193, 1223 and 1273 K, with 2, 4 and 6 h of treatment time. The M2 specimens had boron paste thickness of 3 and 4 mm and temperatures of 1223, 1253 and 1273 K for 2 and 6 h. Results indicate that the growth of boron layers obeys power laws of the form $y = \alpha x^{\beta}$, where α and β constants are a function of the material and the interface of interest. Validation of the model was carried out using experimental data with an average error percentage of 7.6% for Fe_2B in 1045 steel, 15.8% for FeB and 3.4% for Fe_2B in M2 steel.

Keywords: Dimensional analysis; Growth kinetics; Boriding process; Boride layers

1. Introduction

Dimensional analysis is a method to reduce the number and complexity of experimental variables affecting a physical problem, through the use of compacting techniques [1]. If a phenomenon depends on n dimensional variables, dimensional analysis can reduce the problem to only k dimensionless variables, where the subtraction $n - k = 1, 2, 3$ or 4 depends on the complexity of the process. Generally, $n - k$ is equivalent to the number of fundamental dimensions that govern the problem. One of the most important benefits of dimensional analysis is the generation of a model, based on scaling laws, that groups every experimental aspect used during the process. In the same way, it helps to predict the behavior of physical phenomena in similar conditions, under the same experimental range [2].

There are different methods used to reduce the number of variables to a lower number of dimensionless groups; Buckingham Pi Theorem is one of the most applied. The theorem is based on the creation of groups of variables in power product form. These groups are dimensionless (Π_1, Π_2, Π_3, etc.) and represent the most important parameters of the process. In this way, a lower number of experiments are assured, as well as the optimization and automation of the physical phenomena.

In this study, dimensional analysis was applied to the growth of boride layers. Via this surface hardening technique, boron atoms are diffused into the surface of several types of ferrous and non-ferrous alloys. Thus, the formation of iron borides causes an increase in the life of engineering components exposed to corrosion, abrasion and wear [3,4].

There are three important parameters to be controlled in the paste boride process: time, temperature and the boron potential at the material surface. The influence of the boron potential is reflected, mainly, in the decrease of the activation energy, shown as the diffusion of boron through the [0 0 1] direction in the FeB and Fe_2B phases [5].

In the same way, the influence of boron potentials could produce two characteristic layers at the material surface: a Fe_2B monolayer, applied to engineering components, and a FeB/Fe_2B bilayer, which is not desirable in industrial applications, due to the high intensity stresses states generally located at the FeB–Fe_2B interface [3–5]. Furthermore, these phases are formed according to the chemical composition of the material. It is more likely to observe Fe_2B growth in low carbon and low alloy steels, with a saw-toothed morphology. By contrast, flat

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doi:10.1016/j.apsusc.2005.12.002

growth fronts of a bilayer FeB/Fe_2B are formed when the substrate has more carbon and alloying elements such as molybdenum, tungsten, vanadium and chromium [6].

The present study proposes a dimensional kinetics model for the growth of iron boride phases in AISI 1045 and M2 steels. The dimensional model considers a group of experimental parameters for the process, employing the Pi Buckingham Theorem, in order to determine the power values of the iron borides growth. The validation of the model is carried out using experimental data from the paste boride treatment.

2. Model

The objective of dimensional analysis in this paper is to reduce the mass diffusion problem to a function that depends only on a single independent variable. By reducing the number of independent variables, the experimental process can be optimized. This method not only reduces the number of experiments, but also shows which parameters are the simplest to modify.

2.1. Assumptions

For a diffusion controlled process it assumes [9]:

(a) The growth of borided phases in the paste boriding process is a function of: the boron paste thickness h_o, growth constant k, the treatment time T, the boron concentration at the surface C_s and the concentration at the interfaces present C_o.
(b) The Fe_2B and FeB phase growing obeys the power law, of the form $y = \alpha x^{\beta}$, where x and y are dimensionless parameters; α and β are constants.
(c) The growth of boride layers occurs as a consequence of boron diffusion perpendicular to the specimen surface.
(d) The kinetics of the growth layer is controlled by the boron diffusion in the FeB and Fe_2B layers.
(e) The boron concentration at the surface and at the interfaces does not change during the boriding process.

2.2. Dimensional method

The units of the independent and dependent parameters are defined as: u [L] indicating average thickness of layer FeB and Fe_2B; t [T] corresponding to treatment time; h_o [L] equivalent to the boron paste thickness at the substrate surface; growth constant defined as k [L^cT^{-1}]; C_s and C_o with units of the form [ML^{-3}] are described as the boron concentration at the material surface and in present interphases. Dimensionless numbers are found through the application of the classical method, as proposed in Ref. [1].

For the first dimensionless parameter (Π_1), the terms h_o, t, C_s and u are grouped, resulting in the following expression:

$$L^xT^y(ML^{-3})^zL = M^0L^0T^0 \tag{1}$$

where $x = -1$, $y = 0$, $z = 0$ satisfy Eq. (1). Therefore, the dimensionless parameter Π_1 is defined as:

$$\Pi_1 = \frac{u}{h_o} \tag{2}$$

Π_2 groups h_o, k, t and C_s in the form:

$$L^xT^y(ML^{-3})^z(L^cT^{-1}) = M^0L^0T^0 \tag{3}$$

$x = -C$, $y = 1$, $z = 0$. Under these circumstances, Π_2 results in:

$$\Pi_2 = \frac{kt}{h_o^c} \tag{4}$$

where c is the inverse of the proposed exponent. Lastly, the dimensionless parameter Π_3, considers the variables h_o, t, C_s and C_o:

$$L^xT^y(ML^{-3})^z(ML^{-3}) = M^0L^0T^0 \tag{5}$$

where $x = 0$, $y = 0$, $z = -1$. Eq. (5) is then expressed as:

$$\Pi_3 = \frac{C_s}{C_o} \tag{6}$$

The relation of interest is the iron boride layer thickness as a function of dependent parameters, so:

$$\Pi_1 = f(\Pi_2, \Pi_3) \tag{7}$$

$$\frac{u}{h_o} = f\left(\frac{kt}{h_o^c}, \frac{C_s}{C_o}\right) \tag{8}$$

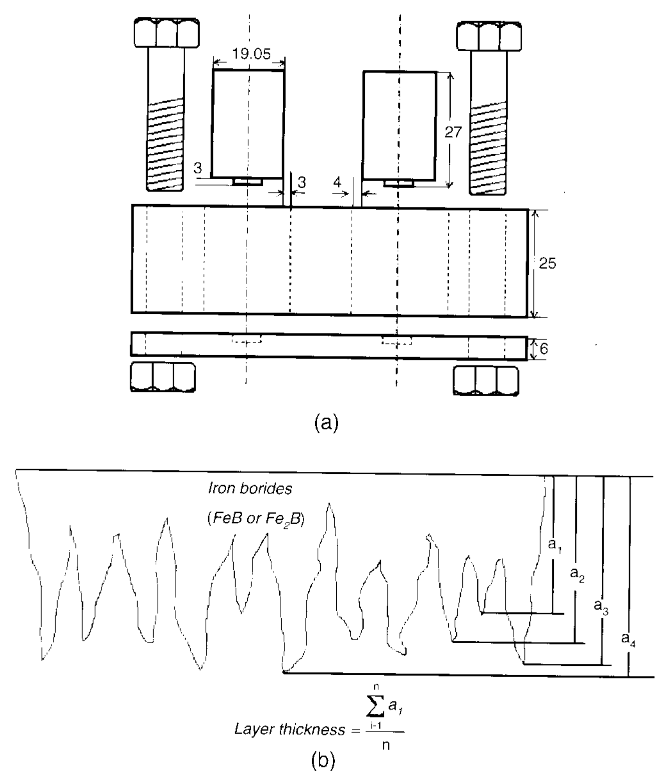

Fig. 1. (a) A schematic representation of the experimental setup for samples to be borided, scale in mm. (b) Procedure to estimate boride layer thickness in AISI 1045 steel [3,10].

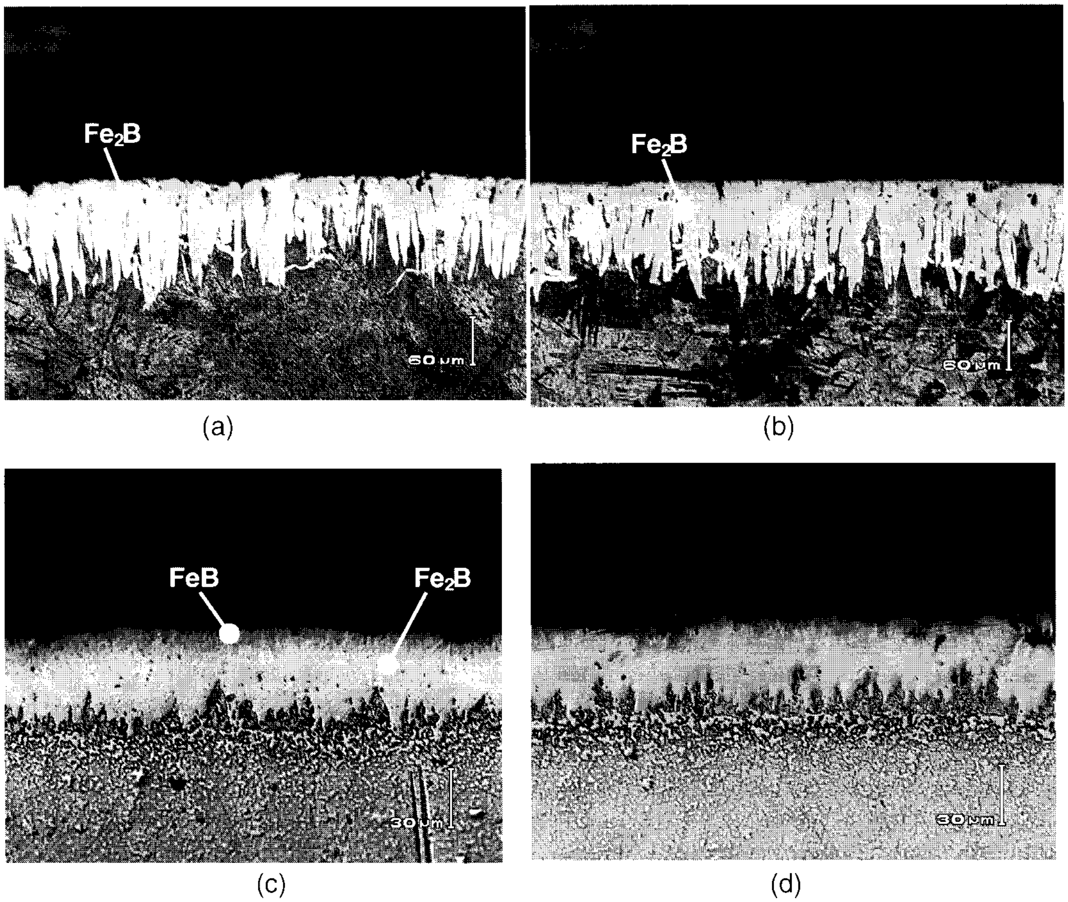

Fig. 2. Cross-sectional views of paste borided samples on AISI M2 and 1045 steels at 1273 K with 6 h of treatment. (a and b) For 1045 steel with boron paste thicknesses of 3 and 4 mm and (c and d) for M2 steel under the same boron paste thicknesses.

It is assumed that boron concentration on the surface and interfaces remain constant during the treatment. The model is valid to be applied to the growth of compact and continuous boride layers at the material surface.[1]

3. Experimental procedure

Cylindrical samples of AISI M2 and 1045 steels were machined and annealed for 1 h at 923 K. Afterwards, the samples were placed into acrylic molds (Fig. 1a), in order to control the boron paste thickness at the steel surface. The water/paste ratio was 0.2. Boron paste consists of B_4C (approximately 76 wt% boron) and cryolithe (Na_3AlF_6). Boriding in 1045 steel was done at 1193, 1223 and 1273 K, with different treatment times of 2, 4 and 6 h, modifying boron potentials in a range of 3, 4 and 5 mm of boron paste. For M2 steel, the boron paste thicknesses used were 3 and 4 mm, with temperatures of 1223, 1253 and 1273 K, and intervals of 2 and 6 h for each temperature. For all the samples, the boriding process was carried out in a conventional muffle furnace under pure argon atmosphere. After the treatment, the pieces were quenched in oil and cross-sectioned for metallographic preparation. The depth of boride layers was measured through optical microscopy with the aid of MSQ PLUS software. In order to minimize the roughness effect at interfaces growth, the layer thickness was defined as the average value of the long boride teeth [3] (see Fig. 1b). A minimulem of 25 measurements were done at different points of the layer for each sample.

[1] For alloyed steels, the boride layers are in the form of (Fe, M)B and (Fe, $M)_2B$. An alloying element M originally present in the substrate can be incorporated in the borides.

4. Results and discussions

Fig. 2 shows the iron boride layers formed at the surface of AISI M2 and 1045 steels. The micrographs reveal two important aspects: first, the chemical composition of AISI M2 steel has a drastic influence on the growth of the FeB/Fe2B bilayer. This is not the case for AISI 1045 steel. Second, there is a clear difference between the layers of AISI 1045 and M2: the first presents a high tendency to columnar growth, and the second shows the reduction in columnarity at the coating/substrate interface [7].

Carbucicchio and Palombarini [8] established the influence of alloying elements on the growth mechanism of iron borides. In their study, the elements present in steels, like Mo, V, Cr and Ni, inhibit the growth kinetics of the layers. Substitutional atoms of those elements tend to concentrate at the tips of the

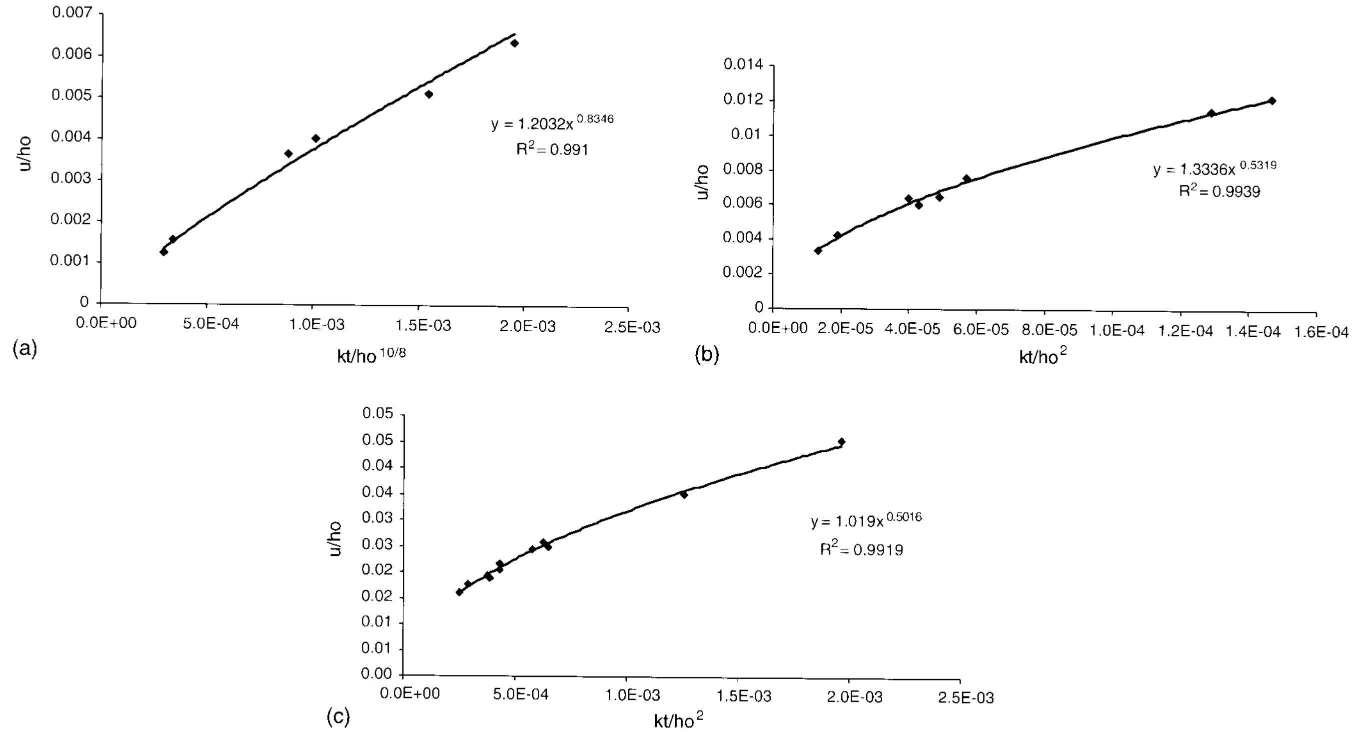

Fig. 3. Dimensionless growth of iron boride layers on M2 steel: (a) FeB and (b) Fe_2B. AISI 1045 steel reflects a Fe_2B phase growth on (c).

boride columns, and this concentration considerably reduces the active boron flux in this zone, consequently, it decreases the columnarity at the interfaces.

The growth of iron borides obeys a diffusion controlled process of the form $y = \alpha x^{\beta}$, where β represents the major adjustment in experimental data used within the process. The parabolic growth hypothesis was employed for M2 steel, where β exponents for FeB and Fe_2B phases are 0.7 and 0.53, respectively. The dispersion was 0.99 for Fe_2B phase and 0.96 for the FeB phase. To improve the data dispersion, the FeB growth was adjusted only to power functions, with 0.7 as an exponential growth. The previous modification was done using a generalized parameter of dimensionless growth kt/h_o^c, where c is the inverse of the proposed exponent. It was found that the dimensionless growth adjusted to a β exponent worth 0.799 with a dispersion value of 0.986. A subsequent iteration was performed, the FeB phase growth was fit to β value of 0.8 as a result the dimensionless growth exponent was 0.83 with a data dispersion of 0.99.

The dimensionless growth for Fe_2B phase in 1045 steel fit the experimental data with a β value equal to 0.50 and a dispersion of 0.99. Fig. 3 shows the curves for M2 and 1045 steel with the dimensionless variable group presented in Eq. (8). These data represent the experiment set done with 3 and 4 mm of boron paste thickness, for less than 6 h of treatment for both steels.

By maintaining α constant, the curve $y = \alpha x^{\beta}$ grows slowly when the β parameter increases, inverting the kinetics for values greater than 1. With the proposed experiments for M2 steel, the dimensionless power growth presents a slower dynamic growth of the FeB phase than in the Fe_2B phase. Also, the Fe_2B phase growth for both steels indicates a controlled growth equivalent to 0.5 according to the experimental data adjustment. The resulting expressions for M2 steel, according to dimensional analysis, are:

$$\frac{u_{\mathrm{FeB}}}{h_o} = 1.2032\left(\frac{kt}{h_o^{10/8}}\right)^{0.8346} \tag{9}$$

$$\frac{u_{\mathrm{Fe_2B}}}{h_o} = 1.3336\left(\frac{kt}{h_o^2}\right)^{0.5319} \tag{10}$$

For Fe_2B phase growth in 1045 steel, the resultant equation is:

$$\frac{u_{\mathrm{Fe_2B}}}{h_o} = 1.019\left(\frac{kt}{h_o^2}\right)^{0.5016} \tag{11}$$

Comparing (10) and (11), for dimensionless growth of Fe_2B phase, it is evident that the process is much faster in AISI 1045 steel.

The influence of temperature is also studied using dimensional analysis and is presented in Fig. 4. The growth kinetics shown by the dimensionless parameter β, establishes that between the temperatures of 1223 and 1253 K, the kinetics is greater than in extreme temperatures like 1193 K for 1045 steel and 1223 K for M2 steel, as well as for 1273 K in both steels. This probably indicates an optimal process temperature, where the growth kinetics of the borided phases has its maximum value. Likewise, when the temperature increases, β converges into values equivalent to 0.5.

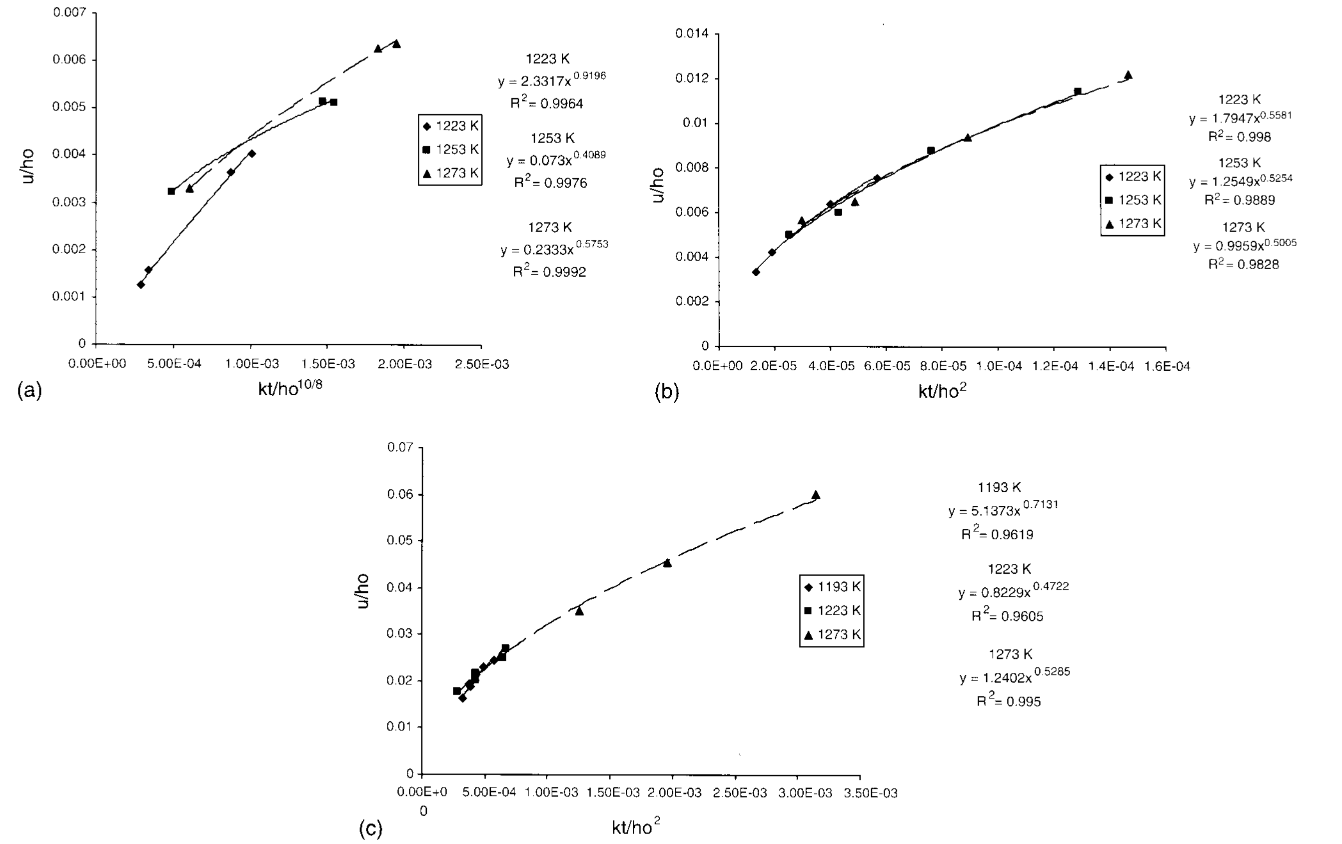

Fig. 4. Temperature influence on β dimensionless parameter for borided phases growth. (a) FeB, (b) Fe_2B, both for AISI M2 steel and (c) Fe_2B for AISI 1045 steel.

Table 1
Validity of dimensionless model for phases (a) FeB, (b) Fe_2B in M2 steel and (c) Fe_2B for 1045 steel

h_o (m)	k (m^2/s)	t (s)	u (m)	kt/h_o^2	u/h_o	Regression	Error (%)
(a) FeB							
0.005	5.6569E−13	14400	8.1065E−05	3.2584E−04	0.016213058	0.018159148	12.0
0.005	5.6569E−13	21600	1.1519E−04	4.8876E−04	0.023037800	0.022254757	3.4
0.005	7.7691E−13	14400	9.4254E−05	4.4750E−04	0.018850872	0.021291784	12.9
0.005	7.7691E−13	21600	1.3534E−04	6.7125E−04	0.027068026	0.026093926	3.6
0.005	5.4564E−12	14400	3.0121E−04	3.1429E−03	0.060241920	0.056602323	6.0
Average							7.6
h_o (m)	k ($m^{10/8}$ s^{-1})	t (s)	u (m)	$kt/h_o^{10/8}$	u/h_o	Regression	Error (%)
(b) Fe_2B in M2 steel							
0.004	6.8421E−11	7200	1.2933E−05	4.8972E−04	0.003233258	0.00224320	30.6
0.004	6.8421E−11	21600	2.0550E−05	1.4692E−03	0.005137379	0.00555012	8.0
0.004	8.5009E−11	7200	1.3177E−05	6.0845E−04	0.003294367	0.00268292	18.6
0.004	8.5009E−11	21600	2.5088E−05	1.8253E−03	0.006272074	0.00663807	5.8
Average							15.8
h_o (m)	k (m^2/s)	t (s)	u (m)	kt/h_o^2	u/h_o	Regression	Error (%)
(c) Fe_2B for 1045 steel							
0.004	5.6640E−14	7200	2.0044E−05	2.5488E−05	0.005010993	0.00480458	4.1
0.004	5.6640E−14	21600	3.5006E−05	7.6464E−05	0.008751535	0.00861859	1.5
0.004	6.6168E−14	7200	2.2566E−05	2.9776E−05	0.005641534	0.00521882	7.5
0.004	6.6168E−14	21600	3.7660E−05	8.9327E−05	0.009415055	0.00936166	0.6
Average							3.4

The validation of the dimensionless model was done with experimental data, using a work temperature range of 1223–1273 K, which was not used for the initial adjustment of the model. Table 1 shows the percentage of error obtained in the model, according to the growth data of FeB and Fe_2B phases, for both steels. The average error of FeB phase is approximately of 16%, and lower than 10% for Fe_2B phase, in both steels.

5. Conclusions

The following conclusions were established:

(a) The use of dimensional analysis reduces the mass diffusion problem into a function than depends only on an independent variable. The reduction of independent variables optimizes the experimental procedure, minimizing the number of tests, in addition to indicating the modified parameters.
(b) The regression of the non-dimensional variables showed that the dimensionless growths of the FeB and Fe_2B layers follow power laws of the form $y = \alpha x^{\beta}$, where constants α and β are a function of the substrate, the thickness of the boride layers generated at the material surface and the treatment time.
(c) The slowest value of β is obtained in the FeB phase, and does not necessarily follow a parabolic growth. On other hand, the dimensionless model shows that the growth of Fe_2B boride phase is faster in AISI 1045 steel than in AISI M2 steel. The power values of Fe_2B, for both steels, obey a diffusion controlled process, which represents a standard value of 0.5 approximately.
(d) The dimensionless β parameter shows the influence of the temperature in the growth mechanism of borided phases in AISI 1045 and M2 steels. The results obtained by the dimensionless model suggest that the growth kinetics of the iron borides layers has its maximum value in the range of 1223–1273 K.

Acknowledgements

This work has been supported by research grant no. 42883/A-1 of the *Consejo Nacional de Ciencia y Tecnologia at Mexico*. The authors wish to thank Mr. Isaac Aguilar Ventura, Mr. Jorge Hadad Bellamy and Susan French for their valuable cooperation.

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