Characterization of boride layers formed at the surface of gray cast irons

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Abstract

The characterization of iron boride layers formed at the surface of gray cast irons is evaluated in the present study. The thermochemical treatment applies the pack-powder boriding process in order to produce the Fe_2B phase at the surface of the material. The treatment was carried out at three different temperatures (1173, 1223 and 1273 K) and four exposure times (2, 4, 6, and 8 h). What is more, the boride layers were evaluated by the Vickers microindentation test, the X-Ray Diffraction method (XRD) and by the Energy Dispersive Spectroscopy method (EDS). Considering the growth fronts obtained at the surface of the gray cast irons, the boride incubation time and the mass balance equation at the interface Fe_2B/substrate, the boron diffusion coefficient on the borided phase was determined in the range of the treatment temperatures. Also, the mass gain on the surface of the borided gray cast irons was calculated assuming that the thermodynamic equilibrium remained constant during the process.

Key words: borides, diffusion, growth kinetics, hard coatings, gray cast irons, boriding

1. Introduction

The use of thermochemical treatments to improve the mechanical, physical and chemical properties of metallic and non-metallic materials has been one of the most important factors to increase the lifetime of mechanical components. Gray cast irons have been used extensively in the automotive industry where the operative conditions of the components are subjected to wear, abrasion and corrosion.

In this case, the boriding treatment is an alternative to increase the different properties at the surface of ferrous and non-ferrous alloys. The boride layers have extremely high hardness (from 1800 to 2000 HV) in comparison with nitriding or carburizing treatments, excellent thermal stability at high temperatures, friction coefficient is very low, and the corrosion resistance at the surface of the base materials in acid and alkaline media is improved [1–3]. Considering the boron potential that surrounds the material, the temperature, the treatment time and the chemical composition of the substrate, an Fe_2B monolayer or FeB/Fe_2B polyphase layers can be identified at the surface of the material. The boride layer has a saw-toothed morphology that increases the adherence of the borided phase with the substrate. According to the thermal, mechanical and physical properties of the boride layers, boronized cast irons can resist extreme conditions of work up to 1223 K.

The growth kinetics of iron boride layers has received a particular interest in the field of the boriding treatment in order to automate and optimize the process. For this reason, different mathematical models have been proposed to determine the boron diffusion coefficient at the borided phases [2–7]. Most of these models consider the thermodynamic equilibrium at the interface during growth and a linear boron concentration profile at the boride layer. The boron diffusion coefficient is obtained by the mass balance equation at the growth interface, considering that the boride layers obey the parabolic growth law $u = k\sqrt{t}$, where u is layer thickness, k is rate constant and t is

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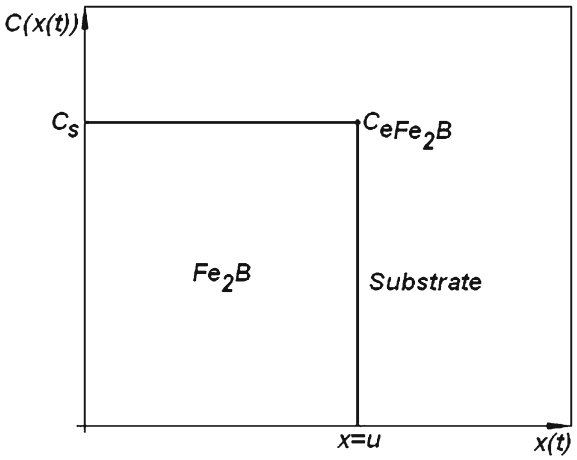

Fig. 1. Boron concentration profile at the Fe_2B boride phase.

time. Nevertheless, the mathematical models are sensitive to the measurement of the boride layer thickness obtained experimentally, to some extent, this causes a lack of information about the boron diffusion coefficients in the borided phases.

Likewise, the dependence between the temperature and the boron mobility at the borided phases can be explained by the Arrhenius equation, which makes possible to obtain the activation energy (Q) of the system.

This study characterizes the surface of gray cast irons hardened by the pack powder boriding treatment. The evaluation of the boron diffusion coefficient ($D_{\mathrm{Fe_2B}}$) was proposed by a mathematical model that considered the boride incubation time at the material surface. Alternatively, there was established the mass gain obtained at the surface of the gray cast irons. The XRD method shows the presence of the Fe_2B layer at the surface of the cast iron, and in qualitative form, the EDS method determines the distribution of the alloying elements in the borided layer. Furthermore, the Fe_2B phases were characterized by the Vickers microhardness testing in order to obtain the microhardness profile at the temperature of 1273 K with different exposure times. The results show that the hardness at the surface of the borided gray cast irons is approximately of 2000 HV.

2. Mathematical model

The model considers a saturated substrate with boron atoms, and also the boron potential used is required to form only one phase. The boron concentration $C(x(t))$ at the Fe_2B phase (Fig. 1) depends on both the position (x) and the time (t), where the total derivative of the concentration is expressed as:

$$\frac{\mathrm{d}C\left(x\left(t\right)\right)}{\mathrm{d}x}=\frac{\partial C\left(x\left(t\right)\right)}{\partial x}\frac{\mathrm{d}x}{\mathrm{d}x}=\frac{\partial C\left(x\left(t\right)\right)}{\partial x}, \quad (1)$$

where the mass balance equation at the growth interface is set as:

$$\left(C_{\mathrm{S}}-C_{\mathrm{eFe_2B}}\right)\left.\frac{\mathrm{d}x}{\mathrm{d}t}\right|_{x=u}=-D_{\mathrm{Fe_2B}}\left.\frac{\partial C_{\mathrm{Fe_2B}}\left(x\left(t\right)\right)}{\partial x}\right|_{x=u}, \quad (2)$$

where $\mathrm{C_S}$ and $C_{\mathrm{eFe_2B}}$ are the boron concentrations in the solubility limits corresponding to the equilibrium between the interstitial compound Fe_2B and the substrate. Substituting (1) in (2) yields:

$$\left(C_{\mathrm{S}}-C_{\mathrm{eFe_2B}}\right)\left.\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2\right|_{x=u}=-D_{\mathrm{Fe_2B}}\left.\frac{\mathrm{d}C_{\mathrm{Fe_2B}}(x(t))}{\mathrm{d}t}\right|_{x=u}, \quad (3)$$

considering that the layer growth obeys the parabolic law $x=u=kt^{1/2}$, Eq. (3) is established as:

$$\left(C_{\mathrm{S}}-C_{\mathrm{eFe_2B}}\right)\frac{k^2}{4}\int_{t_0}^{t_1}\frac{\mathrm{d}t}{t}=$$
$$=-D_{\mathrm{Fe_2B}}\left.\int_{C_{\mathrm{S}}}^{\mathrm{C_{eFe_2B}}}\mathrm{d}C_{\mathrm{Fe_2B}}\left(x\left(t\right)\right)\right|_{x=u}. \quad (4)$$

Assuming that the boron concentrations at the boride layer remain constant during the treatment, the $D_{\mathrm{Fe_2B}}$ value is determined:

$$D_{\mathrm{Fe_2B}}=\frac{k^2}{4}\ln\left(\frac{t_1}{t_0}\right), \quad (5)$$

where k is the growth constant, t_0 is the boride incubation time and t_1 represents the total treatment time.

The mass gain at the material surface $G\left(t\right)$ is established by (5):

$$\frac{k}{2}\sqrt{\ln\left(\frac{t_1}{t_0}\right)}\,t^{1/2}=\sqrt{D_{\mathrm{Fe_2B}}}\,t^{1/2}. \quad (6)$$

Multiplying both terms in (6) by $\rho(C_{\mathrm{S}}-C_{\mathrm{eFe_2B}})$, where ρ is the iron density, $G(t)$ in g cm^{-2} is determined by:

$$G(t)=\rho(C_{\mathrm{S}}-C_{\mathrm{eFe_2B}})\sqrt{D_{\mathrm{Fe_2B}}t}. \quad (7)$$

Equation (7) applies to treatment time $t\geq t_{\mathrm{o}}$.

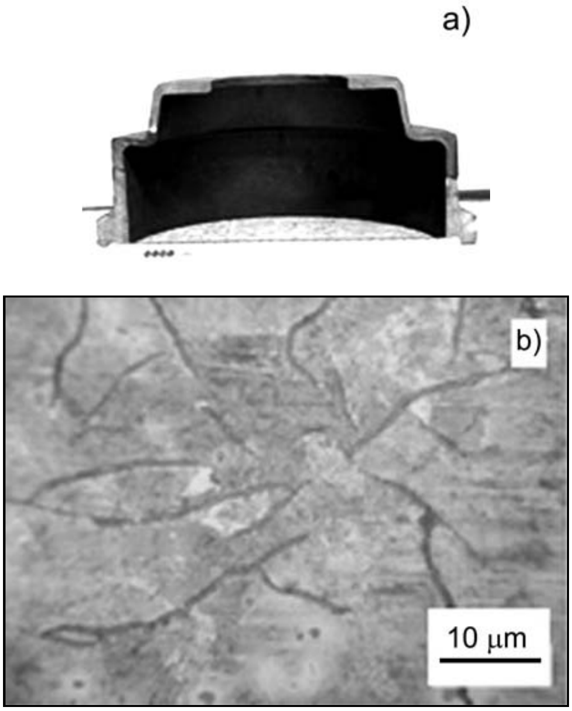

Fig. 2. (a) cross-sectional view of an automobile component made with gray cast iron, (b) microstructure of gray cast iron.

3. Experimental procedure

3.1. Boriding process

Gray cast iron samples class 30 (ASTM A48) with dimensions of 1000 mm^3 and a chemical composition of 3.44–3.45 % C, 1.7–1.77 % Si, 0.5–0.6 % Mn, 0.2 % Cr, 0.45–0.5 % Cu, were sectioned from an automotive component as shown in Fig. 2. The original structure of the samples shows graphite flakes over a pearlitic matrix with a mean hardness of 316 HV.

A stainless steel AISI 304L container was used to carry out the pack powder boriding treatment. The container with the samples was introduced into a conventional furnace where inert atmosphere was not required. The boriding media consisted on B_4C and activators (principally KBF_4), where the boron potential was controlled by the powder quantity placed over and around the material surface. Three temperatures were considered (1173, 1223 and 1273 K) with four exposure times (2, 4, 6, and 8 h). At the end of the process, the container was removed from the furnace and slowly cooled to room temperature.

3.2. Characterization of boride layers

The borided gray cast irons were prepared metallographically for their observation and characterization by optic microscopy and SEM, using an Olympus GX51 and a JEOL JSM 6360 LV, respectively. Fifty measurements were taken of the boride layer thickness in different sections of the material surface, in order to obtain statistically reliable results. The presence of the iron boride formed at the surface of the sample was determined by XRD analysis (D8 FOCUS equipment), using Cu Kα radiation with $\lambda = 1.54$ Å.

Also, microhardness of the boride layers was measured using an HVS 1000 Vickers tester with a 200 g load varying the distances from the surface at 10, 15, 25, and 45 μm. The borided samples at the temperature of 1273 K with the total exposure times were selected for this purpose. The reason of the selected boriding temperature and the different distances from the surface to carry out the microhardness testing is based on the boride layer thickness, being feasible that the indentation area is closed towards the surface of the boride phase. Each hardness value is the average of at least eight indentations for each distance.

4. Results and discussion

The evolution of the saw-toothed growth fronts of iron borides at the surface of gray cast irons is presented in Fig. 3. Also, the distribution and morphology of the graphite flakes seem to be preserved in the boride layer. The XRD analysis over the gray cast iron surface (Fig. 4) reveals the presence of the boride phase Fe_2B at 1273 K with 8 h of exposure time. In the borided layers, in zones corresponding to the boundaries, it is normally possible to find mixed crystals of different phases. Crystals of the Fe_2B type orientate themselves with the z-axis perpendicular to the surface. Consequently, the peaks of the Fe_2B type phases corresponding to crystallographic planes, with deviation from zero of the l index, show increased intensities in the X-ray diffraction spectra [8].

The growth of boride layers is a controlled diffusion process with a highly anisotropic nature. In case of the phase Fe_2B, the crystallographic direction [001] is the easiest path for the boron diffusion in the body centered tetragonal crystalline structure of the Fe_2B phase, due to the tendency of boride crystals to grow along a direction of minimum resistance, perpendicular to the external surface. As the metal surface is covered, an increasing number of Fe_2B crystals comes in contact with adjacent crystals and are forced to grow inside the metal, retaining an acicular shape [9].

The studies developed on borided cast irons [10–13], have determined the presence of polyphase FeB/Fe_2B layers at the surface of the samples. Here, the boron source that provides the boron potential, which surrounds the material surface, seems to have influence on the formation of one phase, and only reaches the concentration limits at the surface to cre-

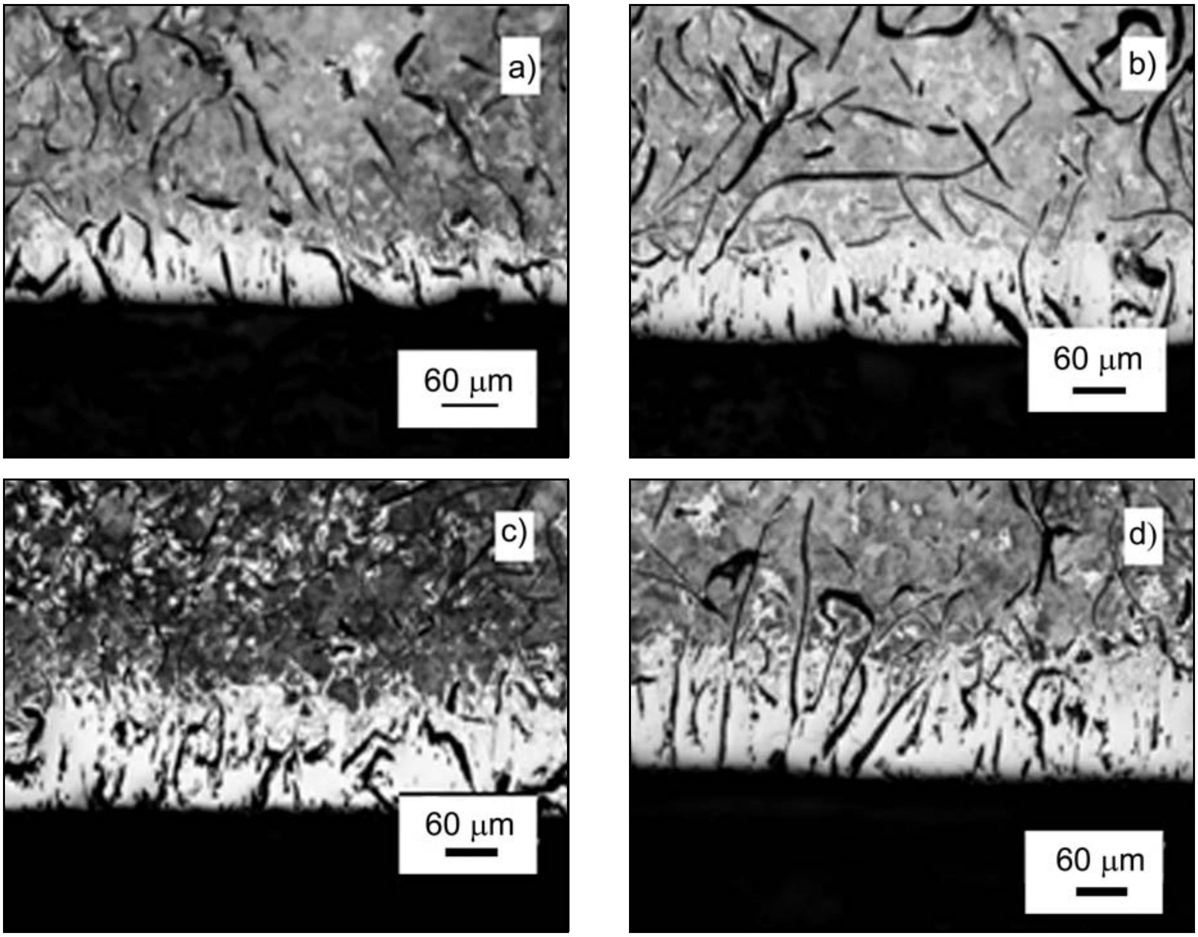

Fig. 3. Cross-sectional views of borided gray cast irons at 1273 K with treatment times: (a) 2 h, (b) 4 h, (c) 6 h and (d) 8 h.

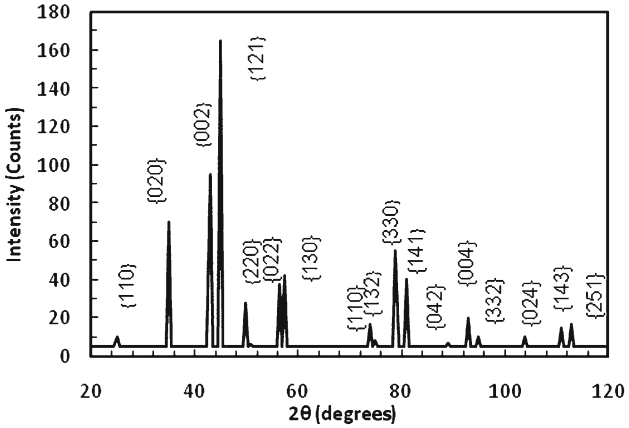

Fig. 4. X-ray diffraction pattern of borided gray cast iron at 1273 K with 8 h of exposure time.

ate the Fe_2B phase. It is known that media with low or intermediate boron potential (as compared to more powerful ones) allow the formation of single Fe_2B layers [14–16]. In industrial applications, it is desirable to have only the phase Fe_2B instead of polyphase FeB/Fe_2B layers due to significant differences between expansion coefficients at both phases, and cracks induced by internal stresses in the interphase are feasible.

The EDS analysis obtained by SEM is shown in Fig. 5. The results show that the chromium dissolves in the iron boride Fe_2B, in fact, the atomic radius of Cr is about the same and larger than that of Fe, and it can then be expected that Cr dissolved on the Fe sublattice of the borides. The carbon and silicon do not dissolve significantly over the phase and do not diffuse through the boride layer, being displaced to the diffusion zone, and forms together with boron, solid solutions like silicoborides and borocementite [5, 12].

The growth kinetics of the Fe_2B layers is depicted in Fig. 6, where the intercept with the abscissa is taken as the incubation time. As explained by Martini et al. (see [22] and references therein), the Fe_2B phase is the first product to form with the growth process inside the substrate along different directions, on the basis of the tip-enhanced growth mechanism. The needles of the boride phase induce in the base metal stresses and lattice distortions, which are high in the substrate

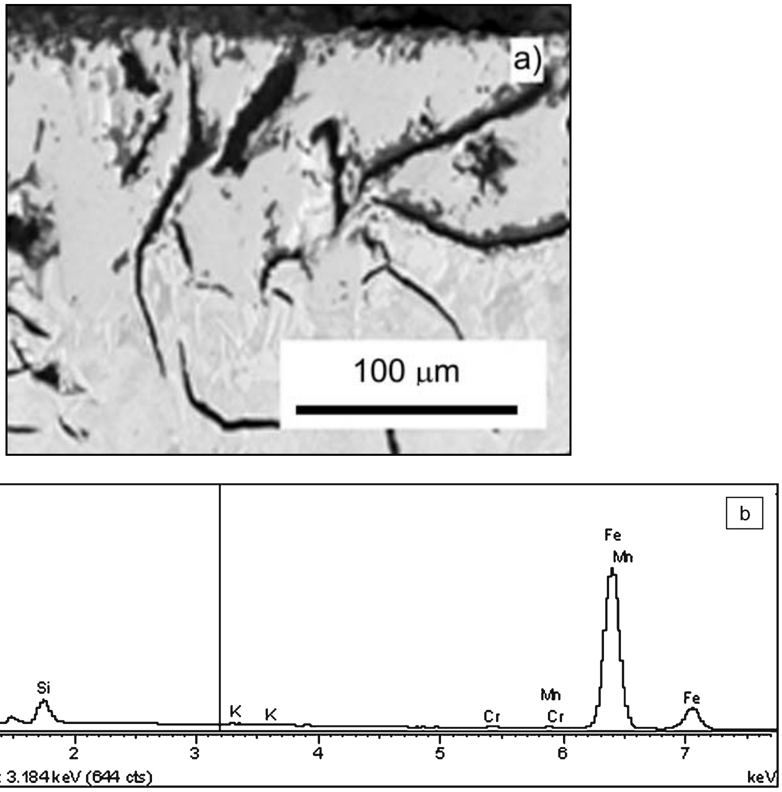

Fig. 5. (a) SEM-BSE image of cross-sectional view of borided gray cast iron at the temperature of 1273 K with 8 h of treatment, (b) EDS spectrum of borided sample.

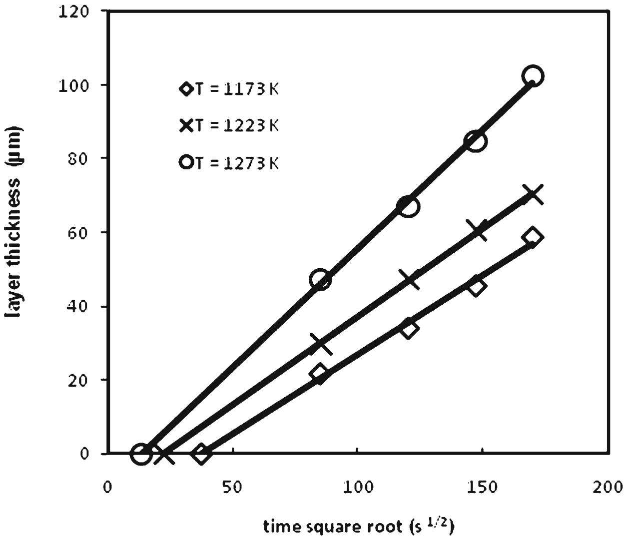

Fig. 6. Evolution of the Fe_2B layer thickness as a function of the time treatment.

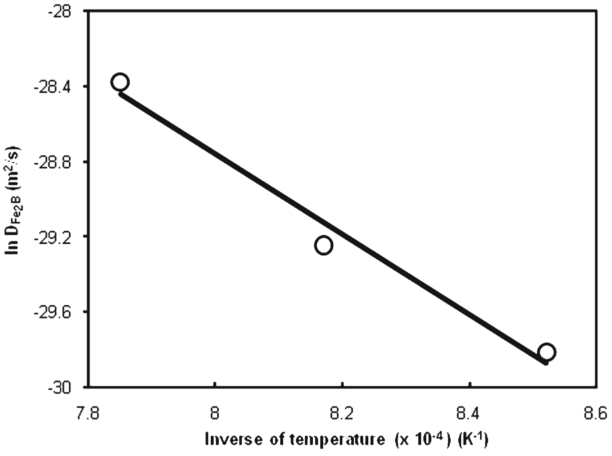

Fig. 7. Arrhenius relationship between the boron diffusion coefficient (D_{Fe_2B}) and the boriding temperatures.

located in front of needle tips. The results of the boride incubation time and the growth constants obtained at the treatment temperatures (Table 1) indicate that the process is thermally activated.

The D_{Fe_2B} values are obtained by Eq. (5) and the experimental results of the kinetic parameters. The dependence between the boron diffusion coefficient and the treatment temperature (Table 2) is expressed by the Arrhenius relation, where the activation energy Q is obtained by the slope of the graph shown in Fig. 7, where $Q = 177.4$ kJ mol^{-1}.

The mass gain at the surface of the gray cast irons surface is determined by Eq. (7). Keddam [17] established that the mass gain per unit surface area $G(t)$ at the surface of AISI 1045 steels is produced

Table 1. Parabolic growth constants and incubation times for the Fe_2B boride layer

Temperature (K)	$k \times 10^{-6}$ ($\mathrm{m\ s^{-1/2}}$)	Incubation time (s)
1173	0.431	1396
1223	0.479	495
1273	0.643	180

Table 2. Diffusion coefficient $D_{\mathrm{Fe_2B}}$ as a function of temperature

Temperature (K)	$D_{\mathrm{Fe_2B}}$ ($\mathrm{m^2\ s^{-1}}$)
1173	1.13×10^{-13}
1223	2×10^{-13}
1273	4.77×10^{-13}

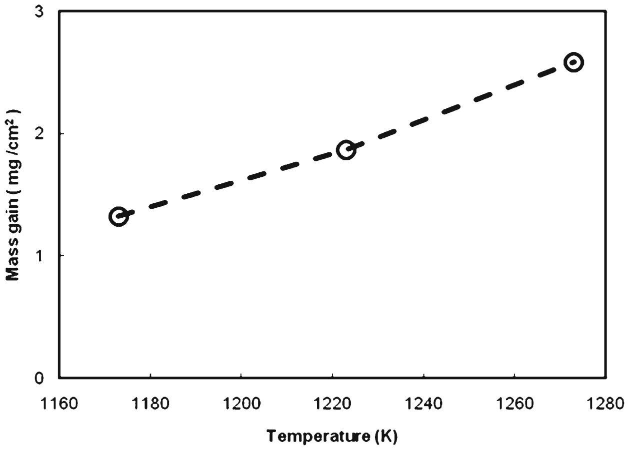

Fig. 8. Mass gain as a function of the temperature process obtained at the surface of gray cast irons.

by the formation of the boride Fe_2B at $t = 0$ covering completely the material surface and following the parabolic growth law. However, Eq. (7) in comparison with the equation proposed by Keddam, considers the mass gain produced for $t \geq t_0$, where t can represent any treatment time and even the boride incubation time. The mass gain associated to the iron boride Fe_2B (Fig. 8) and considering the incubation time, increases along with the treatment temperature.

The microhardness values of gray cast iron boronized at 1273 K with 8 h of exposure time are given in Fig. 9. The formation of the boride layer increases the superficial hardness of the gray cast iron up to 2000 HV. Different studies [17–19] have established that the hardness of the iron borides depends on the presence of thermal residual stresses produced by the iron boride growth, the temperature and the treatment time, the degree of anisotropy of the layer and also by the chemical composition of the substrate. Consequently, the microhardness gradient of the Fe_2B layer is related to the texture of the phase Fe_2B, whose preferential growth is in the direction [001]; the orientation texture increases as a function of the layer thickness and the treatment temperature, until it reaches the maximum value at the layer/substrate interface. On the other hand, according to Galibois et al. [20], the presence of thermal compressive residual stresses produced by the growth of the iron boride and the difference of the specific volume between the substrate and the borided phase, are important factors to take into account in the differences of the microhardness values obtained at the boride layer.

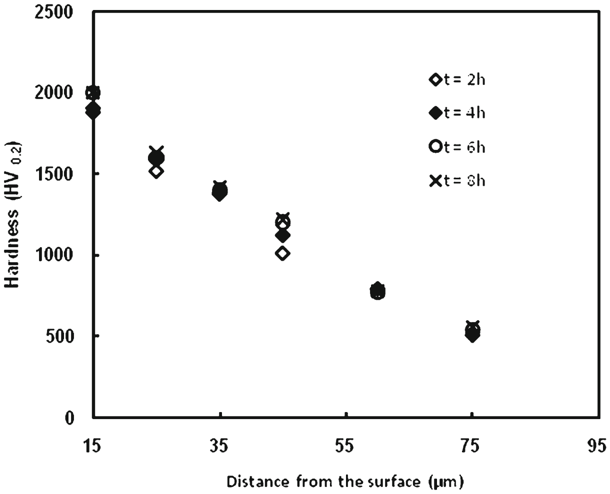

Fig. 9. Microhardness profile obtained for borided gray cast iron for different exposure times at the temperature of 1273 K.

5. Conclusions

This study characterizes the boride layers formed at the surface of gray cast irons. The results show the presence of the Fe_2B layer at the material surface, where chromium was dissolved into the boride layer, while carbon and silicon were diffused away from the boride layer to the diffusion zone. Moreover, the growth kinetics of the boride layers was evaluated by a mathematical model that considered the boride incubation time and the growth constant to determine the boron diffusion coefficient $D_{\mathrm{Fe_2B}}$. The dependence between the boron diffusion coefficients and the treatment temperature is expressed by means of the Arrhenius equation. A diffusivity of boron in Fe_2B created at the gray cast iron surface within the range

$1173\,\mathrm{K} \leq T \leq 1273\,\mathrm{K}$ was obtained:

$$D_{\mathrm{Fe_2B}} = 8.5\times10^{-6}\exp\left(-\frac{177.4\,\mathrm{kJ\ mol^{-1}}}{RT}\right) \quad (\mathrm{m^2s^{-1}})$$

with $R = 8.32$ J mol^{-1} K^{-1}, T in Kelvin and the pre-exponential factor in m^2 s^{-1}.

What is more, it was established that for $t \geq t_0$, the mass gain per unit surface area produced by the formation of the iron boride at the material sample increased in function with the treatment temperature.

Finally, the microhardness profile obtained at the phase Fe_2B was approximately 2000 HV at the outer most part of the layer at 1273 K, while the hardness of the core structure was of 350 HV. This demonstrates that the boriding treatment is feasible to be applied over gray cast irons used in the automotive industry, increasing their mechanical properties at the material surface.

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