CHARACTERIATION OF BORONIZED LAYERS ON X80 WCrV 18-04-01 STEEL AND KINETIC APPROACH FOR BORON DIFFUSION

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ABSTRACT

In the present work, X80 WCrV 18-04-01 steel was borided using a powder method in an electric furnace at a temperature of 1223 K for 1, 2 and 8 h. The powder used is composed of 5 % B_4C, 5 % $NaBF_4$ and 90 % SiC. The boride layers formed on the X80 WCrV 18-04-01 steel was characterized by the optical microscopy and X-ray Diffraction (XRD) analysis. A recent kinetic approach based on the integral method has been used to estimate the boron diffusion coefficients in the bilayer (FeB + Fe_2B) formed on X80 WCrV 18-04-01 steel based on results from the literature. An equation was obtained, after solving the system of algebraic differential equations, to estimate the thickness of the bilayer (FeB + Fe_2B) in order to compare it with the experimental thicknesses. A good agreement was obtained between the predicted and the experimental values. As a result, the activation energy for boron diffusion in X80 WCrV 18-04-01 steel was estimated 212.83 kJ mol^{-1}. The validation of the model was extended by considering the boriding treatment at 1223 K for 1h and 8h, giving a good correlation with the experimental data.

Keywords: *boronizing, iron borides, diffusion, integral method, activation energy.*

INTRODUCTION

Boriding is a thermal diffusion of boron on the surface of the part to be treated. It consists in carrying out the treatment in the temperature range between 800°C and 1050°C, for 1 to 12 hours, in contact with a source rich in boron [1 - 3]. Boron atoms, due to their relatively small size and of a highly mobile nature, can diffuse into ferrous alloys. They can dissolve in iron interstitially, but can react with it to form FeB and Fe_2B intermetallic compounds [4 - 8]. The purpose of boriding is to improve the surface properties resulting in a high surface hardness, better resistance to wear, abrasion and oxidation, as well as resistance to attack by certain acids or alkalis than other thermochemical processes such as carburization, nitriding or carbonitriding [5, 9 - 15]. One of the most important characteristics of the borided surface is to retain its hardness even after additional treatment. [16]

Boriding is widely used in various industrial sectors, such as the chemical industry, textiles, agriculture, mechanical industry and rail transport. It can be achieved by three ways: solid, liquid and gaseous [17 - 19].

Several boriding methods have been developed, that of powders is the most commonly used for its technical advantages, its ease of implementation, the possibility of changing the composition of the powder mixture and for its economic cost which is very low.

The process consists in packing the parts to be treated in a powder mixture and placed in a stainless-steel container [8, 13, 19 - 21].

The type of steel we have selected for the boriding treatment is X80 WCrV 18-04-01 or AISI T1 steel. It is a tool steel generally used for the manufacture of cutting tools such as milling cutters and saw blades. It can also be employed in wear resistance applications or in cold work tools. It should be noted that only one study was conducted on the boriding of this steel [18].

On the kinetic level, mathematical models have been used by several authors [2, 13, 18, 19, 22, 23, 24] to study the growth kinetics of boride layers. One of these approaches, the kinetic model developed by Campos et al. [22] to analyze the kinetics of boriding process. Their model required the knowledge of temperature, time and boron concentration. It is based on Fick's second law and the mass balance equations of the two corresponding growing interfaces (FeB/Fe_2B) and (Fe_2B/substrate) [22].

To verify the validity of this diffusion model, the thicknesses of the layers obtained at 1223 K for 1h and 8 h were compared with the experimental values.

In the present study, a recent kinetic approach called integral method has been successfully applied to the boriding kinetics of X80 WCrV 18-04-01 steel. We first calculated the boron diffusion coefficients through the bilayer ($FeB+Fe_2B$) at each boriding temperature using the integral method.

This model then made it possible to estimate the value of the activation energy for the boron diffusion in the Z80 WCrV 18-04-01 steel based on the experimental results [19].

THE INTEGRAL METHOD

This kinetic approach based on the integral method of Turkmen et al. [14] has been adapted to be applied to the growth kinetics of the bilayer ($FeB+Fe_2B$) formed on X80 WCrV 18-04-01 steel. This diffusion model has been successfully used to simulate the kinetics of the Fe_2B layer on different substrates [2, 14, 18, 19, 25, 26]. The boron concentration profile developed through the bilayer ($FeB + Fe_2B$) is schematically illustrated in Fig 1.

The boron concentration profile has a parabolic shape as sugested by Goodman [27]. During the boriding we noticed the presence of the two phases Fe_2B and FeB, this is why we considered the bilayer ($FeB + Fe_2B$) during the application of this present diffusion model. From Fig. 1, we have:

- C_{low}^{BL} represents the lower limit of boron content in Fe_2B. It is 8.83 % in mass percentage.
- C_{up}^{BL} denotes the upper limit of boron content in FeB. It is 16.40 % in mass percentage.
- u(t) designates the thickness of the layer at a given time.
- C_{ads} represents the adsorbed boron concentration in the boride layer during the boriding treatment.
- C_0 is the boron solubility in the matrix which is very low (≈0 wt.%).

We set the following initial conditions [2, 14, 19, 25]:

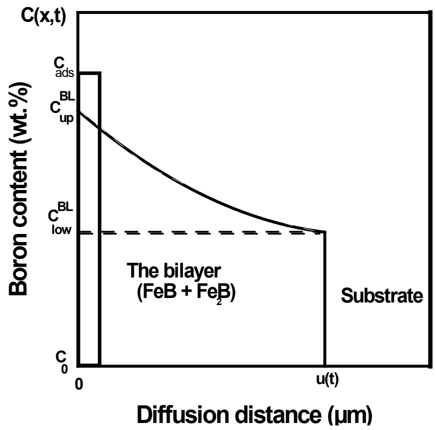

Fig. 1. Boron concentration profile through the bilayer ($FeB+Fe_2B$).

$$C(x, t = 0) = C_0 \approx 0 \text{ wt. \%} \quad (1)$$

The boundary conditions are :

$$C(x = 0, t = t_0) = C_{up}^{BL} \text{ for } C_{ads} > 8.83 \text{ wt. \%} \quad (2)$$

For the integral diffusion model [2, 14, 19, 25], the following system of algebraic- differential equations was considered for predicting the bilayer thickness:

$$a(t)u(t) + b(t)u(t)^2 = (C_{up}^{BL} - C_{low}^{BL}) \quad (3)$$

$$\frac{d}{dt}\left(\frac{a(t)}{2}u(t)^2 + \frac{b(t)}{3}u(t)^3\right) = 2Db(t)u(t) \quad (4)$$

$$2Wb(t) = a(t)^2 \quad (5)$$

with

$$W = \frac{(C_{up}^{BL} + C_{low}^{BL} - 2C_0)}{2}$$

To obtain the expression of the boron diffusion coefficients in the bilayer ($FeB+Fe_2B$) formed on the X80 WCrV 18-04-01 steel, an analytical solution exists for this diffusion problem by setting:

$$u = k_2^{'}\sqrt{t} \quad (6)$$

where $k_2^{'}$ is the parabolic growth constant of the considered interface.

By selecting adequate variables' change [2, 14, 19, 25], the expression giving the diffusion coefficient of boron through the bilayer ($FeB+Fe_2B$) formed on the X80 WCrV 18-04-01 steel is represented by equation (7):

$$D = \eta k_2^{'2} \quad (7)$$

with

$$\eta = \left(\frac{1}{16}\right)\left(\frac{C_{up}^{BL} + C_{low}^{BL}}{C_{up}^{BL} - C_{low}^{BL}}\right)\left(1 + \sqrt{1 + 4\left(\frac{C_{up}^{BL} - C_{low}^{BL}}{C_{up}^{BL} + C_{low}^{BL}}\right)}\right) + \left(\frac{1}{12}\right) \quad (8)$$

Finally, we get the numerical value of h equals 0.6.

Equation (9) provides the predicted value of entire boride layer thickness

$$u(t) = \sqrt{\frac{Dt}{\eta}} \quad (9)$$

EXPERIMENTAL

Material and boriding treatment

The substrate treated by powder boriding is the X80 WCrV 18-04-01 steel. Its chemical composition is (in wt. %): 0.81 C, 0.17 Mn, 0.23 Si, 0.019 S, 0.018 P, 0.08 Ni, 4.25 Cr, 0.09 Mo, 1.08 V, 17.60 W and 0.05 Co. The samples were placed in a hermetic cylindrical crucible made of AISI 304 stainless steel. It contains a mixture of powders consisting of 5 % B_4C, 5 % $NaBF_4$ and 90 % SiC. The boriding was carried out at 1223 K for 1 h, 2 h and 8 h. Once the treatment is complete, the crucible is removed from the furnace and slowly cooled to ambient temperature.

Experimental techniques for characterization

The microstructural observations of the cross-sections of borided samples of X80 WCrV 18-04-01 steel were carried out using an optical microscope. It should be noted that the observations were carried out on the cross-sections previously polished with an abrasive emery paper with increasing granulometry from 240 to 4000 and finished with a diamond solution of 9 and 3 μm.

The phases present in the boride layers formed on the surface of X80 WCrV 18-04-01 steel was verified by X-ray diffraction (XRD) applying a regular 2Θ-ω scanning procedure. An XPERT PRO analytical instrument was used with a copper anticathode whose radiation wavelength λ = 0.154 nm.

RESULTS AND DISCUSSION

Microscopic observations of boride layers

Fig. 2 shows optical micrographs of cross-sections of boride layers formed on X80 WCrV 18-04-01 steel at 950°C for 1 h, 2 h and 8 h. The obtained layers were of a biphasic nature with interfaces having a planar morphology. From Fig. 2, we could not distinguish FeB from Fe_2B but the further XRD analysis confirmed the occurrence of these two iron borides. The thickness of the total layer (Fe_2B+FeB) is between 13.23 ± 0.69 μm after 1 hour of treatment and 37.81 ± 1.78 μm for 8 hours. The morphology of the flat interfaces is due to the effect of the alloying elements present in this steel [28].

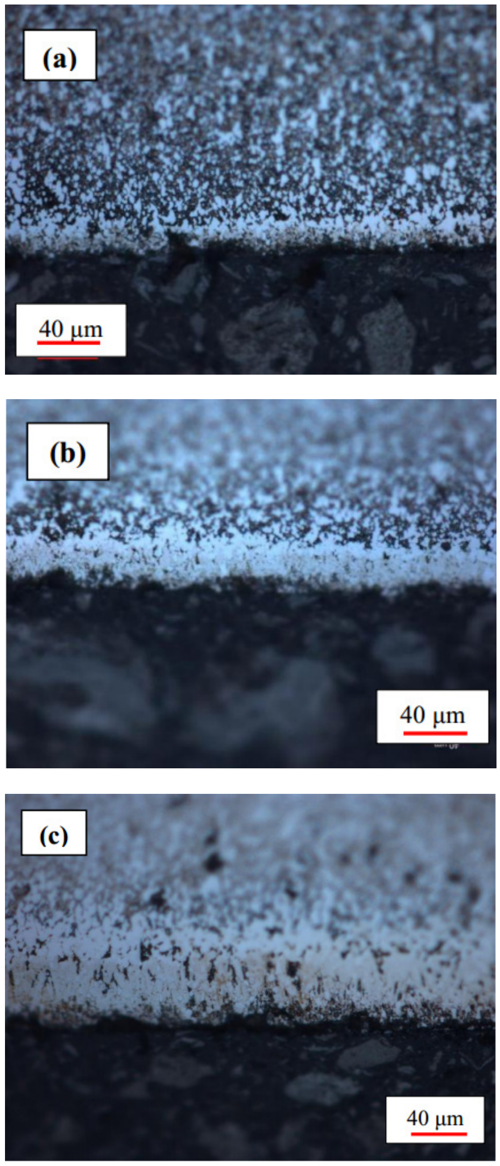

Fig. 2. Optical micrographs taken on the cross-sections of samples borided at: (a) 1 h, (b) 2 h and (c) 8 h.

Fig. 3 shows the evolution of the thickness of the entire boride layer as a function of the square of treatment time. It is noted that the kinetics of formation of the total layer (FeB+Fe_2B) obeys the parabolic growth law.

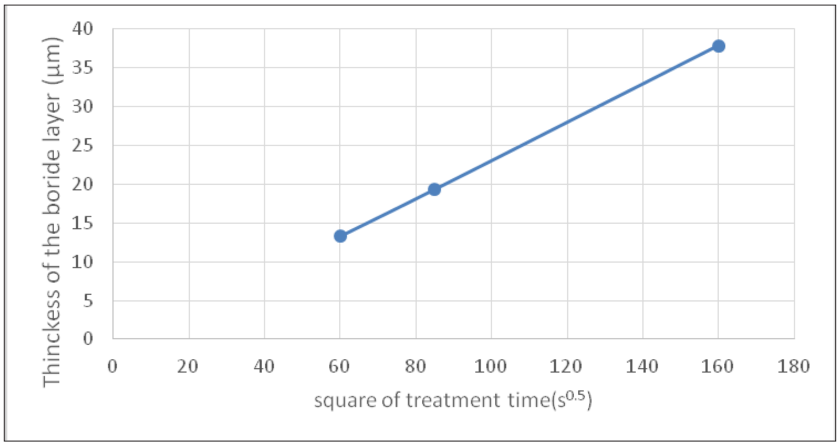

Fig. 3. Evolution of the thickness of the boride layer as a function of the square root of treatment time.

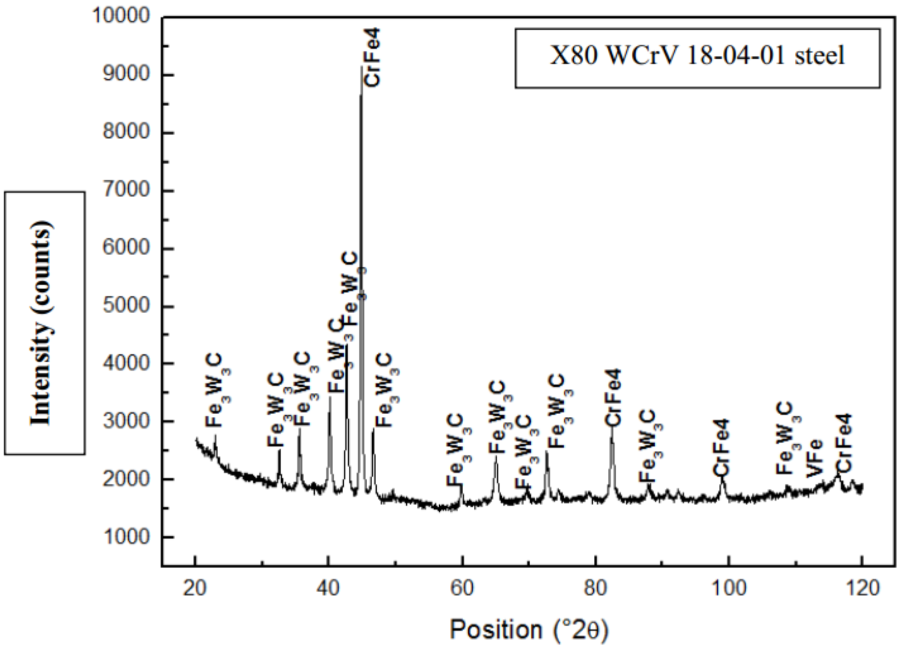

Fig. 4. X-ray diffraction diagram obtained on the surface of steel without boriding.

XRD analysis

Fig. 4 shows the X-ray diffraction patterns of the untreated steel. This diffractogram reveals the presence of a Fe_3W_3C tungsten carbide type. Fig. 5 gives the X-Ray diffraction spectra recorded on the surfaces of the borided samples at 950°C for 1 h, 2 h and 8 h. It reveals the presence of diffraction peaks of the two boride phases FeB and Fe_2B and those of the tungsten carbide Fe_3W_3C. In the present study, metal borides were probably not identified by XRD analysis due to their low volume fractions within the boride layer. In a study by Ozbek and Bindal, the following metal borides (CrB, MoB and Mo_2B) in addition to FeB and Fe_2B were identified in the pack-borided AISI M2 steel using Ekabor [29]. In another study by Campos et al. on the borided AISI M2 steel at 1273 K for 4h, they found out by XRD analysis that the boride layer is composed of FeB and Fe_2B with chromium boride CrB [30]. The AISI M2 steel was also borided by the paste method by Campos et al. at 1273 K for 6 h [30]. However, the chromium borides inside the boride layer were not identified in this case by XRD analysis. It can be seen that the XRD results reported on

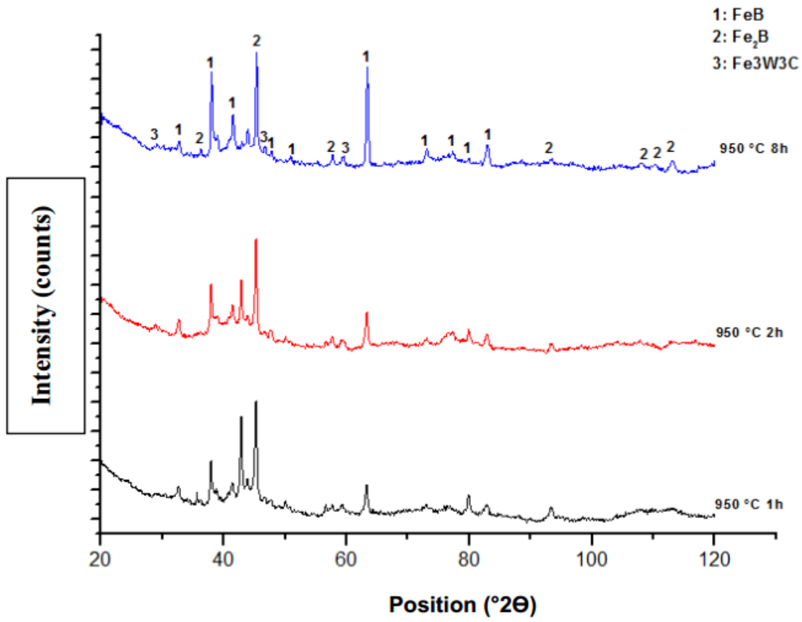

Fig. 5. X-ray diffraction diagram obtained on the surface of boronized steels for 1 h, 2 h and 8 h.

these borided tool steels are not always consistent with the literature data [29, 30].

Estimation of boron coefficient of diffusion

The integral method was used to determine the values of the boron diffusion coefficients in the bilayer ($FeB+Fe_2B$) on the X80 WCrV 18-04-01 steel. The experimental parabolic growth constants k_2' at the ($FeB+Fe_2B$/substrate) interface for the X80 WCrV 18-04-01 steel were derived from the experimental results [18] by adjusting our experimental parabolic growth constant obtained at 950°C with their results [18]. Durborid B_4C was used as a boriding agent in the temperature range of 1123 K to 1273 K with a holding time of 1 h to 8 h. To guarantee the precision of the measurements of the layer thicknesses, an average of eighty measurements was carried out on the different locations of the cross-sections of the borided specimens.

To be able to calculate the boron diffusion coefficients through the entire boride layer for X80 WCrV 18-04-01 steel, it is necessary to determine the experimental value of k_2' obtained at 950°C from our experimental data. The measured entire boride layer thickness was 19.25 µm at 950°C for 2 h. In this case, the k_2' value was determined as 0.2268 µm/s $^{0.5}$ at 950°C (1223 K). The experimental parabolic growth constants obtained on the pack-borided AISI T1 steel [18] were adjusted for our case to estimate the corresponding k_2' values for other temperatures (1123 K, 1173 K and 1273 K) not considered in the present study.

Table 1 contains the determined values of parabolic growth constants k_2' for the X80 WCrV 18-04-01 steel. Table 2 provides the calculated boron diffusion coefficients in the total boride layers for the X80 WCrV 18-04-01 steel by using the integral method on the basis of equation (7).

Determination of activation energy

Using Arrhenius law, we can determine the activation energy Q and the pre-exponential factor D_0. Fig. 6 shows the Arrhenius relationship between the boron diffusion coefficient and the process temperature using the data

Table 1. Mathematically determined values of the parabolic growth constants adjusted according to our case.

Temperature (K)	k_2'(µm/s$^{0.5}$)
1123	0.0892
1173	0.1452
1223	0.2268
1273	0.3421

Table 2. Estimated values of boron diffusion coefficients across the total layer ($FeB+Fe_2B$).

Temperature (K)	$D \times 10^{-14}$ m ^{2} s $^{-1}$ by using Eq. (7)
1123	0.47
1173	1.26
1223	3.08
1273	7.01

Table 3. Experimental values of the thicknesses of the boride layers and the values estimated by the integral method at 1223 K for different times of treatment.

Time (h)	Experimental thickness (μm)	Simulated thickness (μm using Eq. (9)
1	13.23 ± 0.69	13.60
2	19.25 ± 1.10	19.24
8	37.81 ± 1.78	38.48

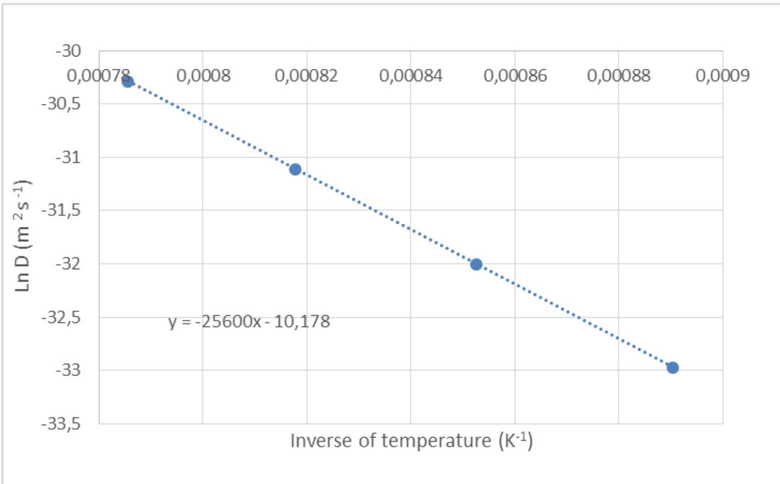

Fig. 6. Arrhenius relationship between the boron diffusion coefficient and the process temperature.

of Table 2. By searching for the slope of Fig. 6, the Q value was deduced to be equal to 212.83 kJ mol^{-1} with a pre-exponential factor D_0= 3.79 x 10^{-5} m^2 s^{-1}. It can be noticed that the obtained Q value from the present study is close to the result found by Ortiz-Dominguez [18] (= 212.76 kJ mol^{-1}) with a difference in the value of pre-exponential factor which is equal to D_0= 1.09 x 10^{-2} m^2 s^{-1} due to the difference in the kinetics of boron diffusion for the X80 WCrV 18-04-01 steel.

Experimental validation of the diffusion model

The total layer thickness ($FeB + Fe_2B$) grown at the surface of the X80 WCrV 18-04-01 steel can be simulated by employing equation (9). From Table 3 it is noted that the predicted values of the thicknesses of the boride layers are in agreement with our experimental results. This present model has been judged capable of simulating the thicknesses of the boride layers obtained at 950°C for 1 h, 2 h and 8 h. As limitation, the present approach did not consider the interaction of boron with carbon during its diffusion at atomic level though the material surface.

CONCLUSIONS

In the present work, the X80 WCrV 18-04-01 steel was hardened by a powder boriding treatment carried out at 950°C with an exposure time of 1, 2 and 8 h.

The kinetics of formation of the total layer ($FeB+Fe_2B$) obtained at 950°C obeyed the parabolic growth law.

A simple equation was used for the experimental validation of the diffusion model. To verify the validity of this model, a comparison was made between the experimental thicknesses of the layers ($FeB+Fe_2B$) and the predicted values for samples borided at 1223 K for 1, 2 and 8 h. A satisfactory agreement was observed when comparing the experimental values of the total layer thicknesses ($FeB+Fe_2B$) with the predicted results.

In addition, the diffusion coefficients of boron in the bilayer ($FeB+ Fe_2B$) were also calculated. As a result, the activation energy value for boron diffusion in X80 WCrV 18-04-01 steel was estimated as 212.83 kJ mol^{-1} using an analytical solution of the integral method.

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