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ISSN 0543-5846
METABK 55(4) 671-674 (2016)
UDC – UDK 669.781.002.4:669.14.018:536.425.669.781:620.18.178.1 = 111

RESEARCH INTO BORIDE LAYERS GROWTH KINETICS ON C45 CARBON STEEL

Received – Primljeno: 2015-11-18
Accepted – Prihvaćeno: 2016-03-20
Original Scientific Paper – Izvorni znanstveni rad

This study focuses on evaluation of borides formed on C45 steel. Pack boronizing is carried out at a temperature range of 870 – 970 °C in durations of 4 to 8 h. Values of frequency factor ($4{,}51 \cdot 10^{-4}$ $m^2 \cdot s^{-1}$) and activation energy ($199{,}63$ $kJ \cdot mol^{-1}$) are determined by means of Arrhenius equation. Analysis is also performed to assess the change in volume share of boride phase and the surface microhardness in the layer cross section. Results indicated that cross sectional changes of volume share of boride phase depends on boronizing temperature and duration. In addition, empirical expression showing functional relationship between them has been obtained.

Key words: boronizing, carbon steel, boride phase, structure, hardness

INTRODUCTION

Boronizing is a thermo-diffusion treatment carried out in order to improve surface properties of treated parts. Obtained surface layer is extremely hard and it improves resistance to abrasive and adhesive wear, corrosion in non-oxidizing weak acids, alkalis and molten metals [1]. Boronizing of carbon steels is usually carried out at temperatures of 800 – 1 050 °C and in treatment durations of 1 to 12 h. Obtained layer may consist of one phase (Fe_2B) or can be dual-phased (FeB + Fe_2B). Although FeB is harder (1 800 – 2 100 HV) than Fe_2B (1 400 – 1 600 HV), it is not desirable because of its brittleness [2 – 5]. The main objective of the present study is to investigate boronizing kinetics on C45 steel, as well as cross sectional changes of volume share of boride phase and hardness of the obtained layers.

EXPERIMENTAL INVESTIGATIONS

The C45 carbon steel is used in the presented study. Pack boronizing is carried out in Durborid 3 solid agent at 870, 920 and 970 °C, for 4, 6 and 8 h. According to selected parameters, 3^2 factorial design with 3 repeats of each case is defined, and 27 specimens with dimensions Ø 16 x 7 mm are cut. After boronizing, all specimens are longitudinally cross-section cut and prepared for metallographic examinations (ground using up to 1 000 grit emery paper, alumina polished and etched with 3 % nital).

RESULTS AND DISCUSSION

Thickness of the boride layer

Borides formed on steel surface are compact and have characteristic saw-tooth morphology (Figure 1). Average boride layers thicknesses are determined by metallographic line method (Table 1).

Table 1 **Boride layer thickness / μm**

	t = 4 h	*t* = 6 h	*t* = 8 h
870 °C	72,7	86,0	94,3
920 °C	106,5	140,4	157,9
970 °C	164,7	211,3	212,5

Although boride layer thickens increases with the increase of boronizing duration and temperature, growth rate slows down with the increase in duration, which corresponds to earlier studies [1, 3, 6]. Since carbon does not dissolve in iron borides, it is suppressed under

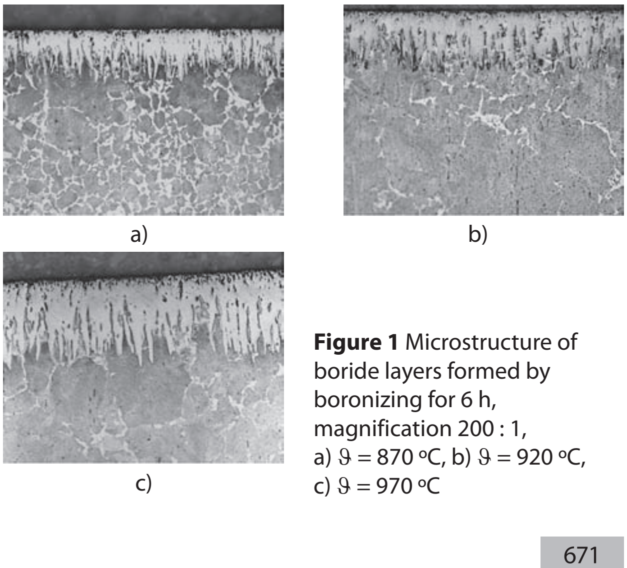
a)
b)
c)

Figure 1 Microstructure of boride layers formed by boronizing for 6 h, magnification 200 : 1, a) ϑ = 870 °C, b) ϑ = 920 °C, c) ϑ = 970 °C

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boride layer to create “carbon barrier” in diffusion zone, which slows down the growth of boride layer.

Kinetic studies

Growth kinetics of boride layer is analysed by using classic kinetic method based on Arrhenius equation (1), i.e. its modified version (2).

$$D = D_0 \cdot e^{-\frac{Q}{R \cdot T}} \qquad (1)$$

$$\ln D = \ln D_0 - \left(\frac{Q}{R}\right)\frac{1}{T} \qquad (2)$$

where T is temperature / K, D_0 is frequency factor / $m^2 \cdot s^{-1}$, Q is activation energy / $J \cdot mol^{-1}$, R is the gas constant / $J \cdot (mol \cdot K)^{-1}$. According to (2), there is a linear relationship between natural logarithm of growth rate constant and reciprocal diffusion temperature.

Diffusion process obeys parabolic law:

$$d^2 = D \cdot t \qquad (3)$$

where d is diffusion layer thickness / m, D is growth rate constant / $m^2 \cdot s^{-1}$, t is diffusion duration / s. Figure 2 shows the change in boride layer thickness with respect to boronizing duration for different temperatures.

Taking the square root of (3) results in:

$$d = \sqrt{D} \cdot \sqrt{t} \qquad (4)$$

Dependence between boride layer thickness and square root of boronizing duration is shown in Figure 3.

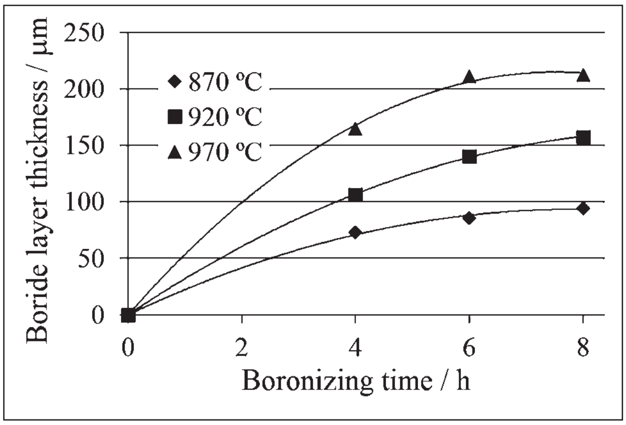

Figure 2 Boride layer thickness as a function of boronizing duration

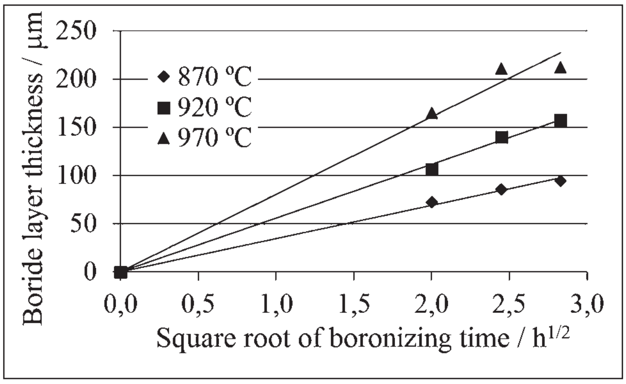

Figure 3 Boride layer thickness as a function of square root of boronizing duration

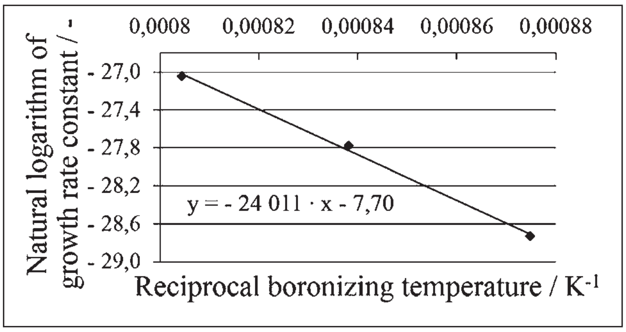

Figure 4 Natural logarithm of growth rate constant as a function of reciprocal boronizing temperature

Figure 2 and Figure 3 confirm diffusion nature of boronizing described with (3) and (4). The plot in Figure 3 reveals that thickness of diffusion layer linearly increases with square root of duration, which is in accordance to (4). The growth rate constants are estimated from slopes of straight lines in Figure 3. The growth rate constants are $3{,}33 \cdot 10^{-13}$, $8{,}64 \cdot 10^{-13}$ and $1{,}8 \cdot 10^{-12}$ $m^2 \cdot s^{-1}$ at temperatures 870, 920 and 970 °C, respectively. Figure 4 shows dependence between natural logarithm of growth rate constants and reciprocal values of boronizing temperatures.

It is evident from Figure 4 that boronizing follows Arrhenius equation (1), i.e. its modified version (2). According to (2), activation energy and frequency factor are estimated from the slope and y-intercept of the straight line in Figure 4. The frequency factor is $4{,}51 \cdot 10^{-4}$ $m^2 \cdot s^{-1}$ and the activation energy is 199 630 $J \cdot mol^{-1}$. If considering used equations and determined data, expression for boronizing of C45 steel in observed temperature range and duration is derived as follows:

$$d = \sqrt{4{,}51 \cdot 10^{-4} \cdot t \cdot e^{-\frac{199\ 630}{R \cdot T}}} \qquad (5)$$

Volume share of boride phase

Change of volume share of boride phase concerning cross section of the layer is estimated by the line method at every 20 μm (as in Figure 5). Volume share of boride phase is equal to the ratio of the sum of all line segments that pass through this phase and the total length of the line. Change of volume share of boride phase concerning cross section of the layer is shown in Figure 6.

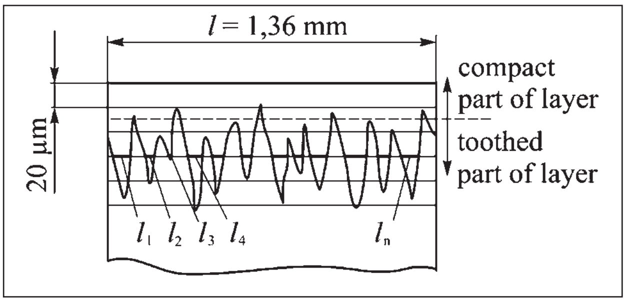

Figure 5 Determination of volume share of boride phase

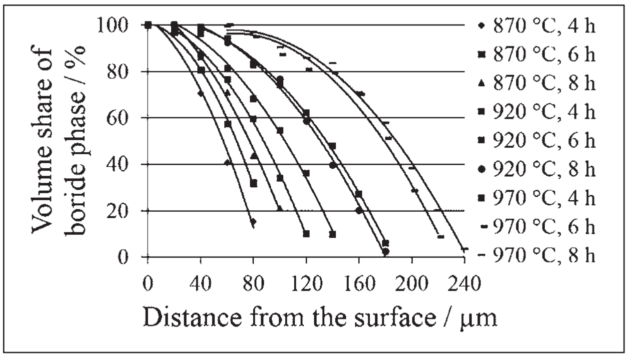

Figure 6 Change of volume share of boride phase

Mathematical model valid for boronizing of C45 steel in observed temperature range and duration is obtained by statistical methods:

$$V = -2572{,}43 + 5{,}60 \cdot \vartheta - 0{,}003 \cdot \vartheta^2 + 60{,}51 \cdot t - 1{,}25 \cdot t^2 - 9{,}31 \cdot l - 0{,}003 \cdot l^2 - 0{,}05 \cdot \vartheta t + 0{,}01 \cdot \vartheta \cdot l + 0{,}09 \cdot t \cdot l \qquad (6)$$

where V is volume share of boride phase / %, J is boronizing temperature / °C, t is boronizing duration / h, l is distance from the surface / µm.

Microhardness of boride layer

Cross sectional microhardness is estimated at every 20 mm by means of the Vickers method (HV 0,1). Fe_2B hardness varies in range from 1 463 to 1 646 HV 0,1 with average value of 1 549 HV0,1. Hardness of base material in diffusion zone (between teeth and just below boride layer) is higher than the hardness of the core, but hardness values decrease with increasing distance from the surface. This phenomenon is the result of increased carbon content due to its suppression under boride layer. The Table 2 presents the change of hardness of base material measured on specimen boronized at 920 °C for 6 h. Change of cross sectional surface hardness is determined on the basis of volume share of boride phase and base material, as well as measured hardness according to expression:

$$H_L = \nu_B \cdot H_B + (1 - \nu_B) \cdot H_{BM} \qquad (7)$$

where H_L is hardness of surface layer at observed depth, H_B is hardness Fe_2B, H_{BM} is hardness of base material at observed depth, n_B is volume share of Fe_2B at observed depth, $(1–n_B)$ is volume share of base material at observed depth. Average value of Fe_2B hardness (1 549 HV 0,1) is used as the hardness of the "hard" phase. Cross sectional surface hardnesses obtained according to (7) for specimen boronized at 920 °C for 6 h are given in Table 2.

Figure 7 shows typical appearance of hardness curve obtained on the basis of results according to (7). Surface layer consists of three areas. Area I is compact part of boride layer, characterized by a slight decrease in hardness and high hardness values due to large share of boride phase. Area II is "toothed" part of the layer characterized by an intense decrease of hardness, primarily due to reduced volume share of boride phase, but also due to decrease in hardness of base material in diffusion zone. Area III is base material

Table 2 **Change of cross sectional hardness for specimen boronized at 920 °C for 6 h**

Distance from the surface /µm	Microhardness / HV 0,1	
Base material		Surface layer
20	-	1 549
40	950	1 526
60	827	1 414
80	640	1 258
100	427	1 038
120	330	769
140	257	383
160	231	231

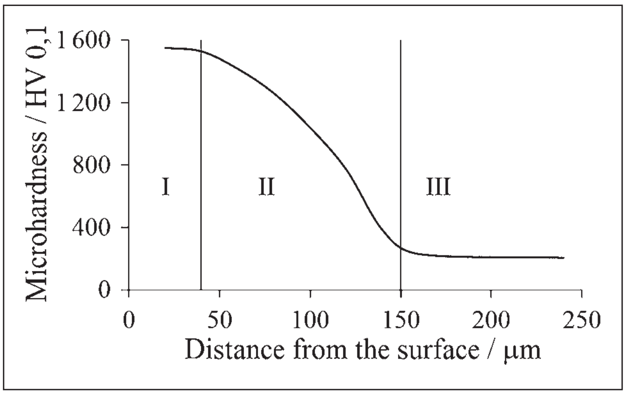

Figure 7 Typical appearance of hardness curve

CONCLUSION

Taking into account all results obtained in this study, the following conclusions are drawn:

Thickness of boride layer strongly depends on boronizing temperature and duration. Use of classic kinetic method based on Arrhenius equation has confirmed the diffusion nature of boronizing, and empirical expression for boronizing of C45 steel has been obtained. This expression is convenient for technological and industrial application.

Variation of boronizing parameters influence on volume share of boride phase and mathematical model showing functional correlation between volume share, distance from the surface and boronizing temperature and duration has been obtained.

Microhardness of Fe_2B varies in range from 1 463 to 1 646 HV 0,1. Change of cross sectional surface hardness is determined on the basis of volume share of boride phase and measured hardness. Based on the microhardness, surface layer consists of three areas. Area I is compact part of boride layer. The best wear resistance is expected in this area due to high hardness and compactness of boride layer. Area II is "toothed" part of the layer. Compared to compact part of the layer, lower wear resistance can be expected in this part of layer. Area III is base material with lowest wear resistance.

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Note: Responsible person for the English translation is Martina Šuto, MA