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AN INVESTIGATION OF BORIDE LAYERS GROWTH KINETICS ON CARBON STEELS

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Original scientific paper

Kinetics of boride layers formation on C15 and C70W2 carbon steels has been investigated in this paper. Pack boronizing was carried out in temperature range 870 ÷ 970 °C with durations 4 ÷ 8 h. Average thickness of boride layers obtained on C15 steel ranges was from 69,9 to 239,2 μm, and on C70W2 steel from 60,6 to 181,2 μm. Microhardness of boride layers was estimated by means of Vickers HV 0,1 method. It was determined that hardness values of Fe_2B iron boride obtained on both steels were almost equal, and did not depend on temperature and duration of boronizing. Based on the average thickness of boride layers and through usage of classical kinetics method, values of activation energy and frequency factor were determined. Based on these values, practical empirical expressions for boronizing of C15 and C70W2, indicating the dependence of boride layer thickness on boronizing temperature and time, were derived.

Keywords: *activation energy, boride layer, boronizing, carbon steels, diffusion, kinetics*

Istraživanje kinetike rasta boridnih slojeva na nelegiranim čelicima

Izvorni znanstveni članak

U ovom radu analizirana je kinetika nastanka boridnih slojeva na nelegiranim C15 i C70W2 čelicima. Boriranje u krutom sredstvu provedeno je u temperaturnom intervalu 870 ÷ 970 °C u trajanju 4 ÷ 8 h. Prosječna debljina boridnih slojeva na čeliku C15 kreće se u intervalu 69,9 ÷ 239,2 μm, a na čeliku C70W2 u intervalu 60,6 ÷ 181,2 μm. Mikrotvrdoća boridnog sloja određena je Vickersovom metodom HV 0,1. Utvrđeno je da je tvrdoća željeznog borida Fe_2B približno jednaka za oba čelika i da ne ovisi o temperaturi i trajanju boriranja. Na osnovu prosječnih debljina boridnih slojeva i uz pomoć klasične metode za boriranje oba čelika određene su vrijednosti aktivacijske energije i faktora frekvencije. Na osnovu ovih vrijednosti za oba čelika dobiveni su praktični empirijski izrazi koji pokazuju ovisnost debljine boridnog sloja o temperaturi i trajanju boriranja.

Ključne riječi: *aktivacijska energija, boridni sloj, boriranje, nelegirani čelici, difuzija, kinetika*

1 Introduction

Tools and the majority of machine parts are commonly exposed to wear during their use. In such working conditions, surface properties are often most important for their reliable and long service life. In order to improve wear resistance, a number of surface hardening treatments are developed within surface engineering, and one of them is boronizing.

Boronizing is a thermo-diffusion process in which boron atoms, due to their small diameter and high mobility at elevated temperatures, diffuse into a metal surface and form intermetallic compounds with atoms of base metal. Resulting boride layer, which may consist of either single-phase or multi-phase borides, is extremely hard and increases abrasive wear resistance of the surface layer. Moreover, boronizing also improves resistance to adhesion wear and corrosion. All mentioned means that with proper selection of boronizing parameters and materials, machine parts lifetime can be extended 3 ÷ 10 times [1].

Although boronizing is most suitable for carbon and low alloyed steels, it can be also applied on Ni, Co, Ti, W and Mo based alloys and sintered hard materials [2-5]. Boronizing of carbon steels is usually carried out at temperatures 800 ÷ 1050 °C and treatment times 1 ÷ 12 h [3-6]. Obtained surface layer, with characteristic saw-tooth morphology, may consist of one iron boride phase (Fe_2B) or can be dual-phased ($FeB+Fe_2B$). Although FeB is harder (1800 ÷ 2100 HV) than Fe_2B (1400 ÷ 1600 HV), it is considered as undesirable due to its brittleness. Furthermore, since FeB and Fe_2B borides have different coefficients of thermal expansion, crack formation on FeB / Fe_2B interface can often be observed [1, 7, 8]. When high loads are applied, presence of these cracks and high internal stresses can often lead to spalling.

Boronizing can be carried out in solid, liquid or gaseous media, and the most frequently used is pack boronizing.

Many of process parameters (i.e. boronizing temperature and time, boron potential, substrate material) affect boronizing. In order to obtain desired properties of boride layer, very important is to establish the process parameters that affect boronizing. The main objective of the present study is to investigate boronizing kinetics on C15 and C70W2 steels during pack boronizing. In this paper, the influence of boronizing time, temperature and carbon content on the thickness and morphology of boride layers obtained on C15 and C70W2 steels is analyzed.

2 Experimental investigations

Two of carbon steels, C15 and C70W2, are used for this study, and their chemical composition is given in Tab. 1.

Table 1 Chemical composition of boronized steels, Wt. %

	C	Si	Mn	P	S	Cu
C15	0,17	0,24	0,38	0,023	0,005	0,04
C70W2	0,72	0,211	0,286	0,014	0,017	-

In order to ensure the same diffusion mechanism (diffusion in austenite) for both steels, boronizing process is carried out at 870, 920 and 970 °C for durations of 4, 6 and 8 h. According to selected parameters, 3^2 factorial design with 3 repeating of each case is defined for both steels. 27 specimens with nominal dimensions ∅16 × 7 mm have been cut.

Before boronizing, the surfaces of specimens were cleaned and ground using 600 grid emery paper. Pack boronizing was carried out in Durborid 3 powder (solid medium for boronizing temperatures 800 ÷ 1000 °C) in electric furnace without protective atmospheres.

After boronizing, all specimens were longitudinally cross-section cut using electrical discharge machining and prepared for metallographic examinations (ground using 1000 grid emery paper, alumina polished and etched with 3 % nital). The morphology and types of borides formed on the surface of the treated steels were confirmed by means of optical microscopy and scanning electron microscopy (SEM). Average boride layers thicknesses were determined using metallographic line method (shown in Fig. 1) and digital Leica MW software [9, 10].

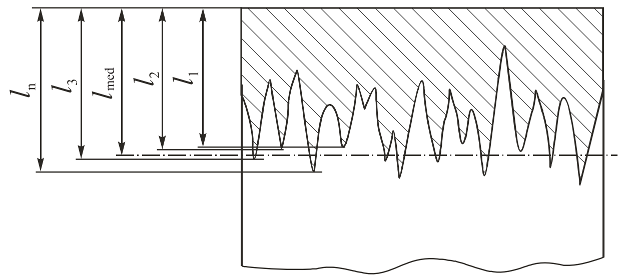


Figure 1 Determination of boride layer thickness [5]

The microhardness of boride layers was measured using a Vickers microhardness tester under test load of 0,981 N (HV 0,1).

3 Results and discussion

3.1 Boride layer properties

Optical microscopy and SEM examinations revealed that borides formed on both steels are compact and porosity free and have characteristic saw-tooth morphology, but toothness is more pronounced on C15 steel. Since carbon practically does not dissolve in iron borides, it will be suppressed under boride layer, creating so-called "carbon barrier" in diffusion zone. Increased carbon content in diffusion zone reduces not only thickness of boride layer, but also its toothness. This is in accordance with previous studies and knowledge that saw-tooth morphology is less pronounced on steels with higher content of alloying elements, or in the case of carbon steels, with higher carbon content. By boronizing high carbon steels, boride layers tend to be flat and poorly adherent to base metal [3-5, 11, 12].

Higher share of pearlite, apparent in diffusion zone, was created due to increased content of carbon suppressed from the surface inward.

In case of C15 steel, it can be observed that at lower boronizing temperatures and times, borides grow in a more columnar nature. Increasing the time and temperature, saw-tooth morphology is less pronounced. Although this phenomenon is not so obvious on C70W2 steel, it is possible to claim that saw-tooth morphology depends not only on chemical composition of treated steel, but also on boronizing temperature and time.

Microstructure of specimens boronized at higher temperatures (920 °C and 970 °C) indicates the presence of another phase in boride layer. Since XRD was not conducted, it cannot be held for certain which phase is present, but its morphology indicates FeB phase.

Microhardness of Fe_2B iron boride has been estimated by means of the Vickers method. Average values of measured hardness are given in Tab. 2. The results indicate that, in the case of carbon steels, the boronizing temperature and time do not significantly affect Fe_2B hardness.

The boride layer thicknesses, given in Tab. 3, are calculated as a mean of 20 measurements conducted on each sample according to design of experiment (3 samples for each of the boronizing times and temperatures).

Tab. 3 clearly shows that boride layer thickness increases with increasing boronizing time and temperature. It can also be seen, that boride layers formed on C15 steel are thicker than those on C70W2 steel, which is in accordance with previous statement that increased carbon content reduces thickness of boride layer.

3.2 Kinetic studies

In this paper, boride layer growth kinetics is analyzed taking into account classical kinetic method based on Arrhenius equation [2, 7, 8, 11, 13, 14]. Most of diffusion process obeys parabolic law described by:

$$d^2 = D \cdot t, \tag{1}$$

where:
d – is diffusion layer thickness, m
D – is growth rate constant, m^2/s
t – is diffusion time, s.

It can be seen that the thickness of diffusion layer linearly increases with square root of time as follows:

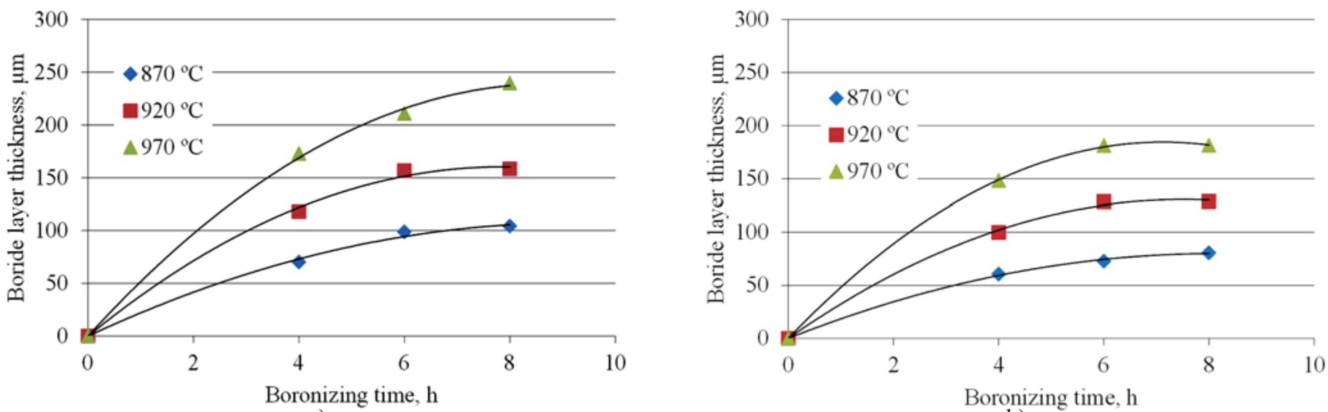
$$d = \sqrt{D} \cdot \sqrt{t}. \tag{2}$$

Table 2 Microhardness of Fe_2B iron boride

Steel	Microhardness of Fe_2B, HV 0,1									
	ϑ = 870 °C			ϑ = 920 °C			ϑ = 970 °C			Average hardness
	t = 4 h	t = 6 h	t = 8 h	t = 4 h	t = 6 h	t = 8 h	t = 4 h	t = 6 h	t = 8 h	
C15	1527	1544	1479	1443	1562	1555	1545	1570	1645	1541
C70W2	1545	1555	1488	1538	1557	1565	1560	1601	1603	1557

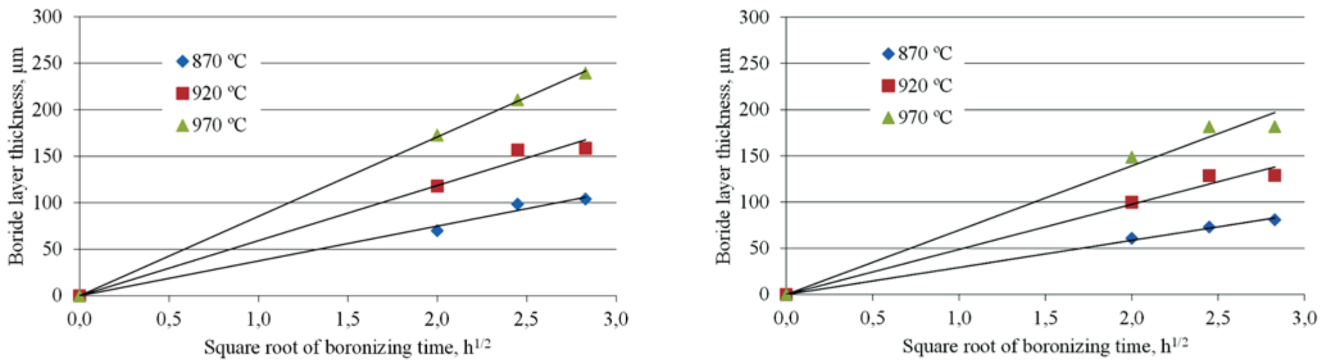
Table 3 Boride layer thickness

Steel	Boride layer thickness, μm								
	ϑ = 870 °C			ϑ = 920 °C			ϑ = 970 °C		
	t = 4 h	t = 6 h	t = 8 h	t = 4 h	t = 6 h	t = 8 h	t = 4 h	t = 6 h	t = 8 h
C15	69,9	98,4	103,9	117,9	156,7	158,3	172,7	210,6	239,2
C70W2	60,6	72,8	80,6	99,7	128,5	128,9	148,2	181,0	1181,2



a) b)

Figure 2 Boride layer thicknesses as a function of boronizing time: a) C15 steel, b) C70W2 steel



a) b)

Figure 3 Boride layer thicknesses as a function of square root of boronizing time: a) C15 steel, b) C70W2 steel

Growth rate constant D depends on diffusion temperature and this relationship is expressed by an Arrhenius equation:

$$D = D_0 \cdot \mathrm{e}^{-\frac{Q}{RT}}, \tag{3}$$

where:
T – is temperature, K
D_0 – is frequency factor, m^2/s
Q – is activation energy, kJ/kmol
R – is the gas constant, kJ/(kmol·K).

Taking the natural logarithm of Eq. (3) it follows:

$$\ln D = \ln D_0 - \left(\frac{Q}{R}\right)\frac{1}{T}. \tag{4}$$

Eq. (4) reveals linear relationship between natural logarithm of growth rate constant and reciprocal diffusion temperature.

The change in boride layer thickness with respect to boronizing time for steel C15 is given in Fig. 2a and for steel C70W2 in Fig. 2b. Graphical representation in Fig. 2 shows that boride layer thickness increases with boronizing time and temperature.

The plot of boride layer thickness versus square root of boronizing time shown in Fig. 3a for C15 steel and Fig. 3b for C70W2 steel reveals linear relationship which is in accordance with Eq. (2).

The graphical representations in Fig. 2 and Fig. 3 also confirm that boronizing obeys parabolic law (1), that is, its modified version (2).

Growth rate constants for each temperature and for both steels estimated from slopes of straight lines in Fig. 3 are given in Tab. 4.

Table 4 Growth rate constants for boronizing of C15 and C70W2 steels

Temperature / °C	Growth rate constant D /m^2/s	
	C15	C70W2
870	$3,904 \times 10^{-13}$	$2,39 \times 10^{-13}$
920	$9,768 \times 10^{-13}$	$6,62 \times 10^{-13}$
970	$2,027 \times 10^{-12}$	$1,34 \times 10^{-12}$

The results given in Tab. 4 show that for both steels growth rate constant D increases with boronizing temperature. For each temperature, growth rate constant D is higher for steel C15 than for C70W2, which confirms that growth rate of boride layer controlled by boron diffusion decreases with increasing carbon content.

Relationship between natural logarithm of growth rate constants and reciprocal values of boronizing temperatures for boron diffusion in both steels is given in Fig. 4.

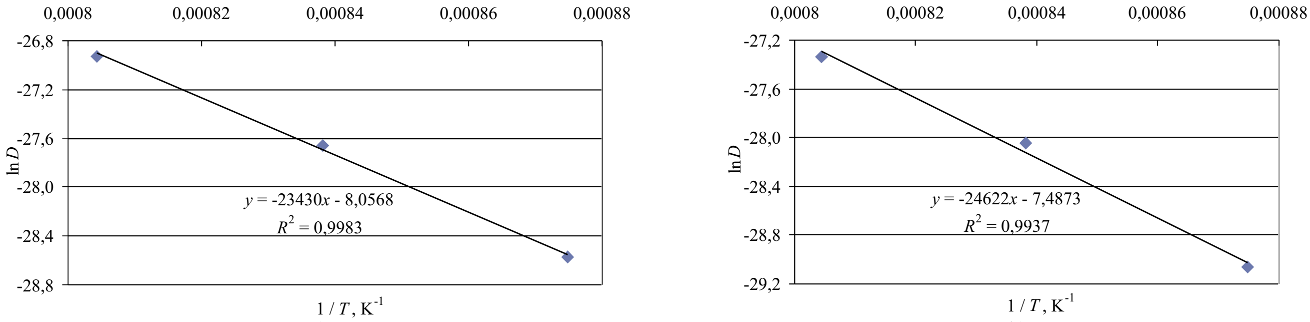
The plots in Fig. 4 reveal linear dependence and confirm that boronizing follows Arrhenius equation [2, 7, 8, 11, 13, 14].

Consequently, activation energy was determined from the slope of straight line and the frequency factor from intercept of the extrapolated straight lines and ordinate axis.

Frequency factor and activation energy for boronizing C15 and C70W2 steels are given in Tab. 5.

Table 5 Frequency factor D_0 and activation energy Q for boronizing C15 and C70W2 steels

Frequency factor D_0/m^2/s		Activation energy Q /kJ/kmol	
C15	C70W2	C15	C70W2
$3,17 \times 10^{-4}$	$5,6 \times 10^{-4}$	194,80	204,71



a) b)

Figure 4 Natural logarithm of growth rate constant as a function of reciprocal boronizing temperature: a) C15 steel, b) C70W2 steel

Frequency factor and activation energy values of boronized C70W2 steel are higher than values of boronized C15 steel. Activation energy affects growth rate constant, and consequently the boride layer thickness, more than frequency factor. Activation energy exponentially decreases growth rate constant, so this is the reason for thicker boride layers obtained on C15 steel, despite the lower values of frequency factor and activation energy.

Considering equations (1) and (3) and data given in Tab. 5, expression for boronizing of C15 steel is:

$$d = \sqrt{3{,}17 \cdot 10^{-4} \cdot t \cdot \mathrm{e}^{-\frac{194800}{R \cdot T}}}, \tag{5}$$

and for boronizing of steel C70W2:

$$d = \sqrt{5{,}6 \cdot 10^{-4} \cdot t \cdot \mathrm{e}^{-\frac{204710}{R \cdot T}}}. \tag{6}$$

Expressions (5) and (6) can be used either for:

- Prediction of boride layer thickness with respect to boronizing time and temperature
- Selection of boronizing time or temperature for obtaining desired boride layer thickness.

4 Conclusion

Taking into consideration all results of this study, the following conclusions can be established:

1) Boride layers formed on C15 and C70W2 steel are compact and porosity free, with pronounced saw-tooth morphology. Nevertheless, comparing saw-tooth morphology, it is obvious that boride layers obtained on C70W2 steel are smoother than on C15 steel. Taking this into account, it is possible to say that increased carbon content acts in the way to reduce characteristic toothness of boride layer, which is in good agreement with earlier studies.
2) Microhardness of Fe_2B iron boride obtained on C15 steel varies in the range of 1443 ÷ 1645 HV 0,1, and for the Fe_2B iron boride obtained on C70W2 steel in the range of 1488 ÷ 1603 HV 0,1. Almost equal hardness values indicate that, in the case of carbon steels, boronizing temperature and time do not affect significantly the Fe_2B hardness.
3) The thickness of boride layer strongly depends not only on boronizing temperature and time, but also on carbon content. Increase of boronizing temperature and time increases boride layer thickness, while increase of carbon content acts in the opposite way.
4) The use of classical kinetic method based on Arrhenius equation has confirmed the diffusion nature of boronizing. Frequency factor and activation energy values for both steels have been established. These values are higher for boronizing of C70W2 steel, than for boronizing of C15.
5) Empirical expressions for boronizing of C15 and C70W2 steel have been derived from classical kinetic equations. These expressions are convenient for technological and industrial application, and could be used for estimation of boride layer thickness in dependence on boronizing parameters (temperature and time).

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