

## TEMPERATURE BEHAVIOUR OF THE BORIDE LAYER OF A LOW-CARBON MICROALLOYED STEEL

### TEMPERATURNO VEDENJE BORIDNEGA SLOJA NA MALOGLJIČNEM MIKROLEGIRANEM JEKLU

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In this work, the boronizing of low-carbon microalloyed steels was carried out in a solid medium using the powder-pack method. After boronizing, a boride layer and the presence of both FeB and Fe<sub>2</sub>B phases in the boride layer were revealed with classic metallographic techniques and X-ray diffraction (XRD) analysis. The presence and distribution of alloying elements on the boride phases was measured using glow-discharge optical emission spectrometry (GDOES) and the distance between the surface and the substrate was taken as the layer thickness. It was found that higher boronizing temperatures resulted in an increase in the layer thickness, from 7 μm to 105 μm. In addition, microhardness tests of the boronized steel samples showed a significant increase in the surface hardness caused by the increased boronizing temperature. The boride layer had a hardness of over 910 HV<sub>0.1</sub> and 1320 HV<sub>0.1</sub> for 973 K and 1273 K, respectively, while the substrate's hardness was approximately 145 HV<sub>0.1</sub>. Kinetic studies showed that the diffusion process is thermally activated, with the mean value of the activation energy being close to 194 kJ/mol.

Keywords: low-carbon microalloyed steel, microhardness, boronizing, activation energy

To delo obravnava boriranje maloogljičnega mikrolegiranega jekla v trdnem mediju z uporabo metode zasutja v prah. Po boriranju je bila v boridnem sloju odkrita prisotnost FeB in Fe<sub>2</sub>B s klasično metalografijo in z rentgensko difrakcijsko (XRD) analizo. Po drugi strani pa je bila izmerjena prisotnost in razporeditev legiranih elementov v boridni fazi z oblačno razelektrivno optično emisijsko spektrometrijo (GDOES) in razdalja od površine do podlage pomeni debelino plasti. Ugotovljeno je bilo, da višanje temperature boriranja poveča debelino sloja od 7 μm do 105 μm. Dodatno so preizkusi mikrotrdote boriranih vzorcev jekla pokazali občutno povečanje trdote površine boriranih vzorcev s povišanjem temperature boriranja. Boridni sloj je imel trdoto več kot 910 HV<sub>0.1</sub> in več kot 1320 HV<sub>0.1</sub> pri 973 K oziroma 1273 K, medtem ko je bila trdota podlage okrog 145 HV<sub>0.1</sub>. Študij kinetike je pokazal, da je difuzijski proces toplotno aktiviran, povprečna vrednost aktivacijske energije pa je bila blizu 194 kJ/mol.

Ključne besede: maloogljično mikrolegirano jeklo, mikrotrdota, boriranje, aktivacijska energija

## 1 INTRODUCTION

Low-carbon microalloyed steels are widely used in mechanical engineering, particularly in pressure vessels and pipelines transporting oil and natural gas, due to their high strength, good toughness and weldability<sup>1</sup>. In considering engineering materials, up to now numerous studies have been carried out relating to microstructural and mechanical properties. As a result, it has been shown that the mechanical properties of engineering materials largely depend on the modifications made by case hardening or coating<sup>2</sup>. Thus, new studies have focused on surface treatments such as boronizing, chromium coating and ion implantation. Boronizing is a thermochemical surface-hardening treatment similar to carburization, which enriches the steel surface with boron so that boron atoms diffuse into the surface of the material at high temperatures<sup>3</sup>. In reference<sup>4</sup> it is indicated that the surface hardness of the resulting boride layer can exceed 2000 HV, providing a good resistance to abrasive and adhesive wears. However, the main disadvantage of boronizing is the embrittlement of the boronized layers. One of the methods to overcome this shortcoming is

forming a single Fe<sub>2</sub>B phase on the metal surface through the proper choice of boronizing parameters<sup>5</sup>. On the other hand, it has been shown that alloying elements such as carbon, silicon, nickel, chromium, and manganese also affect the morphology, thickness, and the nature of the boride layers consisting of either FeB or Fe<sub>2</sub>B or sometimes both, which are formed in the iron-based alloys<sup>4,6,7</sup>. In relation to this, Li et al.<sup>8</sup> showed that the thickness of a boride layer parabolically increases with time and that its thickness value is in the range of 8–33 μm. In this study it has been found that the process temperature plays a much more important role in the layer-thickness increase than the treatment duration, as the boride layers formed at 950 °C show a greater thickness than at 900 °C. This behavior has been explained with the increased diffusion and accelerated formation of the boride layer. Thus, it can be said that the characteristics of a boride layer depend on the physical state of the boronizing source used, the boronizing temperature, the treatment time, and the properties of the boronized material<sup>9–11</sup>.

It is of great importance to establish the process parameters that affect the boronizing kinetics in order to

control automated procedures and to obtain optimal properties<sup>12</sup>. Despite the significance of the boronizing process in the industry, little is known in the literature about the modeling of the layer-growth kinetics. Therefore, the purpose of this study is to investigate the microstructural properties and diffusion mechanisms in the boride layer that was formed in a solid medium using the powder-pack method at several treatment temperatures.

## 2 EXPERIMENTAL METHOD

The chemical compositions of the test materials are listed in **Table 1**. The samples were cut in the dimension of 3 mm × 3 mm × 20 mm. The boronizing of the low-carbon microalloyed steels was achieved in a solid medium using the powder-pack method. In this method, a commercial Ekabor-II boron source and an activator (ferro-silicon) were thoroughly mixed to form the boriding medium. The samples were boronized in an electrical resistance furnace in the temperature range of 973–1273 K for 4 h. After the boronizing treatment, the samples were removed from the furnace, cooled in air, sectioned from one side, grinded up to 1200-grid emery paper, and polished using 3 μm alumina pastes. The polished samples were then dried and metallographically etched with a 4 % Nital solution. The presence of borides on the surface of the boronized low-carbon microalloyed steel was determined by using an X-ray diffractometer (Rigaku D-MAX 2200) with a Cu-K $\alpha$  radiation with the wavelength of 0.15418 nm. Metallographic sections were prepared to observe morphological details by using optical microscopy and scanning electron microscopy (SEM JOEL 5600LV). To determine the hardness of the low-carbon microalloyed steel, a Vickers microhardness tester with a load of 100 g was used. Many indentations were made on each coating film

under each experimental condition to check the reproducibility of hardness data.

**Table 1:** Chemical composition of the low-carbon microalloyed steel in mass fractions, w/%

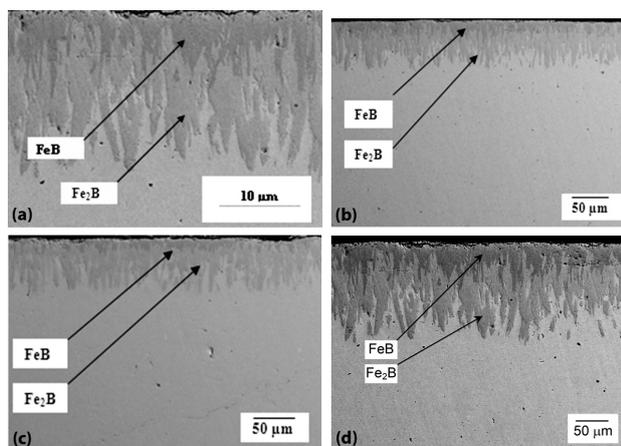
**Tabela 1:** Kemijska sestava maloogljivega mikrolegiranega jekla v masnih deležih, w/%

C	Si	Mn	P	Mo	Mg	Cr	Al	Nb	Fe
0.044	0.353	1.345	0.011	0.023	0.010	0.010	0.030	0.030	Bal.

## 3 RESULTS AND DISCUSSION

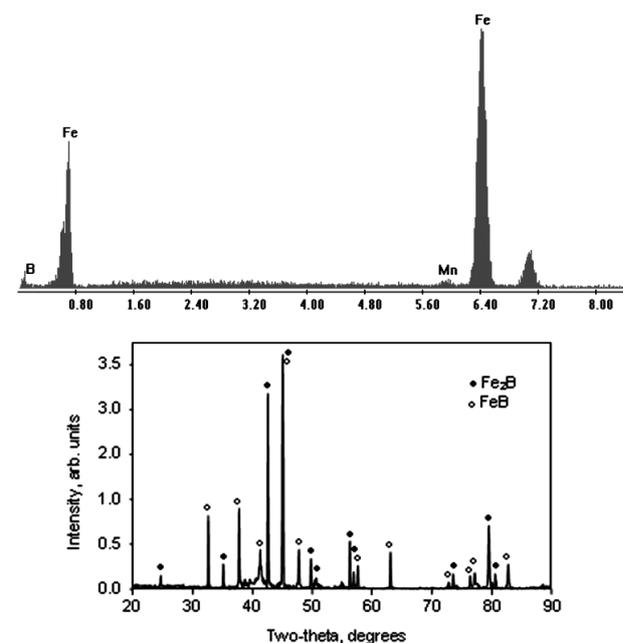
### 3.1 Microstructure

As seen in **Figures 1a-d**, SEM examinations reveal that borides formed on the surface of low-carbon microalloyed steels have a columnar morphology. Moreover, three distinct regions were identified on the surface of steels: (i) the boride layer, (ii) the transition zone and (iii) the matrix. In many studies, it has been shown that the surface-boronizing treatment can form FeB and Fe<sub>2</sub>B layers on the surface of a steel substrate. For a double-phase boride layer, the near surface is the FeB phase and the Fe<sub>2</sub>B phase is between the FeB layer and the substrate<sup>13</sup>. This morphology is a characteristics property of the boride layer in steels and depends on the concentration of alloying elements as well as on the treatment temperature and time<sup>14</sup>. In the present study, borides were identified via the X-ray diffraction (XRD) and energy-dispersive X-ray analysis (EDS). The obtained figures indicate the presence of the two elements: B and Fe (**Figure 2**). In the XRD figure, the peaks relative to



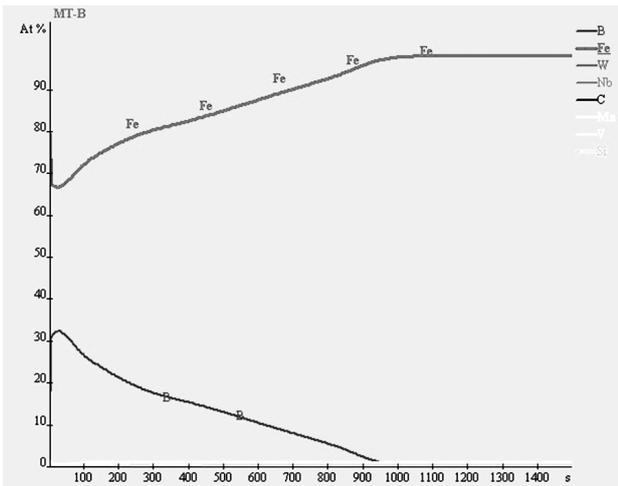
**Figure 1:** SEM images of the cross-sections of low-carbon microalloyed steels boronized for 4 h at: a) 973 K, b) 1073 K, c) 1173 K, and d) 1273 K

**Slika 1:** SEM-posnetek prereza maloogljivega mikrolegiranega jekla, boriranega 4 h pri: a) 973 K, b) 1073 K, c) 1173 K in d) 1273 K



**Figure 2:** a) EDS and b) XRD patterns of low-carbon microalloyed steels boronized at 1173 K for 4 h

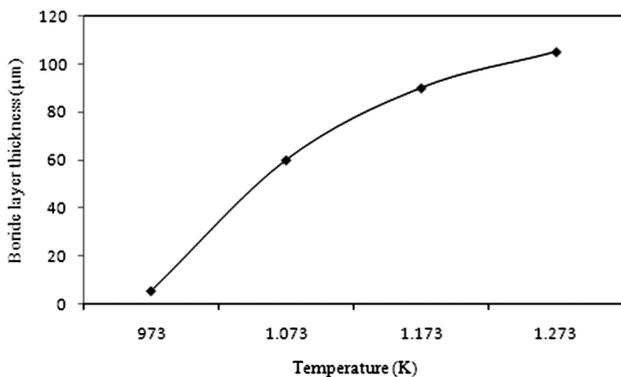
**Slika 2:** a) EDS- in b) XRD-posnetek maloogljivega mikrolegiranega jekla, boriranega 4 h pri 1173 K



**Figure 3:** GDOES profiles of low-carbon microalloyed steels boronized at 1173 K for 4 h

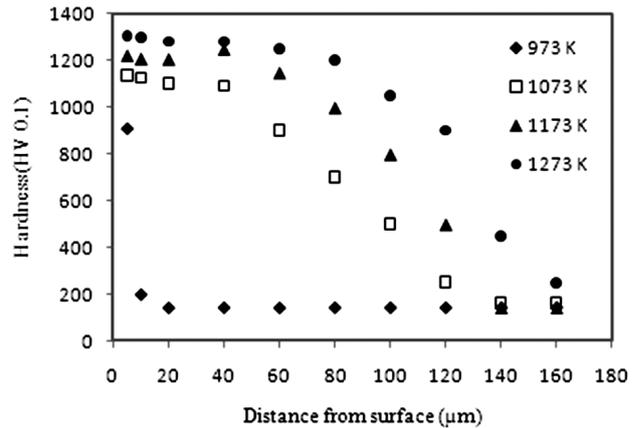
**Slika 3:** GDOES-profil skozi borirano plast po 4-urnem boriranju na 1173 K

the two iron borides, FeB and Fe<sub>2</sub>B, were easily detected. On the other hand, **Figure 3** shows the B and Fe concentrations measured with the glow-discharge optical emission spectrometry (GDOES) technique as a function of the sputtering time. This figure shows that although the concentration of the alloy elements such as W, Nb, C, Mn, Si and V remains constant below the surface, the boron concentration is high at the surface but decreases gradually by about the mole fraction 33 % between the surface and the transition region. This profile exhibits a diffusion-type distribution. This indicates that the iron boride was formed during the boronizing process. As indicated above, the relative concentration of boron should be high at the surface and it then decreases with distance. This behavior is a typical characteristic of a thermochemical treatment such as boronizing<sup>12</sup>. **Figure 4** shows a graphical representation of the variation of a boride layer thickness with temperature obtained from optical and SEM photographs; it was observed that the



**Figure 4:** Boride layer thickness as a function of temperature of low-carbon microalloyed steels boronized for 4 h

**Slika 4:** Debelina plasti borida kot funkcija temperature boriranja maloogljirnega mikrolegiranega jekla



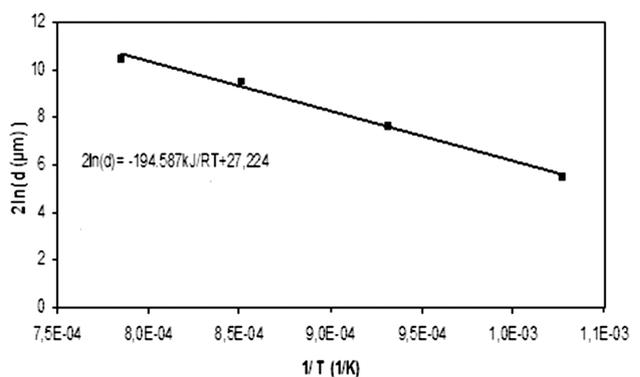
**Figure 5:** Microhardness profiles of low-carbon microalloyed steels boronized at different temperatures for 4 h

**Slika 5:** Profil mikrotvrdote po 4 h boriranja maloogljirnega mikrolegiranega jekla pri različnih temperaturah

thickness of the boride layer increases with increasing temperature. In the literature it has been pointed out that the thickness of a boride layer depends strongly on the boronizing time, the chemical composition of the material to be boronized, the process temperature, and the techniques used, such as gas, liquid and pack boronizing<sup>8-11,15</sup>. In the present study the chemical composition of the material to be boronized, the process time and the technique are fixed, the only parameter that changes is the boronizing temperature. Thus, we say that the boride layer thickness increases when the boronizing temperature is increased due to the diffusion of boron atoms.

### 3.2 Microhardness

The microhardness measurements were carried out on the cross-sections from the surface to the interior as a function of depth and temperature. The microhardness profiles, plotted as a function of both depth and temperature for the boronized low-carbon microalloyed steels during the 4-hour treatment are displayed in **Figure 5**. From this figure we can see that the microhardness



**Figure 6:** Reciprocal temperature dependence of the boride layer thicknesses formed on low-carbon microalloyed steels after 4 h

**Slika 6:** Odvisnost debeline boridnega sloja, nastalega na maloogljirnem jeklu po 4 h, od recipročne vrednosti temperature

profile of the boronized low-carbon microalloyed steels varies with processing. The surface hardness reaches the maximum values of 1320 HV<sub>0.1</sub> and 910 HV<sub>0.1</sub> for the temperatures of 1273 K and 973 K, respectively. The hardness of the transition layer ranges from 500 HV<sub>0.1</sub> to 600 HV<sub>0.1</sub> as a function of temperature. A higher hardness in the transition layer is due to the solid-solution hardening between Fe, B and Mn. In addition, the matrix that is not affected by the treatment has its hardness close to 145 HV<sub>0.1</sub>. To sum up, the hardness measurements carried out by means of the Vickers indentations from the surface to the interior of the specimen showed that the hardness of the boride layer is much higher than that of the matrix (**Figure 5**). This is a consequence of the presence of hard FeB and Fe<sub>2</sub>B phases as determined with different methods. In addition, the microhardness of the boride layer increases with the increased boronizing temperature due to the increasing rate of boron diffusion.

### 3.3 Evaluation of the activation energy of boron diffusion

To examine the activation energy, the relation between the boride layer thickness and the boronizing temperature is given by:<sup>14,16,17</sup>

$$d^2 = k_{\alpha} \cdot t \cdot \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

where  $d$  is the average thickness of the boride layer ( $\mu\text{m}$ ),  $k_{\alpha}$  is the pre-exponential constant (independent temperature), ( $\mu\text{m}^2/\text{s}$ ),  $t$  is the boronizing time (s),  $Q$  is the diffusion-activation energy (J/mol),  $R$  is the universal gas constant  $R = 8.314 \text{ J}/(\text{mol K})$ , and  $T$  is the boronizing temperature (K). Equation 1 can be rewritten as follows:

$$2 \ln(d) = \left(-\frac{Q}{RT}\right) + \ln(k_{\alpha} \cdot t) \quad (2)$$

The thicknesses of the boride layers formed on the low-carbon microalloyed steels were measured by means of optical microscopy and SEM. After fitting the logarithmic values of the average thickness of the boride layer as a function of inverse temperatures, the diffusion-activation energy can be defined from the slope (**Figure 6**). It is generally assumed that boron tends to segregate to the prior austenite grain boundaries, which has been confirmed in a number of investigations<sup>18–20</sup>. In reference<sup>21</sup>, it has been explained that boron is in an interstitial solution in  $\alpha$ -iron and the activation energy of the boron diffusion in  $\alpha$ -iron is 269 kJ mol<sup>-1</sup>. On the other hand, an investigation of the results of the diffusion of boron in low-carbon iron with an application of a high-sensitivity method of track autoradiography on polymetric detectors was conducted. It is shown that, in the body-centered cubic iron, the diffusive-boron mass transport is carried out by vacancy diffusion, while in the face-centered cubic iron this is done by interstitial

diffusion. The diffusion of boron in iron is accompanied by high-density dislocations. The solubility of boron in the low-dislocation-density iron is very small and its temperature dependence is slight<sup>22</sup>. In this study, the calculated activation energy for the formation of the boride layer on the surface of the low-carbon microalloyed steels was 194 kJ mol<sup>-1</sup>. The activation energy for the formation of the boride layer in low-carbon steels was found to be 172 kJ mol<sup>-1</sup>, 123 kJ mol<sup>-1</sup>, 129 kJ mol<sup>-1</sup> and 145 kJ mol<sup>-1</sup> for the electrochemical<sup>23</sup>, plasma-paste<sup>24</sup>, superplastic<sup>25</sup> and plasma-sintering boronizing<sup>26</sup>, respectively, which was lower than that measured in the present study for the powder-pack method. So, it is possible to claim that the diffusivity of B atoms in the boronized low-carbon steels obtained with the powder-pack method is lower than that of the electrochemical boronizing of the low-carbon steel because of the presence of alloying elements. In other words, it could be suggested that the formation of the boride layer during the powder-pack boronizing is more difficult to achieve than with the other boronizing methods such as electrochemical, plasma-paste, superplastic and plasma-sintering boronizing due to the diffusion of boron in the low-carbon microalloyed steels.

## 4 CONCLUSIONS

The following conclusions can be drawn:

- The microstructure of borided-steel surfaces showed three distinct regions: the boride layer, the transition zone and the matrix. The prominent phases formed in the surface layer of the boronized low-carbon microalloyed steels were Fe<sub>2</sub>B and FeB, which were revealed by XRD and EDS analyses.
- Depending on the process temperature, the boride layer thickness of the coating ranged between 7  $\mu\text{m}$  and 105  $\mu\text{m}$ . The increasing boronizing temperature resulted in a thicker boride layer.
- The hardness of the diffusion layer was found to be much higher than that of the matrix for boronized steels. On the other hand, the thickness of FeB increases with the temperature; this mainly happens because at a high temperature boron diffusion occurs fast, hence the hardness value measured on the surface is high due to a thicker formation of FeB.
- The aim of the present study was to estimate the boride layer thickness as a function of the process temperature, which can be useful in engineering applications. Kinetic studies showed a nearly parabolic relationship between the layer thickness and the process temperature, and the activation energy was 194 kJ/mol. This value is close to  $Q$  for the diffusion of boron in the bcc/fcc iron (ferrite/austenite).

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