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# The Influence of Industrial-Scale Pack-Boroding Process Time on Thickness and Phase Composition of Selected Cold-Work Tool Steels

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**The boride coatings are characterized by attractive set of properties such as high hardness and wear resistance, corrosion resistance in higher temperatures and no wettability by liquid metals like aluminum and zinc. This type of coating might be used for manufacturing of different parts from tool steels. In present article the influence of pack boriding time (2, 4, 6h) on microstructure and phase composition of obtained coatings is scrutinized. The pack boriding process was conducted on two groups of cold work tool steels: low-Cr content: 145Cr6, 90MnCrV8, 60WCrV8 and high-Cr content: X165CrV12, X153CrMoV12. The commercial boriding pack Ekabor 2 was utilized and the process was carried out using industrial CVD device (Bernex BPX Pro 325S). The conducted research showed that the boride coatings formed on the substrate of high-chromium steels were characterized by a lower total thickness. On low-chromium steels, FeB phase was discontinuous as an irregular islands located in the near-surface area. On the other hand, for high-chromium steels, a continuous layer of needle-like borides was formed.**

**Keywords:** boride coatings, pack boriding, FeB, $Fe_2B$, tool steel

## 1 Introduction

Steel is still the basic material used e.g. for tools. High carbon content, combined with a properly selected amount of alloying elements, allow for long-term operation in demanding conditions [1,2]. During the exploitation of tools, many phenomena occur, that cause their degradation: abrasive and adhesive wear, cracking, chipping [3,4]. Therefore, an extremely important issue is to increase the durability of tool steels, which reduces costs associated with their replacement or purchase. This is achieved by developing new grades of steel, sintered carbides and cermetals, or by appropriate modification of their surface layer [5]. There are many ways to improve materials properties through various surface engineering processes, such as: application of wear-resistant coatings and use of heat- and thermo-chemical treatment [6-8]. Diffusion boriding belongs to the last group. It allows to increase the hardness and wear resistance of tool steels surface layer [9-11].

During diffusion boriding, workpiece surface is enriched by diffusing boron atoms. After reaching appropriate concentration, $Fe_2B$ and FeB phases are formed. The process can be carried out in a variety of medium: liquid [12], gaseous [13,14], in fluidized bed [15] or solid [16] or in fluidized bed. There are many variants of this process [17-20], but due to its simplicity and low costs, pack boriding is the most commonly used [21,22]. Elements made of various types of steel are most frequently subjected to boriding at a temperature of 850 - 1000°C, for 1 - 10 h. Morphology of the resulting borided coatings depends on the carbon and alloying elements content in treated steel. On the substrate of low-alloy and low-carbon steels, two zones of needle-like structures are formed: external FeB and internal $Fe_2B$ [23,24]. Increased carbon and alloying elements content changes the morphology of boron layers. Carbon and alloying elements (mainly Cr, Mo, W, V) inhibit the growth of boride layer and flatten its front [25,26]. Needles become blunted and thick until they disappear completely. This results in a flat borides/metal interface [27,28].

Microstructure of boride layer is not the only factor that significantly affects its properties. Also, very important is thickness of obtained phases, which can be freely adjusted by changing the boriding parameters (time, temperature, concentration of boriding medium). For this reason, numerous studies are carried out on the kinetics of this process, because its determination makes it possible to assess saturation rate of steel with boron atoms [29-32]. On the basis of experimental results, contour diagrams are developed. They allow forecasting the thickness of resulting phases, depending on time and temperature of the process [30,32,33]. In the case of pack boriding, it depends on the following sub-processes: the formation rate of gaseous boron compounds and active boron atoms, their subsequent adsorption on the surface, the diffusion of boron atoms into steel, the rate of diffusion of other steel components pushed out in front of the growing borides. Boride layers formation rate is controlled by the slowest processes, i.e. diffusion in the solid state. Studies of the layer growth kinetics enable to determine diffusion coefficient D and process activation energy Q [25]. Activation energy of boron diffusion is interpreted as the amount of energy necessary to initiate boron atoms movement in [001] direction, which minimizes the stresses arising during growth of boron layer. It is also an energy barrier. Its exceedance allows the diffusion of boron into the metallic substrate [34]. Q value depends among others on: boriding method, process temperature, chemical reactions occurring during boriding and substrates chemical composition. Alloying elements and carbon create a diffusion barrier, that slows down the flux of active boron atoms into the material. Therefore, activation energy Q is higher for steels containing more carbon and alloying elements [30].

Modeling boriding kinetics allows for the efficient selection of process parameters in order to obtain the desired layer thickness for specific applications. In the literature there are many types of diffusion models, that derive from different assumptions [35-38]. In papers [34,39,40], mass balance equations at the borides/substrate interface were solved, which allowed to determine the boron diffusion coefficients in FeB and $Fe_2B$ phases formed on various steel grades. It was also proposed to utilize a dimensional analysis based on Buckingham's Pi theory, which was used to determine the relationship of four variables with the boron layer thickness. Results were consistent with experimental data [41]. Ortiz-Dominguez et al. [42] and Türkmen et al. [43]developed an analytical solution of the diffusion model using the integration method. In article, [44] parabolic law was used to describe the boride layers growth. This approach is based on partial chemical reactions taking place in the area of two emerging interfaces. The growth kinetics of $Fe_2B$ and FeB phases is described by a system of ordinary differential equations used to determine the change in both borides thickness during the process. Artificial neural networks turned out to be an interesting tool for simulating steel boriding [45-47]. They comprise three layers: input, hidden and output. In order to optimize the designed network, a back-propagation algorithm is used to train it, as it minimizes the mean square error between predicted result and actual value. Applied methodology allows obtaining 95% agreement when predicting the hardness of borided layer as a function of time and distance from the sample surface, for different process temperatures. Main advantage of neural networks is the ability to self-learn, while its greatest drawback is the ability to verify predicted values of variables (e.g. thickness of boride layer) only in the scope of conducted experimental research.

In our previous research [48,49] we studied the formation of boride coatings on selected types of tool steels. In present article the influence of diffusion process time on structure, thickness and phase composition on boride coatings was investigated. Research was conducted using commercial pack boriding materials and industrial-scale CVD system.

## 2 Experimental

The substrate material used in the study was supplied in the form of bars with a diameter of ϕ30 or ϕ35 mm, (depending on availability) from which 30 mm high samples were cut. The processes were carried out on 5 selected tools steel grades (Tab 1) in as-recieved condition which were divided into two groups: low-Cr content: 145Cr6 (NC6), 90MnCrV8 (NMV), 60WCrV8 (NZ3) and high-Cr content: X165CrV12 (NC 10), X153CrMoV12 (NC11 LV). The next stage was grinding using an ATM-M SAPHIR 330 grinder-polisher with water-resistant abrasive papers of 80 to 500 mesh. The samples prepared in this way were subjected to diffusion boriding. The boriding process parameters were selected based on our previous research [48,49]. The diffusion boriding processes were carried out using commercial EKABOR-2 (Bortec, Germany) powder with the following composition (wt. %): 90%, SiC, 5% $B_4C$, 5% $KBF_4$. The process was conducted using an industrial CVD system Bernex BPX Pro 325S (IHI-Bernex, Switzerland) at 1000°C for 2, 4 and 6 hours in an inert Ar atmosphere. After the boriding process metallographic assessment for samples preparation was conducted. The microstructure was observed using a Phenom XL scanning electron microscope (SEM) equipped with an EDS spectrometer - (Thermo Fischer Scientific, USA). Obtained boride layers were assigned to different groups according to the classification proposed by Voroshnin and Lyakhovich [25]. The coatings thickness was measured in 5 areas and average value was calculated.

***Tab. 1** Chemical composition of substrate materials (wt. %) - tested tool steels grades according to standards: PN-EN 10088-1:2014, PN-EN 10085:2003, PN-EN 10084:2008, PN-EN 10083-3:2008, PN-89/H-84030/02:1989, PN-EN ISO 4957:2004, PN-86/H-85023:1986*

| **Low-Cr steels** | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **145Cr6 (NC6)** | | | | | | | | | | | | |
| **C** | **Mn** | **Si** | **P** | **S** | **Cr** | **Mo** | **Ni** | **V** | **Co** | **Cu** | **W** | **Fe** |
| 1.30-1.45 | 1.40-1.70 | 0.15-0.40 | <0.03 | <0.03 | 1.30-1.65 | - | - | 0.10-0.25 | - | - | - | rest |
| **90MnCrV8 (NMV)** | | | | | | | | | | | | |
| **C** | **Mn** | **Si** | **P** | **S** | **Cr** | **Mo** | **Ni** | **V** | **Co** | **Cu** | **W** | **Fe** |
| 0.85-0.95 | 1.80-2.20 | 0.10-0.40 | <0.03 | <0.03 | 0.20-0.50 | - | - | 0.05-0.20 | - | - | - | rest |
| **60WCrV8 (NZ3)** | | | | | | | | | | | | |
| **C** | **Mn** | **Si** | **P** | **S** | **Cr** | **Mo** | **Ni** | **V** | **Co** | **Cu** | **W** | **Fe** |
| 0.55-0.65 | 0.15-0.45 | 0.70-1.00 | <0.03 | <0.02 | 0.90-1.20 | - | - | 0.10-0.20 | - | - | 1.70-2.20 | rest |
| **High-Cr Steels** | | | | | | | | | | | | |
| **X165CrV12 (NC10)** | | | | | | | | | | | | |
| **C** | **Mn** | **Si** | **P** | **S** | **Cr** | **Mo** | **Ni** | **V** | **Co** | **Cu** | **W** | **Fe** |
| 1.50-1.80 | 0.15-0.45 | 0.15-0.40 | <0.03 | <0.03 | 11.0-13.0 | - | - | - | - | - | - | rest |
| **X153CrMoV12 (NC11LV)** | | | | | | | | | | | | |
| **C** | **Mn** | **Si** | **P** | **S** | **Cr** | **Mo** | **Ni** | **V** | **Co** | **Cu** | **W** | **Fe** |
| 1.45-1.60 | 0.20-0.60 | 0.10-0.60 | <0.03 | <0.02 | 11.0-13.0 | 0.70-1.00 | | 0.70-1.00 | - | - | - | rest |

## 3 Results and discussion.

### 3.1 Microstructures and phase composition of f low-Cr cold-work tool steels after boriding treatment

Total thickness of coatings obtained on 145Cr6 (NC6) steel increased with boriding time from 12.2 μm to 76.9 μm (Fig. 1,2) After 2 h, layer consisted only of pointed $Fe_2B$ needles with a thickness of 12.2 μm. After 4 – 6 h needle-like FeB and $Fe_2B$ were formed and confirmed by a XRD analysis (Fig. 3a). Their total thickness was: after 4 h of the process 45.0 μm, including 9.5 μm FeB; after 6 h: 76.9 μm, including 14.9 μm (Fig. 1,2). Observed FeB layer was discontinuous and had uneven thickness (Fig. 2). It allows to assign this microstructure to model no. XI according to Woroshnin and Lyachowich [25]. After boriding for 2 and 4 h, many bright phases located under $Fe_2B$ layer were visible. They may contain increased amount of alloying elements and could be formed due to the process of pushing them back in front of the growing borides [25]. Characteristic needles were also observed by Bartkowska et al.[48]. They borided 145Cr6 steel and obtained acicular boron layers, below which were precipitates of chromium carbides. The process was carried out in a powder containing boron carbide, kaolin and ammonium chloride at 950°C/6 h.

Pack boriding of 90MnCrV8 (NMV) steel for 2 - 6 h produced borided coatings with a total thickness of 12.1 - 97.3 μm (Fig. 1,2). After 2 h, continuous layer of acicular $Fe_2B$ (12.1 μm) was formed. Contrary to samples after 4 – 6 h of treatment, no FeB peaks was observed (Fig. 3b). Boriding in 4 h resulted in the formation of an outer, discontinuous FeB layer (8.0 μm), while the total layers thickness reached 47.5 μm. There were some bright phases located beneath $Fe_2B$ layers for samples treated for 2 and 4 h. After 6 h, borided zone consisted of: an external, discontinuous and unevenly thick FeB layer (8.8 μm) and an internal, continuous $Fe_2B$ layer in the form of thick, blunted needles (Fig. 2) Microstructure was classified in both cases as model no. XI [25].

60WCrV8 (NZ3) steel was borided for 2 - 6 h forming boride coatings with a total thickness in the range of 11.3 – 77.0 μm (Fig. 1,2). After 2 h of the process, layer was made of acicular $Fe_2B$ phase, 11.3 μm thick. After 4 and 6 h, the borided zone had a two-phase structure with a total thickness of 38.0 μm and 77.0 μm. It consisted of a discontinuous FeB layer (thickness: 6.2 μm and 14.7 μm, respectively) and a continuous $Fe_2B$ layer in the shape of thin needles (Fig. 2). Presence of all borides were confirmed by XRD analysis (Fig. 3c). These needles were thinner compared to 145Cr6 and 90MnCrV8 steel (Fig. 2). The reason of such borides morphology is lowered amount of carbon in 60WCrV8 steel. Resulting micro-structures were assigned to model no. XI [25].

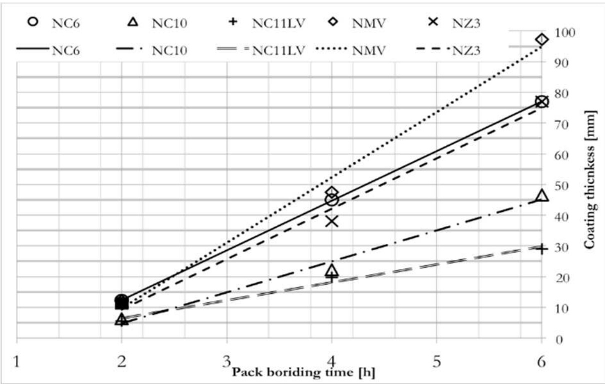


***Fig. 1*** *Kinetics of pack boriding process on different tool steels*

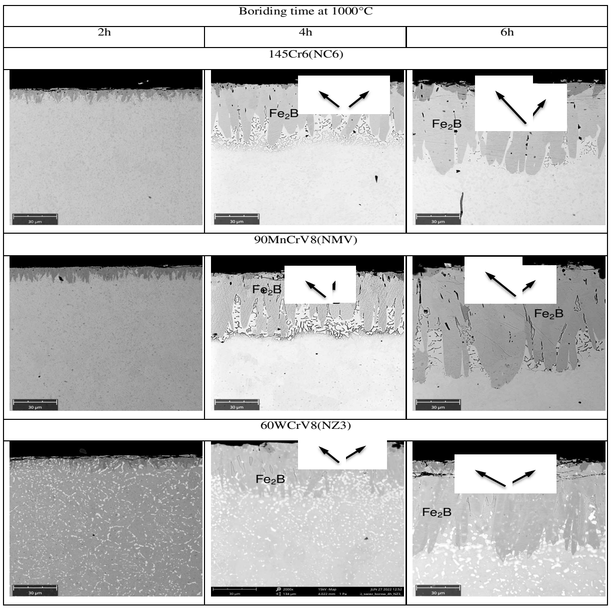


***Fig. 2*** *The microstructure of low-Cr cold work tool steels :145Cr6(NC6), 90MnCrV8(NMV) and 60WCrV8(NZ3) after 2, 4 and 6 hours of pack boriding proces at 1000°C*

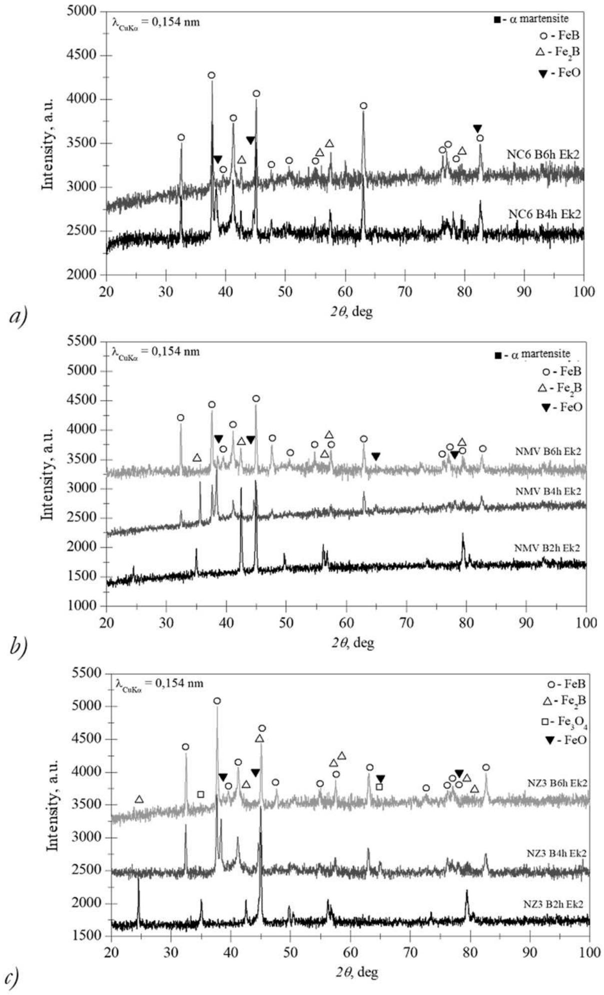


***Fig. 3*** *XRD phase analysis of borided cold-work tool steels: (a) 145Cr6 (NC6), (b) 90MnCrV8 (NMV), (c) 60WCrV8 (NZ3)*

## 3.2 Microstructures of high-Cr cold-work tool steels after boriding treatment

Elements present in high-alloy steels (e.g. chromium, molybdenum, vanadium) concentrate on top of forming borides, inhibiting their growth and causing a change in their morphology. Resulting coatings will have a flat boride/metal interface [26].

Boriding of high-chromium cold work steels X165CrV12 (NC10) and X153CrMoV12 (NC11LV) in 2 - 6 h resulted in the formation of boride coatings with a thickness of 6.2 - 46.5 μm and 5.6 - 28.9 μm, respectively (Fig. 1). The reason for lower thickness of boride layers on X153CrMoV12 steel may derive from the influence of Mo and V, which strongly inhibit their growth [25]. After boriding for 2 h, a continuous layer of acicular $Fe_2B$ borides (Fig. 4) with a thickness of 5.6 μm (X165CrMoV12) and 6.2 μm (X153CrMoV12), respectively, was formed. Increased process time (4 – 6 h) allowed to form a two continuous boride layers: outer FeB and inner $Fe_2B$ (Fig. 4,5). FeB phase had an acicular structure, while the $Fe_2B$ borides exhibited flat borides/substrate interface (Fig. 4,5).

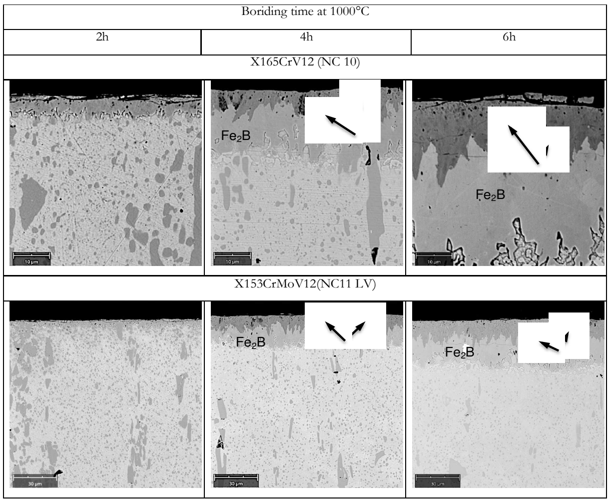


***Fig. 4*** *The microstructure of high-Cr cold work tool steels : X165CrV12 (NC 10) and X153CrMoV12 (NC11 LV) after 2, 4 and 6 hours of pack boriding process at 1000°C*

For X165CrV12 steel, their total thickness was: 22.2 μm, including 9.7 μm FeB (4 h) and 46.5 μm, including 19.9 μm FeB (6 h). For X153CrV12 steel, their total thickness was: 19.8 μm, including 10.3 μm FeB (4 h) and 28.9 μm, including 17.1 μm FeB (6 h). The formation of these phases was confirmed by XRD phase analysis (Fig. 5). Resulting microstructures were classified as model no. I according to Woroshnin and Lyachowich [25]. Similar boride structure obtained Hudakova et al.[49]. They borided K110 steel for 30 - 150 minutes at 1030°C, using Durborid powder. A boride layer consisting of 2 zones was obtained: outer FeB and inner $Fe_2B$. Total thickness of layers increased with process time and ranged from 50 μm to 90 μm. It was also noticed that vanadium reduces the thickness of formed boride coatings.

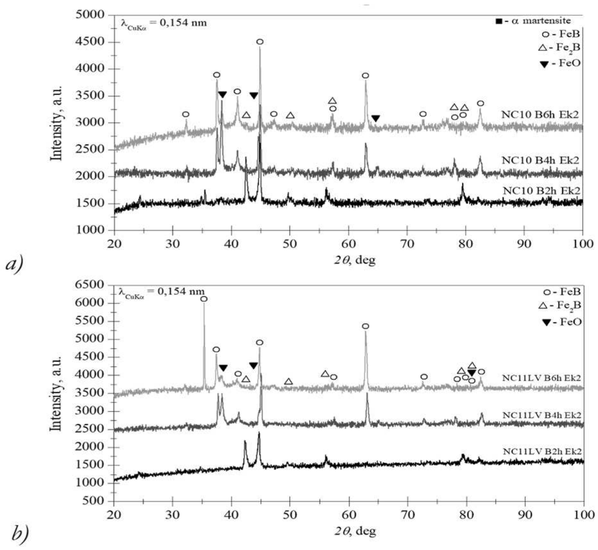


***Fig. 5****. XRD phase analysis of borided high-Cr cold-work tool steels: (a) X165CrV12 (NC10), (b) X153CrMoV12 (NC11LV)*

## 4 Conclusions

In this research selected cold-work tool steels were borided at 1000 °C for 2, 4, 6h using EKABOR-2 powder. The effect of process time and substrate chemical composition on borides growth kinetics and their morphology was investigated. Presence of all phases was confirmed by XRD analysis (Fig. 3,5). After 2 h of treatment all boride layers had the same structure - solely continuous $Fe_2B$ layer. Visible changes appeared after 4 - 6 h of boriding. For low-Cr steels, FeB phase was located in isolated pockets, wile for high-Cr substrates it formed continuous layers. Alloying elements, especially chromium, have powerful effect on thickness, composition and morphology of boride coatings. High amount of carbon and/or alloying elements, which retard borides growth (Cr, Mo, W, V), results in thin boride layers [25]. For this reason, compared to low-chromium steels, the boron layers formed on the substrate of high-chromium steels were characterized by a lower total thickness. Thus, the lowest boriding kinetics among all analyzed steel grades exhibited X153CrMoV12 steel. On the other hand, 90MnCrV8 steel contains the least alloying elements and moderate amount of carbon. Consequently, it had the highest boriding kinetics. On low-Cr steels, FeB phase was discontinuous, forming an isolated islands located in the near-surface area (Fig. 2). However, for high-Cr steels, a continuous layers of needle-like borides were formed (Fig. 4). Noteworthy was the difference in borides/metal interface. For high-Cr steels it was flat, while for low-Cr substrates, acicular. In conclusion, increased chromium content observed in high-Cr cold-work tool steels (Tab. 1) had two-fold effects. For one it diminished the total boride thickness and changed the interface into flat one. For second it favored the formation of continuous FeB layer just beneath the surface.

The obtained results showed that developed boride coatings on selected cold-work steels might be used in different industial tool applications. One of the possibilities are tools for plastic processing of non-ferrous metals, e.g. copper alloys. It is planned to use them in this area. However, it is necessary to carry out full heat treatment of the tools due to the high temperature and long time of the pack boriding proces]. The typical hardening temperature for low-chromium steel is about 840-910$^{o}$C, and for high-chromium steel even above 960$^{o}$C. The last stage of their heat treatment should be tempering at 180$^{o}$C. It will therefore be necessary to continue research on the heat treatment of tools with boride coatings [52,53].

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