CHARACTERISTICS OF SINTERED STEELS BORIDED WITHOUT HALIDES - OVERVIEW

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Abstract

Combined sintering and boriding of Fe-C, Fe-Ni-Mo-C, Fe-Ni-Cu-Mo-C and Fe-Cr-Mo-V-(Mn)-C steel specimens at 1120°C and sintering at 1120°C followed by boriding at 1050°C in boriding mix was carried out in cracked ammonia and hydrogen. The mix consisted of ferroboron and alumina and processing was with or without the assistance of manganese. The surface boride layers, formed on the specimens of uniform thickness and which depended on composition and treatment conditions, were analysed. After boriding Cr-alloyed steels at 1050°C in hydrogen, the microhardness was up to ~1900 HV 0.05 and of those steels containing Ni and Cu, it was 700-900 HV 0.05. The effects of carbon content on the composition of the formed boride layer, core microstructure character and microhardness were demonstrated. The thermodynamic analysis of the Fe-H-N-B-(Mn) boriding of sintered steels system showed a transfer mechanism of boron from the boriding mix onto the metal surface through the BHN$_{10}$ compound.

Keywords: sintered steel, sinter boriding, boriding mix, gas activator, boride layer, microhardness

INTRODUCTION

Boriding is a thermochemical surface treatment process, similar to carburizing or nitriding, which involves diffusion of boron into a base material. The resulting boride layers formed in this way contribute to high hardness of the metallic parts’ surfaces (higher than that obtained by other thermochemical treatment processes), high wear resistance and low coefficient of friction (~0.03). From these reasons it is applied on wrought metals.

Boron is an element of relatively small size, and this allows it to diffuse into a variety of metals. Boron reacts with these metals to form intermetallic borided cases that enhance surface hardness for increased wear resistance. Boriding of wrought metals is a pack cementation technique in which parts are placed in direct contact with a powder material composed from an active source of boron, inert filler and activator. Boriding of wrought metals occurs in the temperature range 815 to 980°C. Process cycle time ranges from one-quarter hour to over many hours. The time and temperature are adapted to the required layer thickness. However, depths greater than 0.025 to 0.125 mm are specified for abrasive wear application, and layers less than 0.025 mm are specified for adhesive wear [1,2].

The rate of boride layer formation depends on the composition of the base material. Boride layer formation is slower on high alloy steels than on plain carbon steels. Boriding can be carried out on most ferrous materials, including sintered iron and steel,
because boriding takes place in the austenite range, air-hardening steels can be simultaneously hardened and borided [3,4].

The combination of a high surface hardness and of low coefficient of friction of the boride layer makes a significant contribution to knowledge to the main wear mechanisms.

Boron reacts virtually with all alloys to form Fe$_2$B. The formation of single phase Fe$_2$B layers with a sawtooth morphology is desirable in the boriding of ferrous wrought steel.

The commonly used boriding compounds for wrought materials include solid boron-yielding substances (B$_4$C, ferroboron, amorphous boron), diluents (SiC, Al$_2$O$_3$), and activators (NaBF$_4$, KBF$_4$, NH$_4$Cl, Na$_2$CO$_3$). Halides are always linked with environmental and corrosion problems. The disadvantages of such boriding treatments are that the processes are inflexible and labour intensive, making the process less cost effective. They cause environmental problems due to the use of halides as activators. Therefore these processes are not used in PM parts production [1,2].

Carbon does not dissolve significantly in the boride layer and does not diffuse through the boride layer. During boriding carbon is driven from the boride layer into the matrix and forms, together with boron, borocementite.

As boron belongs to the elements forming a liquid phase below the common sintering temperature, it can be used as an enhancing element for increasing the density and mechanical properties of sintered components, as well for boriding. Boron forms a eutectic (Fe–3.74B) at 1174°C and has a unipolar solubility with iron. In cases when the prealloyed matrix is used instead of plain iron powder, boron diffuses into the matrix. In this way the extent of densification increases, together with matrix hardness of the borided specimens (bipolar solubility) compared with the Fe–B system.

Only few papers have dealt with pack boriding of PM steels. By pack boriding of sintered iron in a container at 1100°C for 4 h in powder mix consisting of B$_4$C or amorphous boron and NH$_4$Cl as an activator, a thin surface layer with microhardness of 1530 HV 0.1 was formed and increased tensile strength was obtained. The results obtained by pack boriding of iron based specimens with a density of 6.2-7.4 g cm$^{-3}$ at 850°C for 3 h in a powder mix consisting of B$_4$C, KBF$_4$ and SiC are given in Refs. [1,4].

The addition of boron to the sintered material has two roles, namely strengthen the matrix, and under certain conditions to form on the surface of the parts hard boride layers by boriding without halides. Therefore, both roles of boron can be used for systems prepared on the basis of mixed and prealloyed powders.

Overviews of the main results of boriding sintered steels are presented. Two processes without halides were investigated. These were two-stage and one-stage processes in a powder mix consisting of ferroboron, alumina and with and without manganese as possible activator, in cracked ammonia and hydrogen containing atmospheres. Investigated was the effect of boriding on the density, mechanical properties, and mainly on the structure characteristics of the hard boride surface layers characterised by thickness and microhardness. The processes conducted were thermodynamically analysed.

**EXPERIMENTAL PROCEDURES**

The following powders for the preparation of the samples were used:

1. Fe - water atomised iron powder (ASC 100.29, Höganäs), coded here A,
2. Fe - 2% Ni - 0.5% Mo (prealloyed, water atomised powder, Astaloy A, Höganäs), coded here B,
2. - Fe -1.75% Ni - 1.5% Cu - 0.5% Mo (diffusion partially bonded alloy powder, Distaloy SA, Höganäs), coded here C, all these powders with addition of 0.3% graphite and 0.8% HW as lubricant.

- Fe - 1% Cr - 0.3% Mo - 0.3% V (water atomised vacuum annealed powder, 103V, Kawasaki), coded here K1,
- Fe - 3% Cr - 0.3% Mo - 0.3% V (water atomised vacuum annealed powder, 30CRV, Kawasaki), coded here K2,
- Fe - 1% Cr - 0.7% Mn - 0.3% Mo (water atomised vacuum annealed powder, 4100V, Kawasaki), coded here K3.

Admixed with these prealloyed powders were: natural graphite - to powders K1, K2 and K3 of 0.2% (K11, K21, K31), of 0.5% (K12, K22, K32) and of 0.9% (K13, K23, K33), also 0.8% HW as lubricant. 0.2% boron with particle size <40 μm in the form of ferroboron (Fe18B, <40 μm, 18 mass % of boron, balance Fe) was added to both powder groups.

From the powder mixtures tensile strength bars (ISO 2740) were compacted at 700 MPa. The boriding mixture consisted of the base powders, graphite, ferroboron and alumina as diluent for preventing the caking of the boriding mixture with or without addition of manganese.

The following sinter boriding processes were carried out:
- sinter boriding process (combined sintering and pack boriding) at 1120°C for 1 h in a laboratory pusher furnace in cracked ammonia or in hydrogen (one-stage process),
- boriding of sintered samples (sintering at 1120°C for 1 h in cracked ammonia, dew point - 30°C, followed by pack boriding at 1050°C for 1 h and 2 h in hydrogen (two-stage process).

The processes involve packing of the annealed, cleaned, smooth parts into a boriding powder mix in a steel container, placing it into a furnace, and heating up to the process temperature.

The green compacts were packed with the boriding mixture in a steel box, covered with a steel plate. As a reference, green compacts were sintered without boriding.

A part of the borided specimens was austenitized for 0.5 h at 850°C in nitrogen, quenched in oil, and tempered in air for 0.5 h at 200°C. The processed specimens were tested as sintered, as pack borided, and as pack borided and heat treated.

The processes were investigated with the presumption especially of its possible application for PM parts.

Manganese, in the form of high-carbon ferromanganese (75% Mn, 6% C, balance Fe), was used as an activator because in Ref. [5] it was stated that, in addition to halides, also other elements with high vapour pressure, e.g. Cu, S, P, Sb, may act as activators in the pack boriding process. Manganese has significantly higher vapour pressure (19.88 Pa at 1100°C and 3.23 Pa at 1000°C) than, for example, copper (5.94·10⁻² and 6.1·10⁻³ Pa) at the same temperature. Therefore the intense sublimation of manganese during thermal processing, as a consequence of its high vapour pressure, was the reason for its use as a possible activator for pack boriding of sintered steels [6,7]. These data allow an assumption that manganese vapour, together with cracked ammonia or hydrogen protective atmosphere, facilitates the transport of boron to the outer surfaces of specimens and also to inner pore surfaces in the porous materials.
RESULTS

Two processes of boriding sintered steels were studied, namely a two-stage and an one-stage boriding, without the use of halides, in some cases with addition of manganese. One-stage processing was carried out after taking into account the results achieved in the two-stage process.

**Sintering and pack boriding – two-stage process**

Two-stage means that sintering occurred at a higher temperature, 1120°C, than pack boriding, 1050°C. The investigation of such a boriding process for PM parts is undoubtedly better for the furnace and also for the powder parts. For this reason, boriding was carried out using a powder mixture consisting of ferroboron, manganese as an activator, and alumina as a diluent.

**Properties of two-stage borided steels**

Densities of the green, sintered and borided specimens are shown in Fig.1. The sintered density increased by 1.0 to 2.0% compared to the green density. The boriding caused an additional increase in density by 1.7 to 3.6% compared to the sintered values. This proved that even this relatively low-temperature treatment (1050°C) increased the density, indicating an unexpected post-sintering enhancement effect during the boriding process. Higher density levels were obtained with alloyed steels and particularly with the Fe-Ni-Mo-C steel.

The tensile strength values of the steels in all tested states are shown in Fig.2. Boriding of the sintered steels based on the A, B, C powders caused an increase of the tensile strength from 350 to 645 MPa. Thus the tensile strength increased by 50, 53 and 40% for steels A, B and C, respectively, from the values of sintered specimens. The UTS values of the heat-treated borided steels A, B and C, respectively, reached 550 to 835 MPa, i.e. increase of 124, 81 and 70% compared to the non-borided steels.

![Fig.1](image1.png)

*Fig.1. Density of green, sintered, and borided steel specimens Fe-0.3C, Fe-2Ni-0.5Mo-0.3C and of Fe-1.75Ni-1.5Cu-0.5Mo-0.3C; boriding for 2 h at 1050°C [8,9].*

![Fig.2](image2.png)

*Fig.2. Tensile strength of sintered (SINT), sintered and heat-treated (SINT+HT), borided (BOR), and borided and heat-treated (BOR+HT) steels. A (0.12% C, 0.81% Mn), B (0.10% C, 0.84% Mn) and C (0.14% C, 1.12% Mn) [8,9].*

The as sintered carbon in the specimens ranged from 0.1 to 0.14%. During boriding, the manganese content in the borided specimens increased to 0.81–1.12% by
diffusion from the boriding mixture with addition of manganese in the direction to the specimen interior.

The corresponding hardness values of the investigated steels are shown in Fig. 3. The hardness of the borided specimens increased by 96, 125 and 72% for the steels A, B and C, respectively, compared to the sintered. The hardness of the sintered specimens, similarly as tensile strength, was not or minimum affected by heat treatment. With the same carbon content, the heat treatment of the borided specimens increased their hardness by 190, 145 and 103% when compared to the borided for the A, B and C steels, respectively.

Fig.3. Hardness HV 30 of the steels as in Fig.2 [10,11,12].

Fig.4. Microstructures of steels sintered in cracked ammonia for 1 h at 1120°C. Nital etched [8,9].
Figure 4 shows the microstructures of the sintered steels based on the powders A, B and C, respectively, formed by ferrite, ferrite-pearlite and ferrite-coarse bainite. The mean microhardness values of these steels were 122, 151 and 138 HV 0.05. The microstructures of the borided specimens are shown in Fig.5.

Fig.5. Core microstructure of the steels: (a) Fe-2Ni-0.5Mo-0.3C (B), (b) Fe-1.75Ni-1.5Cu-0.5Mo-0.3C (C) pack borided 2 h at 1050°C. Nital etched [9,12].

Fig.6. Microstructures of surface boride layers with subsurface zone formed in specimens borided for 2 h at 1050°C. Nital etched [8,9].
A white boride surface layer was formed on all specimens. The thickness of the white layer depended on the composition of the steel. The eutectic-like surface layer formed on the steel C was the thickest, as shown in Fig. 6. The formation of such a layer on the FeNiCuMoC steel sample at 1050°C resulted from the presence of copper in the steel which gives a low-melting eutectic with boron at 1013°C [13].

Boriding caused an increase of the microhardness values of the microstructure constituents in the specimen cross-section, in contrast to that of the wrought steel specimen on which only a surface boride layer is formed without affecting the substructure of the base material. The microhardness of the surface layer, diffusion zone, core grains and of the eutectics is given in Fig. 7. The structure of the surface layer was eutectic-like.

![Graph showing microhardness values](image)

Fig. 7. Microhardness values (HV 0.05) of the steels after two-stage boriding. SL - surface layer, DZ - diffusion zone, C - core, E - eutectics [8,9].

The microhardness, as a mean value of 20 measurements of the surface layer, was in the range of 699 to 963 HV 0.05, depending on the chemical composition of individual steels. The microhardness of the white surface layer in alloy C was the highest one.

Figure 8 shows the characteristic microstructures of the surface layer, partly with the diffusion zone and the microstructure in the core in the borided state for the Fe-Ni-Cu-Mo-C sample at high magnification and after sintering only. The difference in the character of the sintered and borided specimen core microstructures is shown in Figs. 8(c) and (d). The changes in Mn, Ni and Cu contents, measured in 6 points, from the surface layer to the core of the specimen, caused by boriding are given in Table 1.

Tab. 1. Mn, Ni and Cu content in a cross-section of Fe-1.7Ni-1.5Cu-0.5Mo-0.3C steel sample sintered at 1120°C and after pack boriding at 1050°C for 2 h in boriding mix with manganese in cracked ammonia, see Fig.8 (a), (b), (c). Microanalysis EDAX - LINK, SEM Tesla BS 340.

<table>
<thead>
<tr>
<th>Element</th>
<th>Point</th>
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<tbody>
<tr>
<td></td>
<td>*1</td>
</tr>
<tr>
<td>Mn</td>
<td>16.1</td>
</tr>
<tr>
<td>Ni</td>
<td>1.82</td>
</tr>
<tr>
<td>Cu</td>
<td>2.3</td>
</tr>
</tbody>
</table>

* boride layer, **white layer, * core of the specimen
Large differences in the contents of the analysed elements, from the boride layer to the sample interior, were recorded after this pack-boriding process applied. The highest differences were in manganese concentration, which was a part of the boriding mix. It varied from 17.8 in the boride layer to 11.4% and 4.7% in the subsurface layer down to the sample core concentration of 0%.
In the case of Ni and Cu, coming from the base diffusion prealloyed powder, there was an unexpected reverse diffusion from the core into the surface layer. This was documented by their concentrations registered at points 5 and 6 with zero concentration of Ni compared to those determined at the points 1 to 4. The differences in copper concentration were in the range 1.0 to 2.3%.

**Sinter boriding – one-stage process**

This process was performed with two boriding mixtures differing in their composition. Manganese as an activator of the process was used in the first composition, and in the second the boriding mixture consisted only of ferroboron and alumina. The one-stage pack boriding process was applied and then processed as in the previous case for the steels based on A, B and C powders.

**Sinter boriding with assistance of manganese**

The boriding powder mix consisted, as in previous cases, of ferroboron, ferromanganese as manganese carrier and alumina as diluent. This process, performed at the temperature of 1120°C for 1 h in cracked ammonia, is combined sintering and boriding. As sintered values of the densities and of the shrinkage of the specimens are listed in Table 2. The pack-sinter boriding process caused a marked increase of the density of the steels in comparison with the green and as sintered densities. The alloyed steels, especially the copper-alloyed steel C, showed greater densification after sinter boriding than did the Fe–C steel.

**Tab.2. Density and dimensional changes of samples A, B and C. Sinter pack-boriding for 1 h at 1120°C with assistance of manganese. 600 MPa, cracked ammonia.**

<table>
<thead>
<tr>
<th>Steel</th>
<th>Density [g cm⁻³]</th>
<th>Shrinkage length [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.3C (A)</td>
<td>7.00 7.03 7.13</td>
<td>+0.33</td>
</tr>
<tr>
<td>Fe-2Ni-0.5Mo-0.3C (B)</td>
<td>6.91 7.01 7.16</td>
<td>+0.63</td>
</tr>
<tr>
<td>Fe-1.75Ni-1.5Cu-0.5Mo-0.3C (C)</td>
<td>6.96 7.04 7.21</td>
<td>+0.45</td>
</tr>
</tbody>
</table>

**Fig.9. Boride layers on PM steel samples pack-sinter borided 1 h at 1120°C in cracked ammonia. Steel: (a) - A, (b) - B, (c) - C as in Tab.2. Nital etched [12,13].**
The microstructure of sintered specimens was ferritic–pearlitic depending on the base composition of the matrix. Sinter boriding resulted in formation of white surface boride layers on all steel samples, as shown in Fig.9.

The microhardness values of ferrite in the sintered microstructure, in boride layers and in the core regions, are shown in Fig.10. The highest microhardness of 1370 HV 0.05 was measured on the finest boride layer in material A. There was also a marked increase of the core microhardness compared to the sintered state. This is probably due to modest alloying of the matrix of the alloyed steels with manganese and boron compared with the Fe–C steel.

![Fig.10](image)

Fig.10. Microhardness values of ferrite in sintered reference samples (F) microstructure and of steels sinter pack-borided 1 h at 1120°C. BL - boride surface layer, BZ - diffusion zone, C - core grains. Legend: A, B, C as in Table 2, 15-60 parallel indents for each value [11,12].

The results indicate that sinter boriding process, without halides but with assistance of manganese, can be performed during sintering. It resulted in formation of hard layers with a thickness of 40 to 180 μm on the surfaces of the Fe-C, Fe-2Ni-0.5Mo-C and Fe-1.75Ni-1.5Cu-0.5Mo-C steels with the microhardness of 1100 to 1370 HV 0.05. Compared with microhardness values of the steels treated in two-stage boriding process shown in Fig.7, the microhardness values of the boride layers after one-stage boriding are higher and this process is, from the economical point of view, more effective than the two-stage boriding process.

**Sinter boriding without assistance of manganese**

These experiments were conducted with a boriding mixture consisting of ferroboron and alumina with the aim of verifying whether the use of manganese as a boriding activator is necessary. The first experimental series was carried out as a one-stage process - sinter boriding for 1 h at 1120°C. The second series was carried out for comparison as two-stage boriding - sintering of the samples for 1 h at 1120°C followed by boriding for 1 and 2 h at 1050°C. Both processes were conducted in cracked ammonia.
**Sinter boriding – 1st boriding series**

Figure 11 shows the microstructures of Fe–C specimens sinter-borided in the boriding mix without manganese for 1 h at 1120°C. The uniform thickness of the surface boride layer with a sharp transition into the interior of the sample was the characteristic change of the core microstructure at this process, Figs.11 (a), (b). The uniform surface boride layers were also formed on the Fe-Ni-Mo-C and Fe-Ni-Cu-Mo-C steel samples shown in Figs.12 (a), (b). A marked distinction in the character of the boride layers was observed when compared with, for example, Fig.8.

![Fig.11](image1.png)

Fig.11. Microstructure of Fe-C specimen: (a) surface boride layer, (b) core in Fe-0.3C specimen sinter borided for 1 h at 1120°C in cracked ammonia in a boriding mix without manganese. Nital etched [10,14,15].

![Fig.12](image2.png)

Fig.12. Microstructure of: (a) surface boride layer, (b) core in Fe-2Ni-0.5Mo-0.3C specimen sinter borided for 1 h at 1120°C in cracked ammonia packed in a boriding mix without manganese. Nital etched [11,15,16].

The uniform boride layers were also formed on the FeNiMoC and FeNiCuMoC steel samples shown in Figs.12 and 13. A distinction in the character of the boride layers was observed when compared with Fig.11. As shown in Fig.13 (a), under the boride layer of Fe-1.75Ni-0.5Cu-0.5Mo-0.3C specimen the characteristic subsurface layer was formed, to be compared with Fig.12(a). The core microstructure of the samples is in both cases homogeneous.

The thickness of the boride layer shown in Fig.11 (a) was 140 μm, and 170 μm in those shown Figs.12 and 13. In this case it is necessary to note that, under the boride layer shown in Fig.13, a subsurface diffusion zone was formed.
In Table 3 are listed the microhardness values measured in ferrite, boride layer, diffusion zone and in the core of the specimens.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Microhardness HV 0.05</th>
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<tbody>
<tr>
<td></td>
<td>Ferrite – as sintered</td>
</tr>
<tr>
<td></td>
<td>Boride layer</td>
</tr>
<tr>
<td></td>
<td>Diffusion zone</td>
</tr>
<tr>
<td></td>
<td>Core</td>
</tr>
<tr>
<td>Fe-0.3C</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>1280</td>
</tr>
<tr>
<td></td>
<td>451</td>
</tr>
<tr>
<td></td>
<td>305</td>
</tr>
<tr>
<td>Fe-2Ni-0.5Mo-0.3C</td>
<td>168</td>
</tr>
<tr>
<td></td>
<td>1185</td>
</tr>
<tr>
<td></td>
<td>611</td>
</tr>
<tr>
<td></td>
<td>378</td>
</tr>
<tr>
<td>Fe-1.75Ni-1.5Cu-0.5Mo-0.3C</td>
<td>154</td>
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<tr>
<td></td>
<td>1124</td>
</tr>
<tr>
<td></td>
<td>533</td>
</tr>
<tr>
<td></td>
<td>355</td>
</tr>
</tbody>
</table>

The highest microhardness values were measured in the surface layer on sample of A. The microhardness of the boride layers formed on the surface of both alloy steel samples is on the same level. In contrast, the microhardness of the diffusion zones and in the core of the alloy steel samples is higher when compared to that of Fe-0.3C.

The microhardness of the surface boride layers after one-stage sinter boriding process was lower than after two-stage boriding. This could be explained by longer treatment time (2 h) of two-stage sinter boriding, during which boron diffused through the solid phase from the surface into the matrix. In a one-stage process this would be effected by an increase of solid boron in the boriding mixture, e.g. to 3%. The results indicate that adequate alloying of steels with optimum combination of treatment conditions can yield a good combination of surface layer quality and mechanical properties in manganese assisted pack borided sintered parts.

Two stage boriding – 2nd series of boriding without assistance of manganese

Specimens based on prealloyed Fe-Cr-Mo-V-(Mn) powders (K1, K2, K3) with various starting carbon content were used. Two-stage sinter boriding at 1120°C for 1 h and boriding at 1050°C for 1 h and 2 h in boriding powder mix in hydrogen, in contrast to previously conducted two-stage boriding in cracked ammonia, was carried out. Apparent surface hardness HRC of the borided specimens and HV 10 of as sintered specimens are listed in Table 4. Characteristic microstructures of surface boride layers on K1 and K2 steel
specimens, both with addition of 0.2 and 0.5% graphite two-stage borided for 1 h at 1050°C, are shown in Fig.14.

Fig.14. Microstructure of surface boride layers formed at boriding 1 h at 1050°C on specimens: (a) K1 (Fe-1Cr-0.3Mo-0.3V-0.5C<sub>c</sub>), (b) K2 (Fe-3Cr-0.3Mo-0.3V-0.2C<sub>c</sub>) steel. Etching in (H<sub>2</sub>O, HF, HNO<sub>3</sub>) solution [11, 15].

The thickness of the boride layer shown in Fig.14(a) was 26 μm followed by the diffusion zone, shown on Fig.14(b), of 40 μm.

Tab.4. Apparent surface hardness HRC of samples treated in a two-stage boriding process at 1120°C for 1 h and borided at 1050°C for 1 and 2 h of sintered specimens and hardness HV 10 of as sintered samples.

<table>
<thead>
<tr>
<th>Treatment [°C/h]</th>
<th>Alloy</th>
<th>Fe-1Cr-0.3Mo-0.3V 0.2C</th>
<th>Fe-1Cr-0.3Mo-0.3V 0.5C</th>
<th>Fe-1Cr-0.3Mo-0.3V 0.9C</th>
<th>Fe-3Cr-0.3Mo-0.3V 0.2C</th>
<th>Fe-3Cr-0.3Mo-0.3V 0.5C</th>
<th>Fe-3Cr-0.3Mo-0.3V 0.9C</th>
<th>Fe-1Cr-0.7Mn-0.5Mo 0.2C</th>
<th>Fe-1Cr-0.7Mn-0.5Mo 0.5C</th>
<th>Fe-1Cr-0.7Mn-0.5Mo 0.9C</th>
</tr>
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<tbody>
<tr>
<td>1120/1</td>
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<td>63</td>
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<td>-</td>
<td>79</td>
<td>50</td>
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<td>72</td>
<td>73</td>
<td>76</td>
<td>86</td>
<td>-</td>
<td>-</td>
<td>59</td>
<td>78</td>
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<tr>
<td>1050/2</td>
<td></td>
<td>41</td>
<td>-</td>
<td>76</td>
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<td>86</td>
<td>-</td>
<td>59</td>
<td>78</td>
</tr>
<tr>
<td>*1120/1</td>
<td></td>
<td>98</td>
<td>168</td>
<td>188</td>
<td>122</td>
<td>224</td>
<td>285</td>
<td>92</td>
<td>147</td>
<td>181</td>
</tr>
</tbody>
</table>

*as sintered HV 10 before sinter boriding at 1120°C. C<sub>c</sub>: 0.14 to 0.19% for 0.2%, 0.28-0.32% for 0.5%, and 0.58-0.60% for 0.9% graphite addition

Tab.5. Microhardness HV 0.05 of the surface boride layer and in the core of the K1 and K2 specimens with various graphite addition pack-sinter borided for 1 and 2 h at 1050°C.

<table>
<thead>
<tr>
<th>Treatment [°C/h]</th>
<th>HV 0.05 value</th>
<th>Steel</th>
<th>K1 + 0.5C</th>
<th>K2 + 0.2C</th>
<th>K2 + 0.9C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>layer</td>
<td>core</td>
<td>layer</td>
<td>core</td>
</tr>
<tr>
<td>1050/1</td>
<td>mean</td>
<td>1588</td>
<td>459</td>
<td>1719</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>range</td>
<td>1329-2125</td>
<td>276-534</td>
<td>1426-2148</td>
<td>188-441</td>
</tr>
<tr>
<td>1050/2</td>
<td>mean</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>range</td>
<td>-</td>
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</tr>
</tbody>
</table>
Microhardness values of the surface boride layers and of the core of the specimens K1 and K2 after two-stage boriding without assistance of manganese are listed in Table 5.

The effect of the base composition of the steels, alloyed with carbide- and nitride-forming elements, such Cr, Mo and V, was manifested in their relatively high microhardness values of the surface boride layers and of the specimen cores. Higher graphite additions resulted in higher microhardness values of the boride layer, as well of the core specimens.

The thickness of the boride layers of K1 and K2 steels, accompanied by their relatively very high microhardness values, makes possible a very high abrasive wear resistance of such borided materials. This was documented by testing tribological properties, including seizure testing of Fe-Mn-C and Fe-Mn-B-C steels [16].

DISCUSSION

The interconnected pores have a significant effect on the boriding process, as they increased substantially the reactive surface of the materials. The surface of the interconnected pores at 6.9 g/cm³ density was \( \sim 300 \times 10^3 \) mm²/mm³ and \( \sim 160 \) mm²/mm³ at 7.2 g/cm³ density of a specimen, respectively.

The consequence of the boriding processes applied on sintered steels is the formation of boride hard layers, but also an increase in density, tensile strength and hardness levels compared with as sintered values. Such values cannot be reached even by high alloying and by sintering at higher temperatures. The borided and heat treated Fe-0.3C steel with a density of 7.25 g/cm³ exhibited tensile strength of 550 MPa, the Fe-2Ni-0.5Mo-0.3C steel with density of 7.30 g/cm³ reached a tensile strength of 650 MPa and the Fe-1.75Ni-1.5Cu-0.5Mo-0.3C steel with density 7.45 g/cm³ reached a tensile strength of 835 MPa (Fig. 8).

This was caused by the conducted boriding processes, different to the boriding of wrought steels. In the structure of the steel specimens three zones were formed:
- hard boride surface layers, characterised by the highest microhardness values and by a typical microstructure,
- the diffusion zone below the surface layer with lower microhardness and with a microstructure different to that of the surface boride layer,
- core microstructure of the samples, affected partly by all elements coming from the boriding mixture, which was nearly poreless and was characterised mainly by uniform grains larger than in the as sintered microstructure.

The structural characteristics of the sinter borided Fe-C, Fe-Ni-Cu-Mo, as well as of Fe-Cr-Mo-V, steels clearly demonstrate that surface boride layers cannot be detached from the surface of the sinter borided base materials, which thus are part of the whole borided material, in contrast to boride layers on wrought steels.

Thermodynamic analysis of the sinter boriding of powder steels

The thermodynamics of boriding steels without a manganese addition was more beneficial for the formation of a uniform surface boride layers on the specimens, compared to manganese-assisted boriding. The results proved that the boriding process proceeded in this case in the presence of a gas phase, facilitating the transport of boron from the solid powder mix onto the metal surface and then into the core of the sample. It follows that the activator in this case could be only hydrogen and nitrogen in the atmosphere used. It is a unique situation for powder metallurgy.
From the thermodynamic point of view the model system contains 3 phases:

1. gas phase - ‘sintering’ atmosphere and all potential gas products originating during the process,
2. solid phase - base metal phase and all products originating during the process which become a part of the base metal phase,
3. solid phase - powder boriding mix, which is the source for B (and Mn, when Mn is used as an activator).

The following conclusions can be made from the thermodynamic (TD) analysis of the Fe-B-H-N-(Mn-O) system, considering the mentioned phases:

- transfer of boron from the powder mix containing ferroboron as a boron carrier in the TD model process occurs through the compound \( B_3H_3N_3(g) \),
- presence of oxygen in the system does not affect the composition of the metal phase, but can affect the transfer mechanism of boron from the boriding mix into the metal phase,
- transfer of manganese from the powder mix, if used, is from the thermodynamic point of view an independent process and is realised through the manganese vapour causing only alloying of the matrix including the surface layer, with decreasing concentration from the surface layer to the interior of the sample,
- oxygen in the system from the point of view of the manganese transfer forms MnO in the metal phase if the gas phase contains >0.7% O.

These experiments carried out and the TD analysis proved that the manganese in the boriding powder mix does not fulfil the role of an activator.

Only hydrogen and nitrogen in the atmosphere can be used as an activator in the boriding process of the powder materials. The effect of their mutual portion on the mechanism and kinetics of the reactions can affect the properties of the borided materials. These results, relating to the transfer of boron through a gas activator (BHN\(_{(g)}\)) in the pack boriding process, show that boron can be transferred through the compound BN\(_{(g)}\) \([17,18]\).

The transfer of B through the compound \( B_3H_3N_3(g) \) is universally valid, not only for PM materials, but also for wrought steels. The H-N containing atmospheres, as base sintering atmospheres in powder metallurgy, facilitate further development and possible realization of this process in production of PM parts \([18]\).

**CONCLUSIONS**

Following main results were obtained:

- Manganese assistance in powder boriding mix for sintered steels does not fulfil the role of the activator. Powder boriding mix consisting of boron carrier, i.e. ferroboron and as diluent alumina, is effective for boriding of PM materials and probably of wrought steels in H-N containing atmospheres.
- Hydrogen and nitrogen in the sintering atmosphere fulfilled the role of an activator for sinter boriding (one-stage) and boriding (two-stage) processes for PM steels.
- Transfer of boron from the powder mix containing solid boron carrier proceeds through the compound \( B_3H_3N_3(g) \).
- Uniform surface boride layers on the steel specimens were formed by sinter boriding at 1120°C in cracked ammonia and in hydrogen in 2 component boriding mix.
- Boriding in hydrogen of low chromium alloyed specimens at 1050°C for 1 h caused the formation of surface boride layers with a markedly high microhardness, up to a mean value ~1800 HV 0.05.
- Two-stage boriding in hydrogen of Fe-3Cr-0.3Mo-0.3V-0.9C steel specimen at 1050°C for 2 h caused the formation of a hard surface layer with the microhardness of 1800 to
1900 HV 0.05 and an uniform fine grained microstructure in the whole cross-section of the specimens.

- The boride surface microhardness of Fe-C and Fe-Ni-(Cu)-Mo-0.3C sintered steel specimens which were two-stage borided at 1050°C for 2 h in cracked ammonia reached values from 700 to 950 HV0.05.
- A sawtooth morphology of the borided layer formed on the sintered steels was not formed.
- Borided layers on the surfaces of the sintered steels, according to their microhardness and thickness, fulfil the requirements of up to very high wear resistance applications.
- The surface boride layer formed on the base powder steels is not detachable.

The obtained results on sinter boriding and boriding of PM steels are a contribution to the development of sintered structural parts with high wear resistance.

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REFERENCES
[18] Software: HSC Chemistry 4.1, Outokumpu Research Oy, Pori Finland, June 30, 1999