

FORMATION OF BORIDE LAYERS ON PM STEELS DURING SINTER BORIDING

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Abstract

Simultaneous sintering and pack boriding of PM steels was investigated. The Fe-C, and Fe-Ni-Mo-(Cu)-C powder steels in a boriding mix consisting of boron carrier, manganese and diluent were sintered under standard conditions, i.e. the treatment was carried out at 1120 °C for 1 h in dissociated ammonia. Hard surface layers were formed. The process increased the density and mechanical properties of the materials. Significant changes in microstructure character compared to plain as-sintered one were analysed. The sinter boriding process proceeded under the effect of the formed gas compound $B_3H_3N_{3(g)}$. The sinter boriding process for forming hard surface layer on parts for adhesive or abrasive wear resistance can be applied under conventional sintering conditions in a H/N atmosphere.

Key words: *sintered steel, boriding, activator, mechanical properties, microstructure*

INTRODUCTION

Sintering is the most important and, from a technical viewpoint, the most difficult procedure in the production of sintered materials. Sintering is a process performed in a controlled, mostly reducing, atmosphere, during which a dispersed, fragile body changes into a solid metallic one – which may however still contain pores - with defined physical and mechanical and other required properties. This process takes place in solid state, and therefore is not restricted in alloying in contrast to ingot metallurgy, which is restricted by the solubility of alloying elements. The sintering temperature is commonly in the range of 1100 to 1300°C in dependence on the chemical composition and properties of parts required.

The application of some highly loaded sintered structure parts, mainly in the automotive industry, requires high wear resistance. There are many surface hardening methods, such as e.g. carburising and nitriding, fulfilling the requirements.

High surface hardness and a low coefficient of friction of the boride surface layer makes a significant contribution in combating the main adhesive and abrasive wear of the parts. Pack boriding is the most widely used boriding process in wrought steel parts production because of its relative ease of handling, safety, and the possibility of changing the composition of the powder mix, and the resultant economic savings. Mostly used as boron carrier is ferroboration or boron carbide always with chlorides or fluorides (halogenides) ($NaBF_4$, KBF_4 , NH_4Cl , Na_2CO_3) as activator. Silicon carbide (SiC) and/or alumina (Al_2O_3) serve as diluents, and they do not take part in the reaction [1]. The use of halogenides in the pack boriding process is not realised in powder metallurgy due to environmental and corrosion problems.

The disadvantage of pack and of other boriding processes is that they are inflexible and labour intensive, especially the work in closed containers, and therefore pack boriding is not used as a surface hardening process in powder metallurgy [2,3]. The results of some experiments concerning the pack boriding of sintered steels are given in [4-6].

In [7] it was stated that each element exhibiting high vapour pressure could serve as an activator in the boriding process. On the basis of this information, manganese also can be taken into consideration. Manganese vapour pressure is by some order higher than that of other alloying elements, such as of Cu and Ni mentioned in this work. The vapour pressure of manganese at, e.g. 1100°C, is 19.8 Pa and that of Cu $5.94 \cdot 10^{-2}$ Pa. The consequence of this is the sublimation of manganese also during the heating period for sintering parts containing manganese and the alloying of sintered manganese steel occurs in the solid (iron powder) - gas phase (manganese vapour) [8,9].

In this paper the properties of steel specimens sintered in a pack boriding mixture in cracked ammonia without the use of halogenides, with the aim of simultaneous sintering and formation of a hard boride layer on the surface of the steels, are described.

EXPERIMENTAL PROCEDURE

For the preparation of specimens the following base metal powders were used:

1. Fe – (water atomised iron powder ASC 100.29, Höganäs AB),
2. Fe-2% Ni-0.5% Mo (prealloyed, water atomised powder Astalloy A – Ast.A, Höganäs AB)
3. Fe-1.75% Ni-1.5% Cu-0.5% Mo (diffusion alloyed powder Distalloy SA – Dist.SA, Höganäs AB).

Standard tensile strength bars (ISO 2740), 5 mm thick, were prepared from these powders with the addition 0.3 mass % of graphite and 0.5 mass % of lubricant (zinc stearate) by compaction at 650 MPa. The boriding powder mix consisted of ferroboration Fe18B as the boron carrier, manganese in the form of high carbon ferromanganese milled in air, particle size <45 µm (75 mass % Mn, 6.6 mass % C, balance Fe, OFZ Istebné), and alumina preventing cracking of the boriding agent (diluent), i.e. 20% Fe18B, 5% FeMnC, balance alumina.

The green specimens were packed into the boriding mix within a steel box (300x150x30 mm) covered with a steel plate and treated (sintered) in flowing cracked ammonia (dew point -30°C) at 1120°C for 1 h. Sintering conditions commonly used for structural steel parts were applied for this treatment.

The density (water displacement method, ISO 3369), tensile strength (testing machine TIRATEST 2300, crosshead speed 5 mm/min), and hardness (ISO 4498, Vickers, load 30 kg) were measured. Three specimens for each condition were tested for mechanical properties. For comparison specimens were also sintered without packing in the boriding mix.

Specimens were prepared for microstructure characterization by embedding in a resin under pressure, and by common optical metallography methods were prepared. The microstructure was characterized on an optical microscope NEOPHOT 21. The microhardness was measured on LECO microhardness tester LM-700 AT.

RESULTS

Density

Densities of the green, as-sintered and as-borided materials are shown in Fig.1. A density increase by sintering of 1.0 to 2.0%, in dependence on alloying, was recorded. The sinter borided specimens reached an additional increase in density by 1.7 to 3.6% compared to the as-sintered values, and by 2.7 to 5.4% compared to the green density values. As shown, higher density values were attained with alloyed steels and particularly with the

Dist. SA steel. The length shrinkage of specimens in the range of 0.3 to 0.6% was recorded during this sintering boriding process. The density increase of specimens during this combined process is a proof of its high sintering activity (diffusion processes).

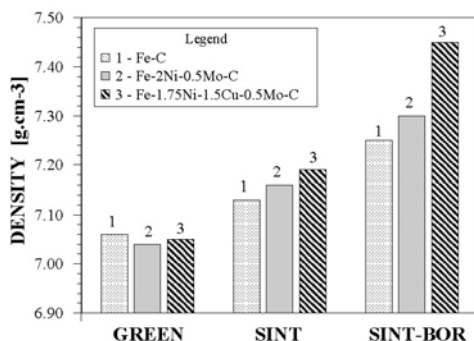


Fig.1. Density of green (GREEN), sintered (SINT) and sinter borided (SINT-BOR) steel specimens. Simultaneous sintering and pack boriding at 1120°C for 1 h in cracked ammonia.

Tensile Strength and Hardness

In Figure 2 are shown the tensile strength values, and in Fig.3 the hardness values of as-sintered and of as-sinter borided specimens.

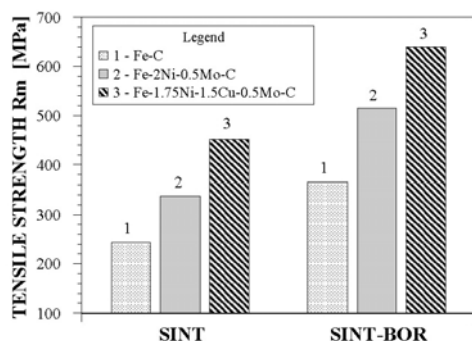


Fig.2. Tensile strength of as-sintered (SINT) and of sinter borided (SINT-BOR) alloys. Simultaneous sintering and pack boriding at 1120°C for 1 h in cracked ammonia.

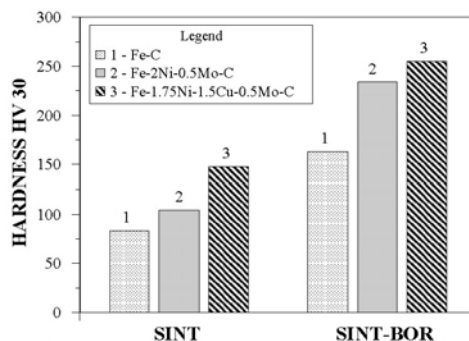


Fig.3. Hardness HV 30 of alloys as in Fig.2.

As shown, compared to the as-sintered state, sinter boriding increased the tensile strength by 50, 53 and 43% for the alloys 1, 2, 3, respectively. Tensile strength values of 582 MPa (Fe-0.3C) to 640 MPa (Dist.SA-0.3C) were attained. The corresponding hardness values increased also by 96, 125 and 72% for the alloys 1, 2, and 3, respectively, compared to the as-sintered state with combined carbon content, which ranged in our case from 0.1 to 0.14 mass %. The as-sintered tensile strength of tested alloys corresponds to that stated in [10].

Microstructure

The microstructure of as-sintered specimens was formed by ferrite, and ferrite-coarse bainite with a tiny amount of pearlite according to the composition considering the mentioned combined low carbon content, as shown in Fig.4. The microhardness values of the microstructure of the as-sintered specimens were in the range 85 – 135, 153 – 220 and 141 – 291 HV 0.05 for the tested alloys 1, 2 and 3, respectively. The microstructure of surface and subsurface layers of the sinter borided specimens is shown in Fig.5. A white surface layer of varying thickness was formed on all specimens. The thickness of this layer depended on the composition of the alloy. The eutectic-like surface layer formed on Dist.SA-0.3C alloy was the thickest. It is possible to say that the presence of copper in this alloy was the cause of the formation of such a thick layer compared to the Fe-2Ni-0.5Mo alloy (2). It is necessary to note that the boride surface layer was not formed as an additional layer on the surface of the specimens as in the boriding of wrought steels. In that case, in the first stage of boriding there is produced a thin, compact boride layer on the surface followed by diffusion in the direction of the bulk, resulting due to an increase of volume in dimensional growth by 5 to 25% of the layer thickness [1]. In the case of pack boriding of sintered steels, the boron from an adequate gas-phase is transmitted to the substrate, in which by diffusion is formed a “boride” layer by the direct boriding of its surface layer, followed with a large diffusion zone in the expanse of pores without dimensional change.

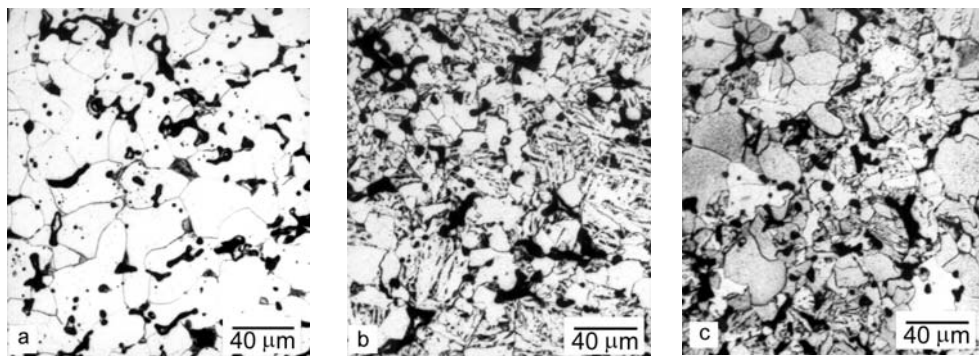


Fig.4. Microstructure of alloys sintered in cracked ammonia at 1120°C for 1 h in cracked ammonia. a (1) - Fe-0.3C, b (2) - Fe-2Ni-0.5Mo-0.3C, c (3) - Fe-1.75Ni-1.5Cu-0.5Mo-0.3C. Optical micrographs, nital etched. (Combined carbon content in the alloys 0.1-0.14%).

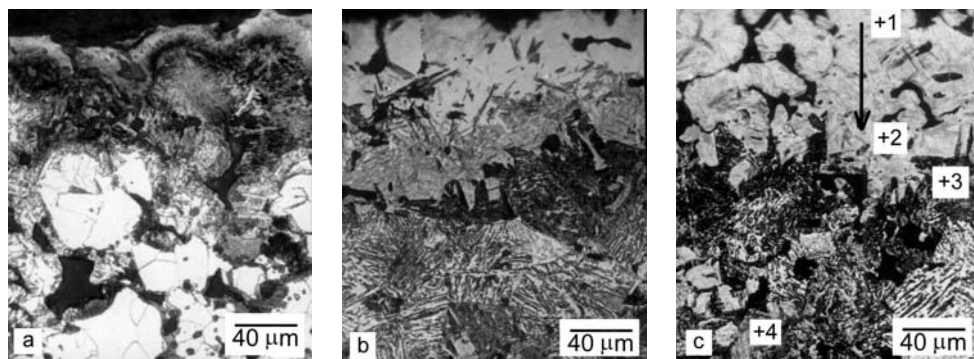


Fig.5. Microstructures of surface and subsurface layers of the sinter-borided alloys as in Fig.4. Optical micrographs, nital etched.

Figure 6 shows the microstructures of the core of the as-sinter borided specimens. The sinter boriding process also significantly changed the core microstructure of the alloys compared to that in Fig.4. The coarsening of the grains and the presence of ferrite and pearlite in the Fe-C alloy was recorded. The determined changes in the microstructure of the specimen cross-section could be caused only through a boron gas phase formed during the process.

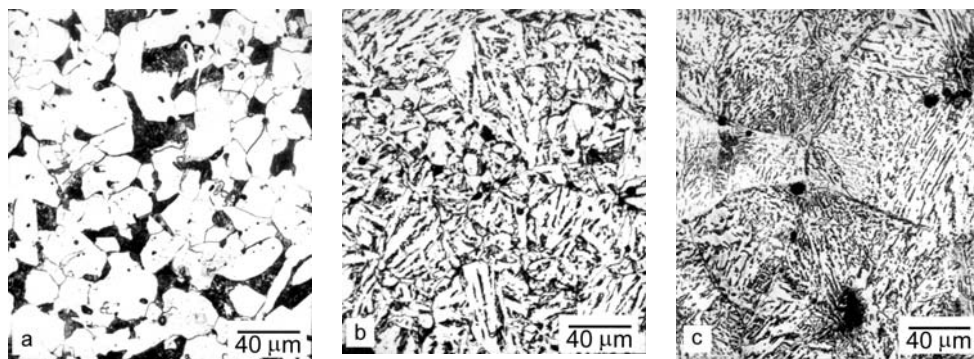


Fig.6. Microstructures of the core of the sinter borided alloys as in Fig.4. Optical micrographs, nital etched.

Microhardness and microanalysis

Sinter-boriding increased the microhardness of the microstructure constituents in the specimen cross-section, as shown in Fig.7. The microhardness of the white surface layer in Dist.SA alloy was the highest. The increase in mean microhardness values of the core grains in the microstructure of alloy steels can be related to the boron as follows from Figs.6b,c. On the other hand, due to the minimal solubility of boron in α -iron, a microhardness increase by sinter boriding of Fe-C steel was not determined.

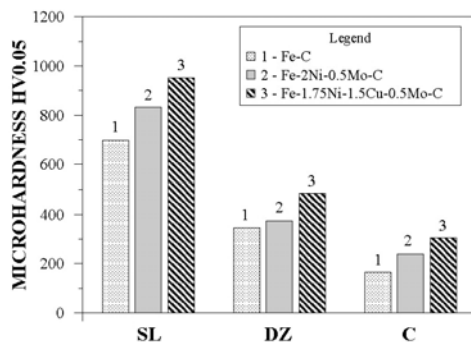


Fig.7. Microhardness (HV 0.05) of sinter borided alloys. SL - surface layer, DZ - diffusion zone, C - core [11].

The EDX microanalysis (LINK analyzer) in the as-sinter borided Fe-1.75-1.5Cu-0.5Mo-0.3C alloy was carried out in a perpendicular direction from surface toward the core in 6 points, and the results are listed in Tab.1.

Tab.1. Microanalysis of Mn, Ni and Cu concentrations in the microstructure of the sinter-borided Fe-1.75-1.5Cu-0.5Mo-0.3C alloy sample. Points 1-4 - Fig.5c (1,2 - white surface layer, point 3 - below the boundary of the surface layer, point 4 - diffusion zone), point 5, 6 - Fig.6c (core) [12].

Element	Analysed point					
	1	2	3	4	5	6
	Concentration [mass %]					
Mn	16.13	17.75	11.58	4.65	0.00	0.00
Ni	1.82	0.53	1.55	1.70	0.00	0.00
Cu	2.31	1.59	3.19	2.10	1.04	1.26

Note: Boron content hardly determinable

A continuous decrease in manganese content from the surface of the sample (16.3%) to the core (0%) is proof of its diffusion into the core only from the surface, and it could be carried out only through the vapour phase from the manganese carrier in the boriding mix. It is necessary also to note the higher concentrations of Ni and Cu in the surface boride layer compared to the core (base alloying element in the alloy, Ni -1.75%, Cu - 1.5%).

DISCUSSION

Boron and manganese are considered in the presented results as the main factors affecting the formation of a hard surface layer on the specimens, the change of the microstructures and increase in density and mechanical properties. The sinter boriding process proceeded through the gaseous compound formed by active constituents of the boriding mix and sintering H/N atmosphere. In this case the surface layer is not the pure Fe_2B or $\text{FeB-Fe}_2\text{B}$ phase known from the boriding of wrought steels, but the $(\text{FeMnB}, \text{Fe,Mn,Ni,Cu,B})$ -layers and therefore their hardness is lower than those of $\text{FeB-Fe}_2\text{B}$ layers. The thickness of the formed surface and diffusion layers was larger than of those formed in the boriding of wrought steel due to porosity. The interconnected porosity of the tested materials served for the entry of the gaseous boriding compound into the entire volume of

the specimens. As a consequence of this process there were new characteristic microstructures of the specimens formed below the diffusion zone.

The microstructures shown in Figs.5,6 compared to Fig.4, respectively are not known due to porosity in the boriding of wrought steels. There are significant differences in the character of the microstructures of the borided samples affected by the basic composition, especially between the Fe-C and both alloyed steels. Due to the very low solubility of boron in iron only a boride layer was formed on the surface of Fe-C specimens, without marked changes of the core microstructure, Fig.4 → Fig.6a even though the boriding gas was present in the pores. Besides this, the possible effect of gaseous manganese, as was previously supposed, did not penetrate the pores and by this did not act as a boriding activator. Only the hard surface layer was alloyed in high concentrations with manganese (gas phase manganisation) as shown in Table 1.

Markedly various core microstructures after sinter boriding were exhibited by the Fe-2Ni-0.5Mo and Fe-1.75Ni-1.5Cu-0.5Mo steels, Figs.6b and 6c. They differ only in copper content, Fig.4. This was only possible as the effect of the gaseous boriding compound which totally changed their character (higher density, coarser more uniform grains). The microanalysis of Ni in the core of the Dist. SA steel demonstrated zero nickel content, Table 1, Fig.6c. This could be explained according to the following assumption, relating to the results attained in plasma-assisted boriding of wrought steel – “It is even more likely that nickel atoms of the bulk would diffuse in the direction of the surface (towards oxygen)” at the simultaneous formation of nickel borides Ni_2B and NiB [13]. “Nickel has been found to concentrate below the boride layer in wrought steel; it entered the Fe_2B layer and in some instances promoted the precipitation of Ni_2B from the FeB layer” as stated in [1]. The same microanalysis including molybdenum should also be carried out in Fe-2Ni-0.5Mo steel. A special character was exhibited by the core microstructure of Fe-1.75Ni-1.5Cu-0.5Mo steel with copper, Fig.6c. As listed in Table 1, the copper content in the core was lower, and in the surface layer and diffusion zone higher than the added one. It means copper diffused from the core in the direction of the surface during the sinter boriding process was used. This was not observed in wrought steel boriding because copper does not belong among its common alloy elements. The core microstructures of the sinter borided alloy steels showed to what extent they were basically affected by boron through the gas phase. The density and mechanical properties of the tested materials as well as a general change of the microstructure character of alloy materials was the effect of enhanced solid-state sintering under the sinter boriding (boron gas phase activated sintering process) used. The effect is higher than that of boron liquid phase sintering [14].

In pack boriding: the direct transmission of a sufficient amount of boron by contact diffusion into the steel surface would be very rare due to the amount of diluent and therefore not liable. The transmission of boron from the gaseous compounds which on the steel surface decompose, e.g. $\text{B}_2\text{H}_6 + 2\text{Fe} = 3\text{H}_2 + 2\text{FeB}$ for processing in hydrogen is viable [6,15]. B_2H_6 (diborane) was the only compound used for boriding from gaseous phase but it is toxic and explosive, and toxic and corrosive are also boron halides (BCl_3 and BF_3), and therefore are not industrially used [13].

Processing in the work was conducted in dissociated ammonia, i.e. in cracked ammonia ($75\text{H}_2/25\text{N}_2$) atmosphere, i.e. the boriding process was also affected by nitrogen. On the basis of some results attained in the gas phase, for wrought steel boriding was suggested the use of a $75\text{N}_2/25\text{H}_2$ gas mixture instead of H_2 gas for its better performance, this because of the production of boride layers with minimum FeB content [1].

It was concluded that manganese, despite its high vapour pressure, is not necessary as an activator of this process. This rebuts the sentence that all elements with high vapour pressure can serve as activator of a boriding process as presented in [7]. The experimental proof of it is also the microstructure, Fig.6c, without manganese in the core, Table 1, in spite of this, that is characteristic for the applied sinter boriding process.

Considering the results attained in the recent sinter boriding process of powder iron and alloy materials, a more detailed thermodynamic analysis of the Fe-B-H-N-(Mn-O) system taking part in the mentioned process was carried out [16]. Hydrogen and nitrogen in the sintering process fulfilled the role of an activator for sinter boriding of the tested PM steels. The transfer of boron from the powder mix containing a solid boron carrier and diluent proceeded through the compound $B_3H_3N_{3(g)}$, which involves both hydrogen and nitrogen also as constituents of the sintering atmosphere.

This indicates a more simple method for the sinter boriding of PM steels under conventional sintering conditions, but also of wrought steels. The addition of a solid activator into the boriding mix is not necessary.

CONCLUSIONS

- The simultaneous sintering in a H/N atmosphere and sinter boriding (pack boriding) in a boriding powder mix consisting of ferroboration, (ferromanganese) and alumina as diluent resulted in the increased properties of Fe-C and alloy steels.
- The formation of hard surface layers with thickness depending on the composition of the alloy was determined. Alloyed materials are more advantageous for the process.
- Marked changes of the core microstructure of the samples, not comparable to the microstructure of as-sintered specimens, were observed. The core microstructures of the alloyed steels exhibited a new uniform coarse grained character.
- The diffusion of nickel and of copper from the core of the alloy specimens in a direction to the surface was by microanalysis demonstrated. This behaviour of nickel and especially of copper and their basic effect on the formation of microstructure of the corresponding alloy steel present a view of sinter borided steels. The mentioned effect of nickel and copper in PM steels used as alloying elements should be, in relation to sinter boriding, studied in more detail from physical-metallurgical as well from economical aspects.
- Selection of alloy elements for production of sintered steels should be adapted to the process for attaining high surface hardness together with high mechanical properties of the materials.
- Manganese, due to its high vapour pressure, as was assumed on the basis of previous literature data, did not act as a boriding activator.
- The transfer of boron from the powder mix containing a solid boron carrier and diluent proceeded through the gas compound $B_3H_3N_{3(g)}$, which involves both hydrogen and nitrogen as constituents of cracked ammonia used as the sintering atmosphere.
- An increase of density, tensile strength and hardness of sinter borided PM steels in H/N atmosphere was the effect of activated solid-phase sintering by $B_3H_3N_{3(g)}$ – boron gas phase activated sintering.

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