

NEW ASPECTS FOR SINTER BORIDING OF PM STEELS

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Dedicated to Prof. Dr. Gerhard Jangg, Dr.h.c. at the occasion of his 75th birthday

Abstract

Sinter boriding at 1120 °C and boriding at 1050 °C in boriding mix consisting of ferrobore and alumina in cracked ammonia and hydrogen of FeC, FeNiMoC, FeNiCuMoC and FeCrMoV(Mn)C steel specimens was carried out. The formed surface boride layers of an uniform thickness in dependence on composition and treatment conditions of the specimens were analyzed. The surface boride layers formed on Cr-alloyed steels with a microhardness up to ~1900 HV0.05 after boriding at 1050 °C in hydrogen were obtained. The effect of carbon content and of composition on the boride layer and core microstructure character and microhardness was demonstrated. The thermodynamic analysis of the Fe-H-N-B-(Mn) system showed the possible transfer mechanism of boron from the boriding mix on the metal surface through the compound $BH_{(g)}$.

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

INTRODUCTION

The combination of a high surface hardness and a low surface coefficient of friction of the boride layer also makes a significant contribution in combating the main adhesive and abrasive wear mechanism. Pack boriding is the most widely used boriding process because of its relative ease of handling, safety, and the possibility of changing the composition of the powder mix, and the resultant economic savings. Silicon carbide (SiC) and alumina (Al_2O_3) serve as diluents, and they do not take part in the reaction [1].

The disadvantages of pack and of other boriding processes are that they are inflexible and labor intensive, especially the work in closed containers in pack boriding, causing environmental problems due to the use of halides as necessary activators [2,3]. Therefore, these boriding processes are not commonly used in PM parts production.

The use of manganese in boriding mix as an activator in place of halides showed the possibility for the boriding of PM parts in common sintering furnaces. The chance to pack boride also PM steels under common industrial conditions without halides as activators, was based on the study that the elements with high vapour pressure such as Cu, S, P, Sb, can be used in boriding process in place of halides [4]. The vapour pressure of manganese is some orders of magnitude higher than that of the above mentioned [5-7]. Therefore, its use as an activator was experimentally verified. In Ref. [8] was presented a sinter boriding process at 1120 °C in cracked ammonia, it means a combined sintering and boriding for Fe-C and Fe-Ni-(Cu)-Mo-C alloys in a boriding mix containing manganese. Surface boride layers with a microhardness up to 1370 HV0.05 on the samples were formed. Another process on the same base was the boriding of sintered materials at a

temperature of 1050°C [9]. This pack boriding process furthermore enhanced the levels of tensile strength and hardness of PM alloys. Beside the formation of surface boride layers the change of the microstructure in whole cross-section of the specimens due to the formation of boron liquid phase at these processes was demonstrated. The real role of manganese in the mentioned pack boriding process of PM steels was not analyzed in detail.

In this paper, main data concerning sinter boriding and the boriding of carbon, and low alloyed nickel and chromium powder materials in a powder mix consisting of ferroboration and alumina without manganese in cracked ammonia and hydrogen, are presented.

EXPERIMENTAL PROCEDURE

For the investigation following base metal powders were used:

1.
 - Fe - water atomised iron powder (ASC100.29, Höganäs),
 - Fe-2% Ni-0.5% Mo (prealloyed, water atomised powder, Astaloy A, Höganäs),
 - Fe-1.75% Ni-1.5% Cu-0.5% Mo (diffusion partially bonded alloy powder, Distaloy SA, Höganäs)
- all with 0.3% natural graphite and 0.8% HW as lubricant addition.

The specimens 10 mm in diameter and 10 mm in height were from these powder mixtures at 600 MPa compacted.

2.
 - 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.

Natural graphite in amount of 0.2% (K11, K21, K31), of 0.5% (K12, K22, K32) and of 0.9% (K13, K23, K33) and 0.8% HW as lubricant was admixed to the powders. From the powder mixtures the impact toughness (10x10x55 mm) and bending strength bars (10x5x55 mm) at 700 MPa were compacted.

The powder boriding mix consisted of ferroboration (Fe18B, <40 µm) and alumina as diluent.

The following pack boriding processes were carried out:

- sinter boriding process (combined sintering and pack boriding) at 1120°C for 1 h in a retort furnace in cracked ammonia or in a tube furnace in hydrogen,
- the boriding of sintered samples (sintering at 1120°C for 1 h in cracked ammonia) followed by pack boriding at 1050°C for 1 h and 2 h in a tube furnace (TU Vienna) in hydrogen was carried out.

RESULTS

Boriding in powder mix with manganese

In this chapter, for a comparison the micrographs of some samples borided in a powder mix containing manganese under the conditions described in Ref. [9] are presented. In Figure 1a is shown the surface boride layer on a Fe-0.3C sample. A small (in thickness) boride layer and being non-steady in relation to the sample surface was in some cases characteristic for this process. This feature of the surface layer can be a consequence of the

dissolution of the base material. As shown in Fig.1b, on the FeNiCuMo sample a eutectic-like thicker surface boride layer was formed resulting from the presence of copper in this alloy. This feature of the layer was proof that under process conditions a boron liquid phase was formed. The progressive coarsening of grains, with an eutectic network as a consequence of a boron liquid phase existing during boriding, also in the core of the sample, was observed as shown in Fig.2. The as-sintered starting microstructure of this alloy is shown in Fig.3.

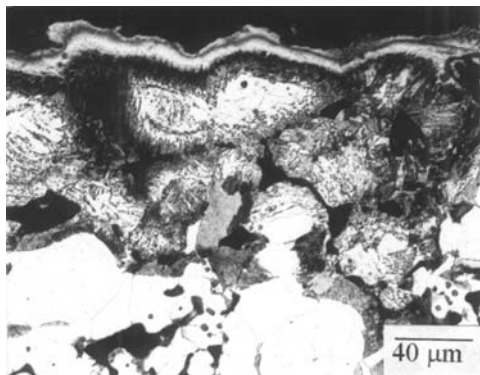


Fig.1. Microstructure of surface boride layer with subsurface zone formed in sintered specimens borided at 1050°C for 2 h in cracked ammonia in boriding mix with manganese.

a) Fe-0.3C (microhardness 700 HV0.05), b) Fe-1.75Ni-1.5Cu-0.5Mo-0.3C alloy (microhardness 920 HV0.05). Nital etched.

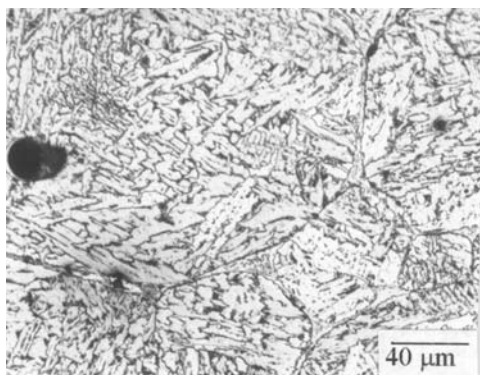


Fig.2. Core microstructure of Fe-1.75Ni-1.5Cu-0.5Mo-0.3C alloy borided at 1050°C for 2 h. Boriding as in Fig.1. Nital etched.

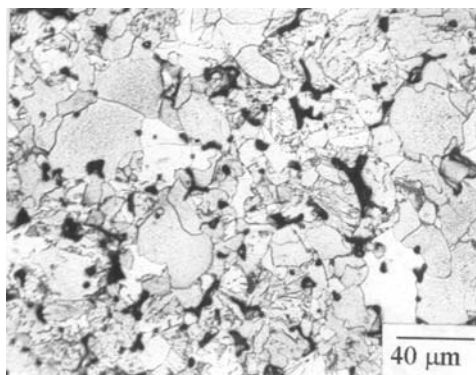


Fig.3. Microstructure of as-sintered alloy as in Fig.2. Sintering at 1120°C for 1 h in cracked ammonia. Nital etched.

The changes in Mn, Ni and Cu contents from the surface (boride layer) up to the core of the FeNiCuMoC specimen, measured in 6 points, are given in Tab.1.

Tab.1. Mn, Ni and Cu content in cross-section of the Fe-1.75a-1.5iCu-0.5Mo-0.5C sample, pack borided at 1050°C for 2 h in boriding mix with manganese in cracked ammonia (see Fig.1b). Microanalysis EDAX - LINK, SEM Tesla BS 340 [10].

Element	Point					
	*1	*2	**3	4	5	+6
	Content [%mass]					
Mn	16.1	17.8	11.6	4.7	0.0	0.0
Ni	1.82	0.53	1.55	1.70	0.00	0.00
Cu	2.3	1.6	3.2	2.1	1.0	1.3

*boride layer, ** white layer, +core of the specimen

A great effect of manganese vapour formation due to the sublimation of manganese in boriding mix and of its condensation on the metal and open pore surface was demonstrated [7]. The depletion in Ni and Cu content in the core of the specimen and enrichment of the surface layer will be necessary to study.

TREATMENT IN POWDER BORIDING MIX WITHOUT MANGANESE

For the experiments, the powder boriding mix consisting of ferroboron and alumina was used.

Sinter boriding in cracked ammonia

The samples of Fe, Fe-2Ni-0.5Mo and Fe-1.75Ni-1.5Cu-0.5Mo alloys, in the form of cylinders ($\varnothing 10 \times 10$ mm) were sinter borided at 1120°C for 1 h in the mentioned powder mix in cracked ammonia. In Figure 4 is shown the surface boride layer with the sublayer zone in the Fe sample. The uniform thickness of the boride layer with a sharp passing into the interior with a change of the microstructure of the specimen was observed. The uniform coarsening of the new ferrite-pearlite grains with eutectic network was demonstrated. The uniform surface boride layer also on the Fe-2Ni-0.5Mo and on Fe-1.75Ni-1.5Cu-0.5Mo samples was formed, as shown in Figs.5, 6. A new microstructure, characteristic for boron liquid phase sintering below the surface zone in the whole cross-section of the samples was formed. A marked distinction in the character of the layer when compared with Figs.1-3 is seen.

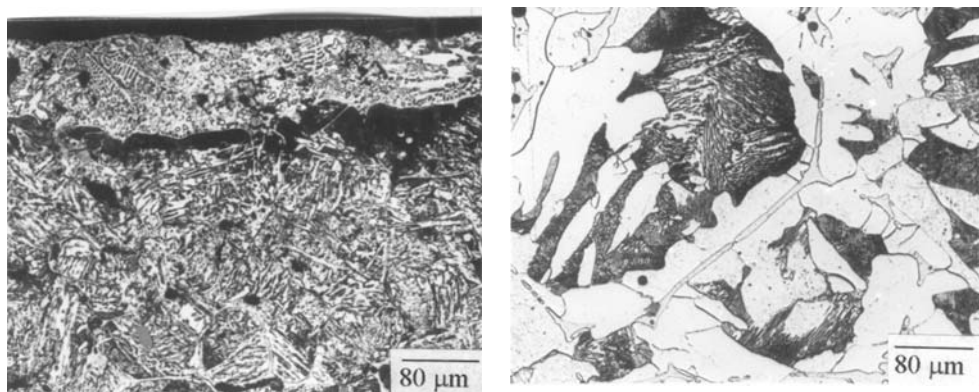


Fig.4. Microstructure of: a) surface boride layer, b) core in Fe-C specimen sinter borided at 1120°C for 1 h in cracked ammonia. Nital etched.

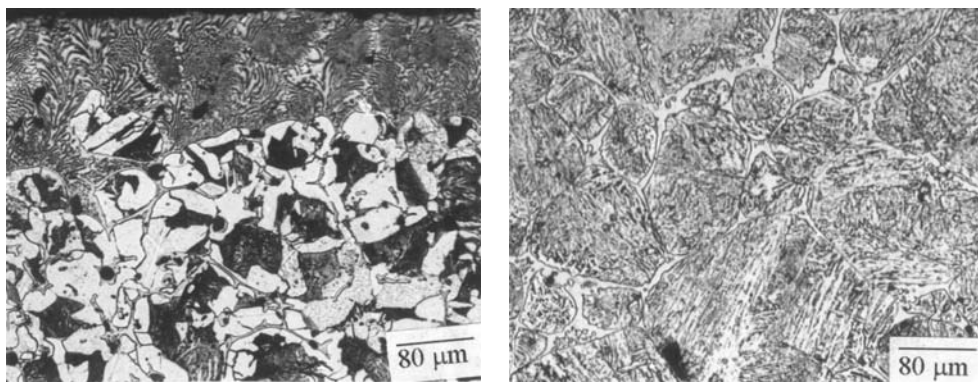


Fig.5. Microstructure of: a) surface boride layer, b) core in Fe-2Ni-0.5Mo-C specimen sinter borided at 1120°C for 1 h in cracked ammonia. Nital etched.

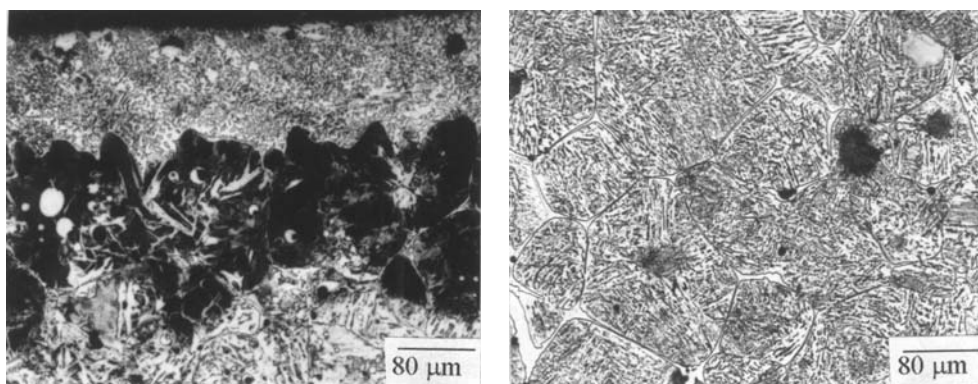


Fig.6. Microstructure of: a) surface boride layer, b) core in Fe-1.75Ni-1.5Cu-0.5Mo-C specimen sinter borided at 1120°C for 1 h in cracked ammonia. Nital etched.

Sinter boriding and boriding in hydrogen

For these experiments the specimens based on prealloyed Fe-Cr-Mo-V-(Mn) powders (K1, K2, K3) were used. Sinter boriding at 1120°C for 1 h and boriding at 1050°C for 1 and 2 h in mentioned boriding powder mix in hydrogen was carried out. Apparent surface hardness of treated specimens is shown in Tab.2.

Tab.2. Apparent surface hardness HRC of samples sinter borided at 1120°C for 1 h and borided at 1050°C for 1 and 2 h and hardness HV10 of as-sintered specimens.

Treatment [°C/h]	Alloy								
	Fe-1Cr-0.3Mo-0.3V			Fe-3Cr-0.3Mo-0.3V			Fe-1Cr-0.7Mn-0.5Mo		
	0.2C	0.5C	0.9C	0.2C	0.5C	0.9C	0.2C	0.5C	0.9C
1120/1	63	-	-	-	-	79	50	-	-
1050/1	56	72	-	73	76	-	-	-	-
1050/2	41	-	76	62	-	86	-	59	78
*1120/1	98	168	188	122	224	285	92	147	181

* as-sintered hardness HV10; C_c: 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

A marked increase in surface hardness in both processes was attained. The hardness of sinter borided and borided specimens increased with increasing carbon content and in relation to the base composition. Especially very high hardness of 86 HRC in K23 (0.9C) alloy borided at 1050°C for 2 h was obtained.

Microstructure

Characteristic microstructure of surface boride layer in K12 and K21 alloy specimens borided at 1050°C are shown in Fig.7. The white layers were formed in the surface material area of the specimens. The change in the feature of the surface boride layer and of the subsurface zone in comparison with Figs.1-6 was affected by the difference in base composition of the specimens.

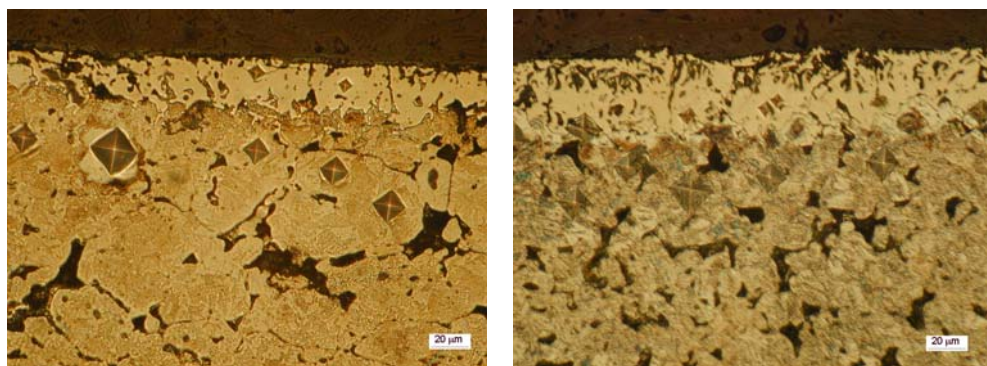


Fig.7. Microstructure of surface boride layer formed at boriding at 1050° C for 1 h on specimen: a) K12 (Fe-1Cr-0.3Mo-0.3V-0.5C), b) K21 (Fe-3Cr-0.3Mo-0.3V-0.2C). Etching in (H₂O, HF, HNO₃).

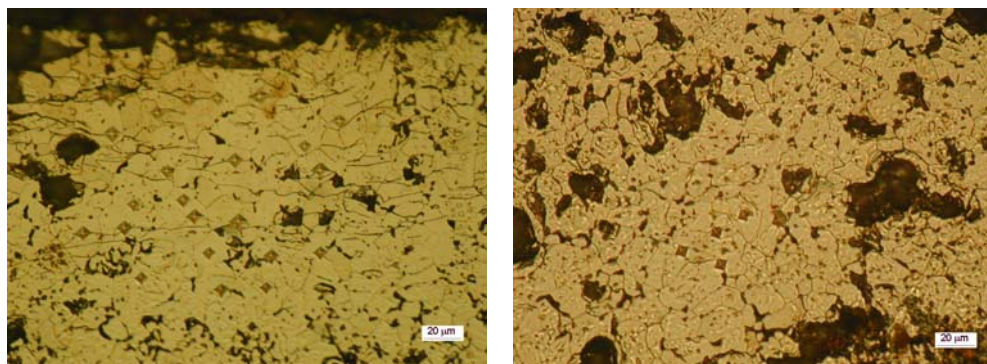


Fig.8. Microstructure of K23 (Fe-3Cr-0.3Mo-0.3V-0.9C) specimen borided at 1050°C for 2 h: a) surface zone, b) core. Etching in (H₂O, HF, HNO₃).

No structurally defined characteristic surface boride layer formation on the specimen K23, in comparison with the sample treated for 1 h (Fig.7) was observed, as shown in Fig.8. A new fine grained ferrite-like microstructure was formed. The same character of the microstructure in the whole cross-section of the specimen (Ø10x10 mm) was formed, as shown in Fig.8b. The formation of the microstructure of such character was not observed in any other alloy. It is possible only to suppose and analyze that the surface

boride layer formed during first time stage of boriding (1 h), during the following stage (2 h) dissolved, and boron diffused into the whole cross-section of the specimen, causing a substantial change in the microstructure character and in properties, especially in increase of microhardness also in the core of the specimen.

Microhardness values of the boride layers and of the core microstructure of these specimens are given in Tab.3. The microhardness values in the surface boride layers were in this case substantially higher than those obtained in Fe-C and Fe-Ni-(Cu)-Mo-C alloys [7, 8].

Tab.3. Microhardness HV0.05 (LECO microhardness tester LM700AT) of the surface boride layer and of the core of the specimens borided at 1050°C for 1 and 2 h.

Treatment [°C/h]	Value	Alloy					
		Fe-1Cr-0.3Mo-0.3V-0.5C		Fe-3Cr-0.3Mo-0.3V-0.2C		Fe-3Cr-0.3Mo-0.3V-0.9C	
		Layer	Core	Layer	Core	Layer	Core
1050/1	Mean	1588	459	1719	320	-	-
	Range	1329-2125	276-534	1426-2148	188-441	-	-
1050/2	Mean	-	-	-	-	1772	1910
	Range	-	-	-	-	1586-2191	1509-2274

The effect of base composition of the alloys, characterized by alloying with carbide and nitride former elements, such Cr, Mo, V, was manifested in relatively high macro- and microhardness values of these alloyed steels, especially of K23 alloy. The thermodynamic and physic-chemical conditions for the formation of a microstructure with such high hardness should be the reason for the basic analysis of the boriding process conditions and materials used.

Thermodynamic

It was proved that the use of the simplest boriding mix consisting of boron donor and diluent was more beneficial for the formation of an uniform surface boride layer on the specimen, compared with manganese assisted boriding. The results showed that the boriding process proceeded also in this case in the presence of a gas phase facilitating the transport of boron from the solid powder mix on the metal surface, and then into the core of the sample. It follows from this, that the activator 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 investigated 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).

From the thermodynamic (TD) analysis of the Fe-B-H-N- (Mn-O) system, considering the mentioned phases, the following results can be concluded [11]:

- transfer of boron from the powder mix containing ferroboron as boron donor, in 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 is from the thermodynamic point of view an independent process, and is realized through the sublimation in form of manganese vapour,
- oxygen in the system, from the point of view of the manganese transfer, forms MnO in the metal phase if the gas phase contains $>0.7\% \text{ O}_2$.

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. Manganese affects the character of surface boride layer and mechanical properties of the alloy. As an activator in the boriding process used may be considered only hydrogen and nitrogen in the atmosphere, and the effect of their mutual portion on the mechanism and kinetics of the reactions, and on the properties of borided materials. These results, relating the transfer of boron through a gas activator ($\text{BHN}_{(\text{g})}$) in pack boriding process, particularize the data in Ref. [12], that the boron can be transferred through the compound $\text{BN}_{(\text{g})}$. The conclusion, considering the transfer of B through the compound $\text{B}_3\text{H}_3\text{N}_{3(\text{g})}$ is universally valid, not only for PM materials. The H-N containing atmospheres, as the base sintering atmospheres in powder metallurgy, facilitate the further development and possible realization of the mentioned process in production of PM parts.

CONCLUSIONS

From the study it was concluded:

- Manganese assistance in powder boriding mix for PM steels is not necessary as activator. Powder boriding mix consisting of boron donor, e. g. ferroboration and of diluent, e.g. alumina, is effective for boriding of PM and probably of wrought steels in H-N containing atmospheres.
- Hydrogen and nitrogen in the sintering atmosphere fulfil the role of an activator for sinter boriding and boriding processes for PM steels.
- Transfer of boron from the powder mix containing solid boron donor proceeds through the compound $\text{B}_3\text{H}_3\text{N}_{3(\text{g})}$.
- Uniform surface boride layers were formed on investigated steel specimens 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 markedly high microhardness up to $\sim 1800 \text{ HV}0.05$.
- 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 new uniform fine-grained microstructure with the microhardness of 1800 to 1900 HV0.05 in it, throughout the cross-section.
- The application of sinter boriding and boriding of PM steels considering mentioned new aspects, may be a contribution to the development of structural material of special properties.

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