

# THEORY AND TECHNOLOGY OF SINTERING, THERMAL, AND CHEMICOTHERMAL TREATMENT PROCESSES

## PHYSICOCHEMICAL CHARACTERISTICS OF POWDER BORONIZING

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Powder boronizing is the simplest and most convenient as well as a comparatively cheap method of surface hardening of parts operating under intense wear conditions. The method is at present used in industry, particularly in the service and maintenance departments of factories and enterprises.

The principal component of powder mixtures for boronizing is boron carbide. The process can be intensified by employing various activating additions [1]. The following mixtures have been used for powder boronizing (wt.%): 1)  $84\text{B}_4\text{C} + 16\text{Na}_2\text{B}_4\text{O}_7 + 1.5\text{NaCl} + 1.25\text{NH}_4\text{Cl}$  [6]; 2)  $50\text{B}_4\text{C} + 50\text{Na}_2\text{B}_4\text{O}_7 + 1.5\text{NaCl} + 1.25\text{NH}_4\text{Cl}$  [7]; 3)  $70\text{B}_4\text{C} + 30\text{Na}_2\text{B}_4\text{O}_7 + 1.5\text{NaCl} + 1.25\text{NH}_4\text{Cl}$  [7]; 4)  $85\text{B}_4\text{C} + 15\text{Na}_2\text{B}_4\text{O}_7 + 2.5\text{KBF}_4$  [8]; 5)  $100\text{B}_4\text{C}$  [4]; 6)  $100\text{B}_4\text{C} + 1.25\text{NH}_4\text{Cl}$ ; 7)  $100\text{B}_4\text{C} + 1.25\text{KBF}_4$ ; 8)  $100\text{B}_4\text{C} + 1.25\text{NH}_4\text{I}$ ; 9)  $80\text{B}_4\text{C} + 20\text{Na}_2\text{CO}_3$  [9]; 10)  $80\text{B}_4\text{C} + 20\text{Fe}_2\text{O}_3$ ; 11)  $40\text{B}_4\text{C} + 60\text{Fe}_2\text{O}_3$ ; 12)  $80\text{B}_4\text{C} + 1.25\text{NH}_4\text{Cl} + 20\text{Fe}_2\text{O}_3$ ; 13)  $80\text{B}_4\text{C} + 20\text{Al}_2\text{O}_3$ ; 14)  $20\text{B}_4\text{C} + 80\text{Al}_2\text{O}_3$  (mixtures 10-14 have been formulated by the authors).

Practical usefulness is the main requirement for a boronizing powder mixture. By this is meant that such a mixture must be characterized by high activity, as measured by the thickness of the coating it produces, and be capable of being used many times without regeneration or comminution. In powder boronizing with mixtures 1-4 fairly high activity is accompanied by some sinterability of the charge. The latter characteristic hinders the extraction of parts from the container after boronizing, which must therefore be performed, at least partly, by hand, and may lead to mechanical chipping of the boronized surfaces. Furthermore, a mixture exhibiting sinterability must be crushed before it can be reused.

From the results of our own investigations into the effect of small activating additions on the boronizing ability of technical boron carbide it follows that the sinterability of a charge depends to a large extent on whether or not it contains a halide activator ( $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{I}$ ,  $\text{KBF}_4$ , or  $\text{AlF}_3$ ).

In our work boronizing was performed for 4 h at a temperature of  $1000^\circ\text{C}$  in a container with a liquid seal. Specimens of chromium stainless steels of various chromium contents and of chromium-nickel steels of compositions chosen from two sections of the Fe-Ni-Cr diagram were used. A technically pure boron carbide powder of grain size No. 5 (mixture 5) proved to be the only virtually unsinterable material; however, it was also the least active of all the materials investigated. Because of this, it was decided to carry out a detailed investigation of sintering processes in a charge consisting of technically pure boron carbide alone.

In order to analyze the processes taking place in a charge, it is necessary to obtain an understanding of the mechanism of formation of a boride layer on a metal being treated. Of particular interest is the question of what chemical reactions can occur at the metal/impregnating-charge interface. The chemistry of the process depends on many factors. Thus, e.g., the number of atoms being adsorbed on the metal surface would be expected to be affected by the process temperature, the partial vapor pressures of the components of the mixture, chemical affinity between the impregnating elements and the metal being treated, the rates of supply of the gaseous mixture being generated to the metal surface and of removal of the reaction products, and the like. At present it is not possible to allow for the interaction between all these factors.

It is known that the higher the absolute value of the negative isobaric-isothermal potential of a chemical reaction, the greater is the probability of the reaction's proceeding to completion [2]. The thermodynamics of boronizing in mixtures containing halide activators has already received a good deal of investigation [3], but the mechanism of impregnation with oxygen transport of boron is not yet fully understood. In the work described below an attempt was made to elucidate the processes occurring during boronizing in a charge without a halide activator.

Calculations of the isobaric-isothermal potentials of reactions which could be involved in boronizing in a technically pure boron carbide charge (Table 1) revealed that impregnation of a metallic surface with boron can

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TABLE 1. Calculated Isobaric-Isothermal Potentials of Possible Chemical Reactions in Boronizing in Technically Pure Boron Carbide

No.	Reaction	Isobaric - isothermal potential of reaction at temp., °K, of			
		298	1000	1100	1200
1	$B_4C + 4Fe \rightarrow 4FeB + C$	-58,60	-61,36	-63,66	-65,75
2	$B_4C + 8Fe \rightarrow 4Fe_2B + C$	-13,86	-9,61	-9,05	-7,76
3	$B_4C + 2Fe_2O_3 + 5C \rightarrow 4FeB + 6CO$	+99,40	-80,06	-107,26	-133,046
4	$B_4C + 4Fe_2O_3 + 11C \rightarrow 4Fe_2B + 12CO$	+202,14	-34,11	-95,25	-142,36
5	$B_4C + 8FeO + 7C \rightarrow 4Fe_2B + 8CO$	+193,1	-14,41	-44,25	-73,36
6	$B_4C + 4FeO + 3C \rightarrow 4FeB + 4CO$	+44,87	-63,76	-81,25	-93,55
7	$2B_2O_3 + 4Fe \rightarrow 4FeB + 3O_2$	+429,0	+380,48	+325,28	+311,01
8	$2B_2O_3 + 8Fe \rightarrow 4Fe_2B + 3O_2$	+545,64	+466,49	+456,40	+447,49
9	$2B_2O_3 + 4Fe + 3C \rightarrow 4FeB + 3CO_2$	+145,24	+56,68	+41,48	+27,06
10	$2B_2O_3 + 4Fe + 6C \rightarrow 4FeB + 6CO$	+232,2	+55,38	+24,68	+1,09
11	$2B_2O_3 + 8Fe + 3C \rightarrow 4Fe_2B + 3CO_2$	+268,89	+182,69	+172,6	+163,54
12	$2B_2O_3 + 8Fe + 6C \rightarrow 4Fe_2B + 6CO$	+348,84	+178,79	+155,8	+134,59
13	$B_2O_3 + Fe + C \rightarrow FeO + CO_2 + 2B$	+133,48	+103,55	+99,85	+95,40
14	$B_2O_3 + Fe + 2C \rightarrow FeO + 2B + 2CO$	+162,13	+101,25	+93,25	+95,75
15	$B_2O_3 + 3Fe_2O_3 \rightarrow 2Fe_3O_4 + 2B$	+332,20	+268,20	+269,45	+251,40
16	$B_2O_3 + 6FeO \rightarrow 3Fe_2O_3 + 2B$	+105,22	+125,10	+127,85	+129,30
17	$B_2O_3 + 5Fe \rightarrow 3FeO + 2FeB$	+250,45	+207,37	+200,89	+194,75
18	$B_2O_3 + 3Fe \rightarrow 3FeO + 2B$	+110,39	+102,45	+102,05	+102,15
19	$B_4C + O_2 \rightarrow 4B + CO_2$	-80,95	-81,7	-81,75	-81,90
20	$2B_4C + 7O_2 \rightarrow 4B_2O_3 + 2CO$	-1307,5	-1141,4	-1120,1	-1099,7
21	$B_4C + 4O_2 \rightarrow 2B_2O_3 + CO_2$	-653,75	-570,7	-550,05	-549,9
22	$B_4C + CO_2 \rightarrow 4B + 2CO$	+41,95	+11,6	+7,25	+3,1
23	$B_4C + 7CO_2 \rightarrow 2B_2O_3 + 8CO$	-165,15	-197,5	-204,04	-209,9
24	$B_4C + B_2O_3 \rightarrow 6B + CO_2 + 1/2O_2$	+205,45	+162,0	+157,75	+152,0
25	$B_4C + 3Fe \rightarrow Fe_3C + 4B$	+18,1	+13,65	+13,30	+12,95
26	$B_2O_3 + 2Fe \rightarrow Fe_2O_3 + 2B$	+109,0	+110,0	+110,65	+111,2
27	$2B_2O_3 + 6C \rightarrow 4B + 6CO$	+376,0	+201,3	+177,6	+155,1
28	$2FeB + O_2 \rightarrow 2FeO + 2B$	-40,69	-28,78	-26,57	-24,32
29	$2FeB + 5/2O_2 \rightarrow 2FeO + B_2O_3$	-367,79	-302,07	-291,29	-282,65
30	$4B + 3O_2 \rightarrow 2B_2O_3$	-572,8	-489,0	-478,3	-468,0
31	$5B_2O_3 + B_4C \rightarrow 7B_2O_2 + CO$	-648,4	-511,45	-504,15	-495,95
32	$B_2O_2 + 2Fe \rightarrow 7FeO + CO$	+51,63	+48,45	+48,20	+24,95
33	$Fe + B \rightarrow FeB$	-17,98	-18,56	-19,13	-19,62
34	$Fe_2B + B \rightarrow 2FeB$	-29,16	-31,5	-32,78	-34,12
35	$2Fe + B \rightarrow Fe_2B$	-6,79	-5,63	-5,47	-5,12
36	$Fe + B_4C \rightarrow 4[B] \text{ (in } Fe_{20}) + C$	-	+77,0	+97,0	-
37	$B_2O_2 + 2Fe + C \rightarrow 2FeB + CO_2$	-19,9	-35,93	-38,95	-42,3
38	$FeB + 4Fe_2O_3 \rightarrow 3Fe_3O_4 + B$	-2,04	-13,135	-14,67	-15,67
39	$B_2O_2 \rightarrow [B]_{M_{Fe}B} + 2B_2O_3$	-241,9	-201,6	-197,3	-193,2

occur through a reactive mechanism, with boron carbide coming into direct contact with the metal (reactions 1 and 2) or reaching the metal through a gaseous phase (reactions 33-35 and 37). It should be noted that the presence of a small quantity of oxygen and carbon oxides in the reaction volume may bring about the formation of boric anhydride and free boron in the actual charge (reactions 19-21, 23, and 28-30).

It has already been established that steel cannot be impregnated by direct contact with boric anhydride ( $B_2O_3$ ) and its vapor [4]. This finding is borne out by thermodynamic calculation (reactions 17 and 18). However the presence in the charge of a small quantity of free carbon (e.g., in the form of carbon black) [5] may shift the equilibrium of the boride formation reaction to the right (reaction 10), in which case the possibility of impregnation with boron as a result of direct contact between solid boron carbide particles, liquid boric anhydride, and metal cannot be ruled out.

A thermodynamic analysis of possible chemical reactions in boronizing with technically pure boron carbide showed that the presence of iron oxides in the charge may promote the appearance of borides in the mixture itself (reactions 3-6). This phenomenon in turn will provide an additional source of atomic boron and boric anhydride as a result of oxidation reactions (28 and 29). The reaction of boric anhydride with boron carbide ensures the formation of the lower boron oxide  $B_2O_2$  in gaseous form (reaction 31), and direct contact between the latter and a steel surface in the presence of free carbon intensifies the boronizing process (reaction 37). The presence of the lower boron oxide in the container atmosphere facilitates the main reaction of the boronizing process (39).

Thus, iron oxides present in the charge may intensify the boronizing process and reduce the depletion of the mixture by ensuring that it is "topped up" with boric anhydride (reverse reactions 15-18, 26, and 32). To verify this hypothesis, boronizing experiments were carried out in a charge consisting of boron carbide and magnetite (enriched Kursk Magnetic Anomaly ore) (mixtures 10 and 11). In these experiments the mixture was found to exhibit no sinterability and comparatively little adhesion to the surface, and its activity was only slightly lower than that of mixtures with halide activators: On 08Kh17 (0.08% C-17% Cr) steel the boronized layers were 140-150 and 150-170  $\mu\text{m}$  thick, respectively. Replacing magnetite with alumina (mixtures 13 and 14) sharply decreased the activity of the charge, as a result of which virtually no boride layer formation was observed. This may be taken as evidence that iron oxides activate the boronizing process in the case of oxygen transport of boron.

It should be noted that iron borides forming on a metal surface and in an impregnating charge readily oxidize (reactions 28 and 29 and reverse reactions 7-9). Because of this, boronizing in a mixture of boron carbide and magnetite should be performed in a hermetically sealed container or in a protective atmosphere.

In an open container boronizing was accompanied by severe corrosion of the boride coating, but a boronized layer was nevertheless obtained. At the process temperatures the boron impregnation reactions probably predominated over the boride oxidation reactions, as otherwise a boronized layer would not have formed at all (reverse reactions 7 and 8). It is possible that the main action of oxygen began during cooling from the boronizing temperatures, because with fall in temperature the probability of oxidation grew (the absolute value of the isobaric-isothermal potential of the reaction tended to increase).

Metallographic examinations of the structure of boride layers on transverse microsections revealed varying degrees of porosity at their boride-layer/matrix interfaces. The size of the pores and their pattern of distribution changed depending on the composition of the impregnating charge. It must be assumed that the decrease in the area of contact between a boride layer and its matrix due to porosity and the large difference in linear thermal expansion between the borides and the metal of the matrix can lead to the exfoliation of the layer.

In the boronizing of a number of chromium and chromium-nickel steels in a mixture of boron carbide and ammonium iodide complete peeling of coatings, in the form of boride crusts, from specimens was observed. Use of chlorine-containing activators ( $\text{NaCl}$  and  $\text{NH}_4\text{Cl}$ ) slightly diminished the extent of peeling of boride layers. In this case the layers exhibited extensive porosity, with pores forming continuous bands at the boride-layer/matrix interfaces. In boronizing in mixtures with fluoride activators ( $\text{AlF}_3$  and  $\text{KBF}_4$ ) the intensity of pore formation was less, the pores were discrete and formed no bands, and there was only slight peeling of the layers.

It must be noted that boronizing without halide additions (10 and 11) with oxygen transport of boron enabled better-quality, dense layers to be obtained with a much lower pore concentration at the boride-layer/matrix interfaces compared with the above-described case. This was probably the reason why the most compact layers were formed in mixtures with an oxygen-containing activator.

Thus, on the basis of this investigation it is possible to recommend mixtures with magnetite for adoption in industry. Such mixtures give high quality of coatings and possess good processing characteristics: They exhibit no sinterability, are comparatively nontoxic and noncorrosive, can be used repeatedly without regeneration or the addition of fresh materials, and suffer little loss of activity compared with halide-containing mixtures. The most suitable for practical application was found to be mixture 10 (80%  $\text{B}_4\text{C}$  + 20% magnetite). One practical drawback of this mixture is that it has a slight tendency to adhere to the surface being treated, but the adhering particles can readily be removed from parts by washing in hot water.

## CONCLUSIONS

1. According to thermodynamic calculations, in the initial stage boronizing may occur through a dual mechanism: simultaneous active diffusion of atomic boron and direct reaction resulting in the formation of higher iron borides.
2. It is demonstrated that in powder boronizing the nature of the activator has a pronounced effect on the concentration and character of distribution of pores in the boride layer and hence on the quality of the resultant coating.
3. On the basis of data yielded by thermodynamic calculations and experimental results it is shown that iron oxides can be successfully employed as activators of the powder boronizing process.

4. Experiments have shown that a powder mixture consisting of 80% boron carbide and 20% magnetite is comparable in activity to mixtures with halide activators, but surpasses them in other respects: It possesses good processing characteristics, is nontoxic, shows no sinterability, and is capable of being used repeatedly without regeneration.

5. Mixtures with oxygen transport of boron offer greatest promise for the boronizing of high-alloy stainless steels.

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