EMINA D. POŽEGA[1], *SVETLANA LJ. IVANOV*[2]
ALEKSANDRA T. IVANOVIĆ[1]

Scientific paper
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Influence different chemical composition and percentage rate of added activators on depth of boride layer

During sintering and chemical-thermal treatment-boriding of samples from iron powder generates adequate boride layer, so in this paper are presented results of research dependence of depth of boride layer from composition of mixture which are used for boronizing process. Basic mixture used for boriding of investigated samples from iron powder is modified by addition of activators different chemical composition and in different percentage rate. The obtained boride layers vary in depth and quality (porosity, the contact with metal). In order to obtain better boride layers and to show certain appearances during boriding, it was necessary to choose mixture for boronising and to determine the most useful activators and their ratio. Processing of eksperimentaly obtained results is carried out by using Simplex method. Results of investigation and mathematical processing allow us to choose composition of mixture for boriding with depth change which is given in advance. It has been observed that simultaneously with boriding also sintering occured, and this fact offers a wide application possibility in the chemical-thermal treatment for sintered materials. It is possible to completely avoid sintering process of products wich are obtained with powder metallurgy.

***Key words**: sintering; boriding; boride layers; activators; Simplex method*

1. INTRODUCTION

Thermochemical boriding of iron alloys both single Fe_2B phase and FeB-base polyphase coating to be obtained and then used mainly to improve surface hardness and wear resistance of components for tribological applications [1-3]. Boride cotings, in fact, display considerable hardness and compactness except for the outermost, few micrometers thick region which,being constituted by differently oriented crystals, is friable and, consequently, should be removed from the component by means of a surface finishing procedure [4].

Iron materials obtained by technology of powder metallurgy - pressuring iron powder and sintering greatly are different from materials formed by classic procedures (casting, plastic deformation) how by matter so by properties.

One of fundamental difference at matter is presence porosity at these materials.

Porosity, deformation bullets, great length boundary bullets and sl. are factor which certainly influense in proces diffusion permeation sintering iron materials. Regime of sintering iron powder are contiguity regimes of chemically-thermical process and because of that sintering of compacts occurs. Within these researches it is necessary to predict possibilities of obtainig boroning layers at the compacts of iron powder, and also possibilities of sintering in presence of chosen activator.

This paper makes contribution to the research work of depth boride layers by boroning compacts from iron powder beside together fluctuation composition mixture for boroning, wherewith obtain difffusing layers with difference depth. This should help us to sort out changes arise due to boroning [5-7], from changes which arise due to activated sintering [8-11, 12, 13]. Transportation process of matter during sintering of metal powder leads to the recovery of greater contact between particles of powder, and finally, to the shrinkage and increase of density.

The mechanism and kinetics of sintered materials diffusing layers differs considerably from that of casting materials [14 -16]. Therefore, the chemical-thermal treatment of sintered materials seems to be very delicate.

The kinetics of diffusing layers formation, the structure, properties and phase composition depend on a large extent of the structural characteristics of sintered materials. Porosity of sintered materials has a significant influence on diffusing layers quality. What should be noticed is the shape, dimensions and even contribution and what is most important, the kind of pores (open or closed).

For chemical-thermal treatment of materials with closed porosity, intrusion of active atoms from satu-

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Address authors: [1]Mining and Metallurgy Institute Bor, POB 152, 19210 Bor, Serbia [2]University in Belgrade, Tehnical faculty in Bor, POB 50, 19210 Bor, Serbia, E-mail: emina.pozega@irmbor.co.rs

rating environment into the inner part of the sample is excluded, so the diffusing layer formation on sintered materials differs from the one on casting materials due to the presence of closed porosity, crystal structure defect, crystal lattice deformity, larger length of grains and subgrain boundaries and the presence of admixtures. Due to the mentioned facts, the diffusion process is accelerated in sintered materials.

The process of saturation with most elements causes lessening of sections and closing of pore channels due to diffusion layers formation on their surface and additional sintering as well. Therefore, it is possible to determine that sintered materials transit very quickly from the semi contiguous porosity to closed porosity materials.

When talking of open porosity materials, active environment penetration through open pores into the inner part of the compact has strong influence on the speed of diffusing layer formation and their structure. When examining saturation of open porosity materials, one should keep in mind that the initial porosity changes in the saturation process. Diffusing layer formation on the open pores surface goes along with volume enhancement, therefore, the section surface of the open pores channel diminishes during the chemical-thermal treatment. Over time, this hinders the penetration of saturating element into the inner part of the compact. Articles published on these problems, allow several assumptions [6, 7, 17]:

1. The closing of pore channels supports saturation with elements by nature similar to Fe (Cr, V, Cu, Ni, Mn).
2. The saturation with elements by nature considerably different from Fe (Al, Si, S) does not make the complete closing of pore channels possible but only lessens the section thereof.
3. Closing of pore channels is intensified by fluid phase formation during the saturation process as well as by the formation of chemical compounds.

During the process of chemical-thermal treatment, due to the vicinity of chemical-thermal treatment to the sintering regime, sintering of compacts occurs. The atmosphere present during saturation considerably stimulates this process, due to which, with the application of gas saturation methods, a „non-porous" transitional zone can form under the diffusing layer, which has a significant influence on exploiting properties of the sample.

The research presented in this article has shown that the boriding process on non-sintered samples is possible.

2. EXPERIMENTAL PART

Results presented in this paper represent modest contribution to study of depth boride layer changes at chemical-thermal treatment – at boroning of iron powder compact. Primary aim was to determine how boroning mixture composition affects on depth changes. The examinations were executed on pressed samples obtained from iron powder (Höganäs, Sweden). The samples were pressed under pressure of 400 MPa. Boroning is performed in mixture whit B_4C, Al_2O_3 and activators. Base components rate was constant, and only was varied activators content in proportion specified by plan. Experiment is planed. Simplex plan of fourth degree whit fifteen experimental points is used. Experiment plan is presented in Table 1.

Table 1 - Plane of experiment and experiments results of depth boride layers changes of pressed and boroned iron powder samples

Number of samples	Contents of activators [%]			Coded values of factors			Depth of boride layers [μm]		
	NH_4FHF	NH_4Cl	KBF_4	X_1	X_2	X_3	δ_1	δ_2	δ_{av}
1	4	0	0	1	0	0	131,25	130,875	131,062
2	0	4	0	0	1	0	134,812	129,25	132,031
3	0	0	4	□	0	1	79,812	104,25	92,031
4	1	0	3	1/4	0	3/4	126,125	122,937	124,531
5	2	0	2	1/2	0	1/2	130,187	126,937	128,562
6	3	0	1	3/4	0	1/4	121,375	138,562	129,969
7	3	1	0	3/4	1/4	0	182,062	161,5	171.781
8	2	2	0	1/2	1/2	0	166,875	146,562	156,719
9	1	3	0	1/4	3/4	0	151,187	161,062	156,125
10	0	3	1	0	3/4	1/4	145,125	123,5	134,312
11	0	2	2	0	1/2	1/2	126,5	129,187	127,844
12	0	1	3	0	1/4	3/4	122,375	120,375	121,375
13	1	2	1	1/4	1/2	1/4	129,937	139,25	134,594
14	1	1	2	1/4	1/4	1/2	116,437	151,375	133,875
15	2	1	1	1/2	1/4	1/4	108	110,875	109,437

Mathematical model is polynomial of fourth degree, since incomplete cubic and cubic model are inadequate. NH_4HF_2, NH_4Cl, and KBF_4 are used in boroning process as activators. Activators percentage ratio is different and in range from 0 to 4 %. Boroning is performed at 950°C and the process time was 4 hours. Depth of boride layers are messured after boronising on universal apparatus for measuring depth. In aim to get reliable data experiment is repeated and results in Table 1 are average value of repeated scan.

3. EXAMINATION RESULTS

On the basis of the obtained results, the following can be concluded.

Explanation of experimental data by simplex method [18, 19] reveals that a strong dependence on depth boride layers changes from composition of boroning mixture (1) exists. Fig. 1 brings out more clearly this influence.

Depth of boride layers are varied, because of different influence of composition mixture. How we can see from table 1. maximum depth of boride layers are obtained by experiment are amount 171,781μm, by composition of activators: 3% NH_4HF_2 and 1%

NH_4Cl. By composition of activators of 4% KBF_4 depth of obtained boride layers has been minimal and number 92,031 μm. This change of boride layers depth, at change of activators percent stake, can be assigned to non uniformly effect of activators.

Due obtained experimental result are calculated polynomial coefficient which are used for graphical review of dependence of depth changes from composition of boronizing mixture (Figure 1).

The depth boride layers changes of boroned samples are given by the Eq. 1:

$$\begin{aligned}\hat{y}_{\Delta\delta} &= 131{,}062x_1 + 132{,}031x_2 + 92{,}031x_3 + 100{,}690x_1x_2 + 68{,}062x_1x_3 + 63{,}252x_2x_3 + 86{,}083x_1x_2(x_1 - x_2) - \\ &- 75{,}080x_1x_3(x_1 - x_3) - 37{,}669x_2x_3(x_2 - x_3) + 288{,}579x_1x_2(x_1 - x_2)^2 + 62{,}760x_1x_3(x_1 - x_3)^2 + 84{,}325x_2x_3 \\ &(x_2 - x_3)^2 - 3342{,}565x_1^2x_2x_3 + 402{,}456x_1x_2^2x_3 + 1131{,}261x_1x_2x_3^2\end{aligned} \tag{1}$$

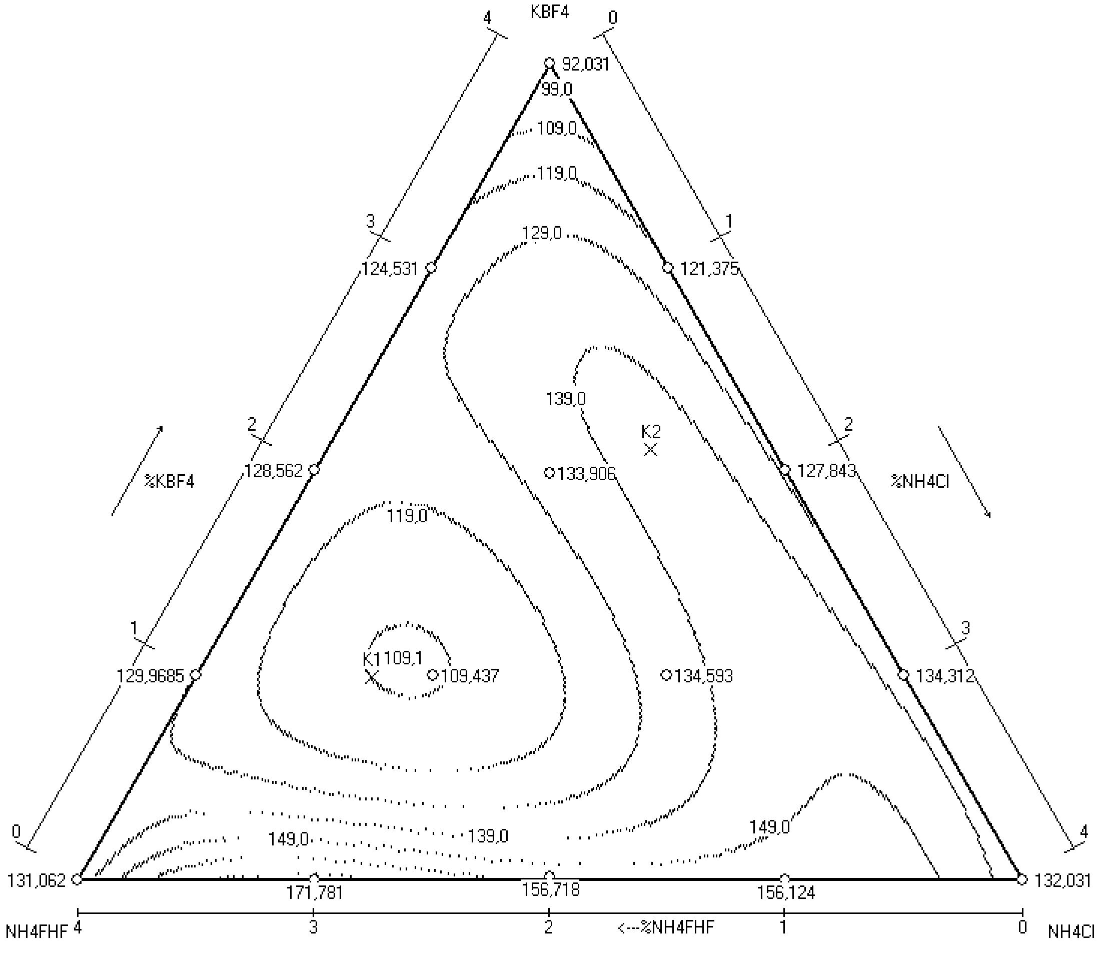

Figure 1 - Dependence of depth changes of pressed and boroned samples from composition of boroning mixture

Graphical review in Figure 1, very clearly illustrate dependence of depth changes with change compoition of boroning mixture. Lines on Figure 1 is presenting projection cut of parallel plane same depths with reaction surface in factor space. Possessing before itself graphical review of such a kind it is possible very simply to choose composition of mixture which will assure in advance defined depth changes. If it is wanted for depth boride layers changes of pressed and boroned samples to be in limit 109 – 119 μm then should be choosen mixture whit addition NH_4Cl, KBF_4 and NH_4HF_2 in ratio (0.4 – 0.8 %) NH_4Cl : (3.4 – 3.7 %) KBF_4 : (0 – 0.6 %) NH_4HF_2 or (0.2 – 1.7%) NH_4Cl : (0.6 – 1.9 %) KBF_4 : (1.5 – 3 %) NH_4HF_2. Opposite to this, maximum depth changes are occurring in area where is relation of activators (0.05 – 3.6 %) NH_4Cl: (0.2 – 3.7 %) KBF_4 : (0.35 – 3.8 %) NH_4HF_2. It is needed to point that this effect of individual activator on depth boride layers changes is matter only for taken limits of concentrations 0 – 4 % and for applied regime of boroning.

After dispersion analysis, which is gave satisfactory results, accomplished is check of mathematical model at controls points K_1 and K_2. By virtue of these checks it is possible to say with probability of 99% that mathematical model is adequate.

Regression polynomial (1), measures reaction surface in every point of factor space. Only problem is that this valuation, respectively her correctness, is not same for all points of simplex yet depend from condition of experiment. Dissipation of results-dispersion-can be estimated for each model, having on mind that for all peaks, or horns, of simplex, regression coefficients are linear function of results [6].

Parallel with measuring depth of boride layer are registered change of mass and change of individual dimension on samples. As operation diffusion atom boron from mixture at callow of samples results manifest increase theirs mass at boroning process. At increase dimension influences formation boride at callow.

Considering expected dependence between obtained depth of boride layers and changes of dimension on samples, as well as dependence between changes of mass(Δm) and changes of samples volume (ΔV), it was necessarily to establish eventual connection. It was needed to deduce dependence between change of volumes and change of mass samples which aroused during boroning. Base on result are represent these dependence on figure 2.(Figure 2 Dependence between depth of boride layer – δ and changes of sample dimensions – Δh), defined by the Eq. 2:

$$\delta = 0{,}0548\Delta h + 132{,}89 \qquad (2)$$

Coefficient of correlation is $r = 0{,}46$. Within boroning process start of boride formation are not accessorized adequate change of dimension Δh, yet increase of dimensions notice from the moment when the layer about 132 μm formation. Gradient of line (Figure 2.) manifested that increase of dimension (Δh) are more intensive from the depth of boride layers at interval registered changes of samples dimension (Δh).

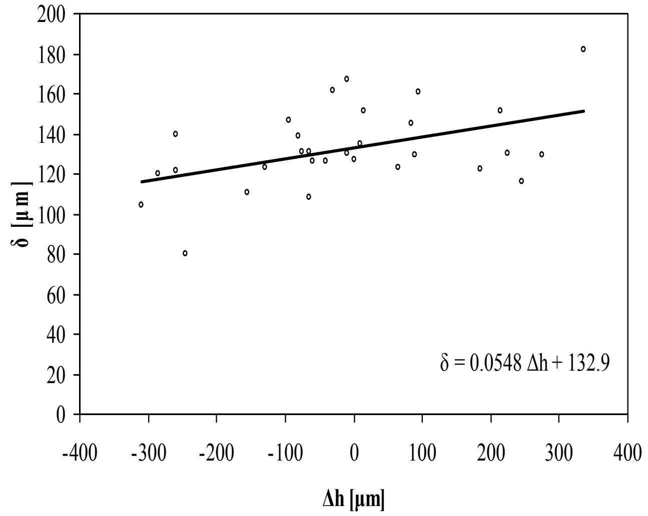

Figure 2 - Dependence between depth of boride layer – δ and changes of sample dimensions – Δh (Coefficient of correlation coefficient is 0.46)

Within the framework of this article, metallographical analysis of the quality of boride samples was executed and the boride layer depth was measured. By metallographic analysis of samples it is found that surface band structure is characteristic for boronising materials from iron powder. On all samples are notices sharp Fe_2B boride, which penetrate inland of samples. Boride layers of samples are differened from each other how by depth layers, so by way of penetration boride at basic metal and way of connecting with basic metal. How is before noted at diffusion and production of diffusion layers on product obtained by process of sinter metallurgy is influenting so many faktors [3-9], betwen of them and composition of boronising mixture. All samples have analogy structure of basic metal, wich is only different by size of porosity.

Figure 3 - Basic microstructure of samples number 21 are consist of bullet dissociated by connected porosity. Porosity are consequence of starting materijal porosity. At boroning came to certainly welding (sintering) single bullets, non-etched (x 300).

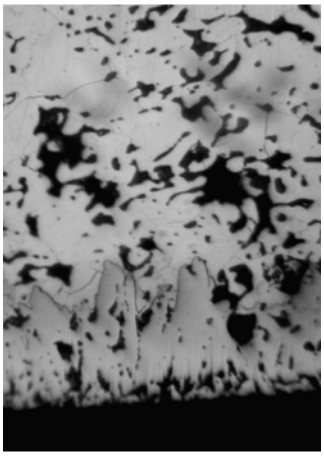

Figure 4 - The microstructure of a boride sample number 11, obtained from iron powder by pressing with the pressure of 400 Mpa. The boroning temperature was 950°C and the process time was 4 hours at mixture of activator: 4% KBF_4. Thickness of the boride layer is 79,812 μm. The pressed sample density was 73,82 % TD and porosity was 19,25 % (x 500).

The obtained compact boride layer consist of colimnar crystals penetrating in a wedge shape into the basic material is noted greater number of acicular boride crystals which deeply penetrating in basic metal (Fig. 6). In view of the great brittleness of boride layers,the bond of boride layer with basic metal realized in a wedge shape enables application of such a boride layer for contact strains.

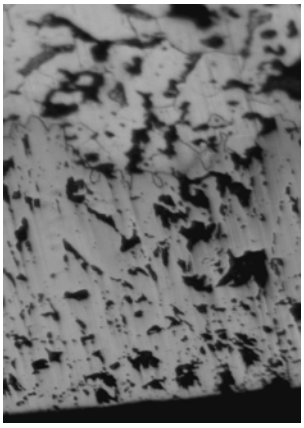

Figure 5 - The microstructure of a boride sample number 23, obtained from iron powder by pressing with the pressure of 400 Mpa. The boroning temperature was 950°C and the process time was 4 hours at mixture of activator: 1% NH_4Cl and 3% NH_4FHF 4%. Thickness of the boride layer is 182.062 μm. The pressed sample density was 75,6 % TD and porosity was 8,79 % (x 500).

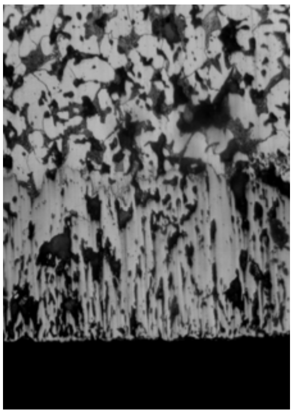

Figure 6 - The mictrostructure of a basic metal sample number 16, obtained from iron powder by pressing with the pressure of 400Mpa. The boroning temperature was 950°C and the process time was 4 hours at mixture of activators: 1% NH_4Cl and 3 % KBF_4. Thickness of the boride layer is 122.375 μm. The pressed sample density was 73.57% TD and porosity was 7.70% (x 500)

CONCLUSION

Results of investigation and conclusion derived by mathematical processing confirm that by boroning in solid mixtures with boron carbide in the presence of activators, boride layers difference both in depth and quality (porosity, the bond whit basic material) were obtained. Because proximity of sintering regime to chemically-thermical treatment during boroning it came also to sintering, as result of this process activation from saturation element side and activated medium. Sintering occurrence during boroning process gives wider possibility for usage of chemically-thermical treatment on sintering materials. Depth and quality of boride layers depends from composition of boroning mixture. Influence of boroning mixture composition on depth changes of pressed and boroned samples from iron powder exist, considering that happened vary of layer depth value. Depending on amount and proportion of activators depth change was 92.031 μm do171,781 μm. Depth of boride layer dependence of concentration activated and absorbed atoms at sample surface (atom of boron). Process of diffusion, apropos directional shift of atoms absorbed on the sample surface, towards his inside, is consequence of tendency for concentrations compensation. Solid solution state whit steady components distribution corresponds state whit minimum free energy.

Exceptionally high values of boride layer depth (even 182,062 μm) were obtained on samples boronized at mixture of activators: 3% NH_4FHF and 1% NH_4Cl, which is completely understandable taking into account that saturation was executed from the gas environment in the presence of a great number of open pores.

Besides this, it is needed to point out that these effects individual activators (NH_4Cl, KBF_4 and NH_4HF_2) on depth changes hold for taken concentration limits 0 - 4%, for used boroning regime and used iron powder compacts pressed with specified pressure. Simplex plans can be used for solving chemically-thermical treatment problems. Accepted mathematical model which is also and adequate, very simply enable to choose mixture composition which can give as in advance specified depth changes of boride layer.

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IZVOD

UTICAJ DODATKA AKTIVATORA RAZLIČITOG HEMIJSKOG SASTAVA I PROCENTUALNOG ODNOSA NA DUBINU BORIDNOG SLOJA

Tokom procesa sinterovanja i hemijsko-termičke obrade-boriranja uzoraka od železnog praha stvara se odgovarajući boridni sloj, zato su u ovom radu predstavljeni rezultati ispitivanja zavisnosti dubine boridnog sloja od sastava smeše koja je korišćena za boriranje. Osnovna smeša koja je korišćena za boriranje uzoraka od železnog praha modifikovana je dodatkom aktivatora različitog hemijskog sastava i procentualnog odnosa. Dobijeni boridni slojevi razlikuju se po dubini i kvalitetu (poroznost, kontakt sa metalom). Da bi se dobili kvalitetni boridni slojevi i da bi se mogle pratiti određene pojave pri boriranu bilo je potebno izvršiti izbor mešavine za boriranje, odnosno odrediti najpogodnije aktivatore i njihov odnos. Obrada eksperimentalno dobijenih rezultata izvršena je Simpleks metodom. Rezultati eksperimentalnih ispitivanja i matematičke obrade omogućili su izbor sastava mešavine za boriranje sa unapred zadanim promenama dubine sloja. Zapaženo je da se istovremeno sa procesom boriranja dešava i sinterovanje i ova činjenica daje široke mogućnosti primene hemijsko-termičke obrade na sinterovane materijale. Moguće je potpuno izbeći proces sinterovanja proizvoda koji su dobijeni metalurgijom praha.

Ključne reči: *sinterovanje, boriranje, boridni slojevi, aktivatori, Simpleks metoda*