

Influence of Composition of Boroning Mixture on the Volume Change of Pressed and Boroned Samples From Iron Powder

Svetlana Ivanov^{1,a}, Emina Požega^{2,b}

¹University of Belgrade, Technical Faculty in Bor, VJ 12, 19210 Bor, Serbia

²Copper Institute, Zeleni Bulevar 35, 19210 Bor, Serbia

^a sivanov@tf.bor.ac.yu, ^b pozegic@ptt.yu

Keywords: Iron Compact; boride layers; sintering

Abstract. The volume change occurs during sintering and chemical-thermal treatment of metal powder samples. The results of investigation of the volume change of pressed and boroned samples from iron powder, depending on mixture composition used for boroning process, are presented in this paper. Basic mixture, used for boroning of investigated samples from iron powder, is modified by the addition of activators with different chemical composition and in different percentage rate, up to 4wt %. Mixtures with ammonium bifluoride, ammonium chloride and boron potassium fluoride were investigated. The research results and mathematical processing enable the choice of mixture composition for boroning based on the volume change given in advance.

Introduction

Chemical-thermal treatment of products obtained by powder metallurgy processes is quite a new method and only few papers deal with boroning of iron powder compacts [1-3, 11, 12]. According to these researches, it is necessary to predict possibilities of obtaining boroning layers at the compacts of iron powder, as well as the possibilities of sintering in the presence of chosen activators.

A contribution to the research work of dimension change by boroning of the compacts from iron powder beside together fluctuation composition mixture for boroning, wherewith obtain diffusing layers with difference depth, is given in this paper. This should help us to sort out changes arise due to boroning [1-3], from changes which arise due to activated sintering [4-7, 10]. 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. Transfer of matter, which leads to shrinkage, appears due to diffusion or viscous flowing at solid state. These processes usually run in particular favourite ways and therefore the value of linear shrinkage is different by different compacts' axes. Investigation of linear shrinkage gives some information about major direction of matter flow during the sintering, and accordingly, makes possible deeper penetration within mechanisms which lead to shrinkage [4, 5].

The mechanism and kinetics of sintered materials diffusing layers differs considerably from that of casting materials [1, 9, 11, 12]. 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 saturating 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 [2, 3, 13]:

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 formed 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 showed that the boriding process on non-sintered samples is possible.

Experimental

The examinations were executed on pressed samples obtained from iron powder (Höganäs, Sweden). The samples were pressed under pressure of 400 MPa. The boriding process is performed at 950 °C for 4 hours in mixture with B₄C, Al₂O₃ and activators. Own authors' experience was used in the selection of the boriding mixture [6, 7], according to which the best results of boride layers depth and quality were achieved using mixture with B₄C. NH₄HF₂, NH₄Cl, and KBF₄ were used as activators in the boriding process, with percentage ratio differing in the range from 0 to 4 wt %. Base components ratio was constant, and only activators content was varied in proportions specified by simplex plan. Dimension of the samples before and after boriding, like boride layer depth, were measured with precision of ±1 μm. In aim to get reliable data, the experiments were repeated and the results shown in this paper were given as average values.

Results and Discussion

Application of the simplex plan of fourth degree with fifteen experimental points has been used in the choice of optimal boriding conditions for the pressed iron powder samples. Mathematical model presents a polynomial of fourth degree, since incomplete cubic and cubic model are inadequate. The results of explained simplex plan are presented in Table 1.

Explanation of experimental data by simplex method [14, 15] reveals that a strong dependence of volume change on boriding mixture composition exists. The volume change of borided samples is given as follows:

$$\hat{y}_{\Delta V} = -0.099x_1 + 2.474x_2 - 1.581x_3 - 1.317x_1x_2 + 5.155x_1x_3 + 5.092x_2x_3 + 8.227x_1x_2(x_1 - x_2) - 9.905x_1x_3(x_1 - x_3) + 10.637x_2x_3(x_2 - x_3) + 18.773x_1x_2(x_1 - x_2)^2 - 11.815x_1x_3(x_1 - x_3)^2 + 22.115x_2x_3(x_2 - x_3)^2 - 74.916x_1^2x_2x_3 - 147.793x_1x_2^2x_3 + 20.285x_1x_2x_3^2 \quad (1)$$

Computer processing of experimental results enabled drawing of the isovolume lines of boroned samples and was presented in the coordinate system concentration - composition of activators (Fig. 1).

After dispersion analysis, which gave satisfactory results, the results were checked by mathematical model at controls points K_1 ($x_1 = 0.72$; $x_2 = 0.68$; $x_3 = 2.60$) and K_2 ($x_1 = 0.68$; $x_2 = 2.48$; $x_3 = 0.84$), and it was confirmed with probability of 99 % that mathematical model was adequate.

Table 1. Obtained volume change and boride layers depth of investigated samples.

Number of samples	Contents of activators [%]			Coded values of factors			Volume change [%]			Depth of boride layers [μm]
	NH_4FHF	NH_4Cl	KBF_4	X_1	X_2	X_3	ΔV_1	ΔV_2	ΔV_{av}	δ_{av}
1	4	0	0	1	0	0	-0.010	-0.187	-0.099	131.062
2	0	4	0	0	1	0	0.983	3.965	2.474	132.031
3	0	0	4	0	0	1	-1.065	-2.097	-1.581	92.031
4	1	0	3	0.25	0	0.75	0.367	-0.106	0.131	124.531
5	2	0	2	0.5	0	0.5	0.458	0.440	0.449	128.562
6	3	0	1	0.75	0	0.25	-1.895	-0.076	-0.985	129.969
7	3	1	0	0.75	0.25	0	3.502	0.395	1.949	171.781
8	2	2	0	0.5	0.5	0	1.627	0.090	0.858	156.719
9	1	3	0	0.25	0.75	0	1.198	2.187	1.693	156.125
10	0	3	1	0	0.75	0.25	6.101	2.796	4.449	134.312
11	0	2	2	0	0.5	0.5	0.176	3.263	1.719	127.844
12	0	1	3	0	0.25	0.75	2.576	-1.723	0.427	121.375
13	1	2	1	0.25	0.5	0.25	2.970	-1.618	0.676	134.594
14	1	1	2	0.25	0.25	0.5	2.657	2.241	2.449	133.875
15	2	1	1	0.5	0.25	0.25	0.611	-0.185	0.213	109.437

Depending on amount and relation of activators, volume change was in the range -0.099 to 4.449 %. During the process of chemical-thermal treatment, due to the vicinity of chemical-thermal treatment to the sintering regime, sintering of compacts occurs. After boroning, dimensions can remain the same or can occur to shrinkage or growth of samples. It can be seen from Table 1 that the influence of boroning mixture composition on the volume change of samples is dual, e.g. at some samples occurred shrinkage, while at some samples increase of dimensions (e.g. growth) occurred. For the samples in which shrinkages occurred, the compactness of boride layer increases, whereas the total sample porosity decreases. Density of compacts increases on account of pore volume decreasing.

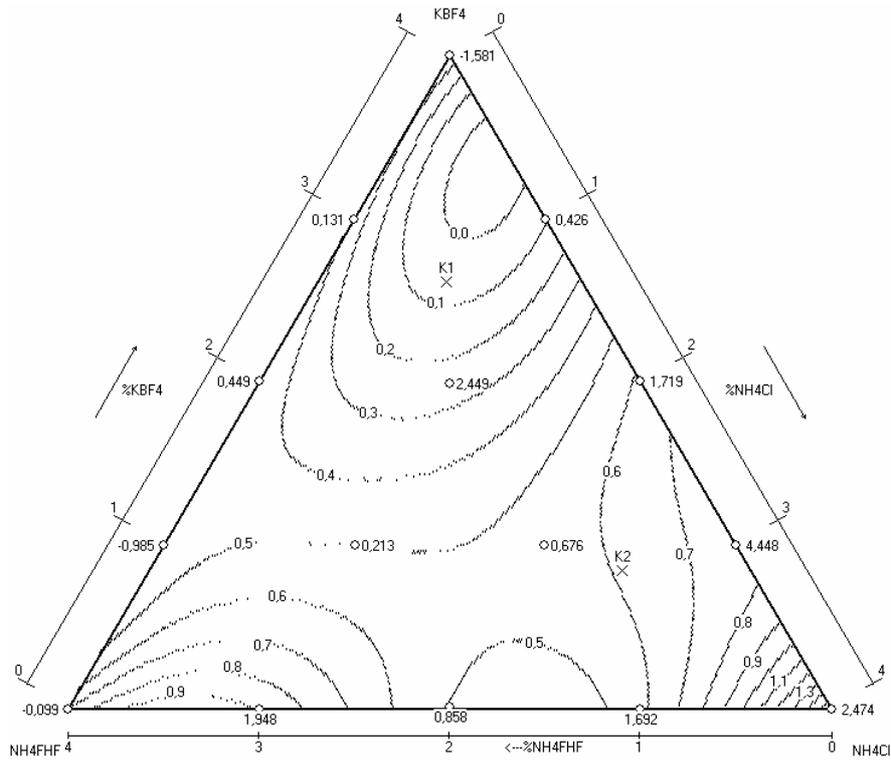


Fig. 1. Dependence of volume change of pressed and boroned samples on the boroning mixture composition

Considering expected dependence between obtained boride layers depth and the changes of sample dimension, as well as dependence between mass changes (Δm) and volume change (ΔV), it was necessarily to establish eventual connection. Fig. 2 and Fig. 3 represented these dependences. Boride formations from start of boroning process were not attended by adequate changes of cross section dimension (Δh). Dimension increase has been noticeable from the moment in which the layer of about 132 μm was formed.

The increase of mass during boroning arisen from the start of process, while volume change was registered from the moment when mass grown to about 0.58 g (Fig. 3).

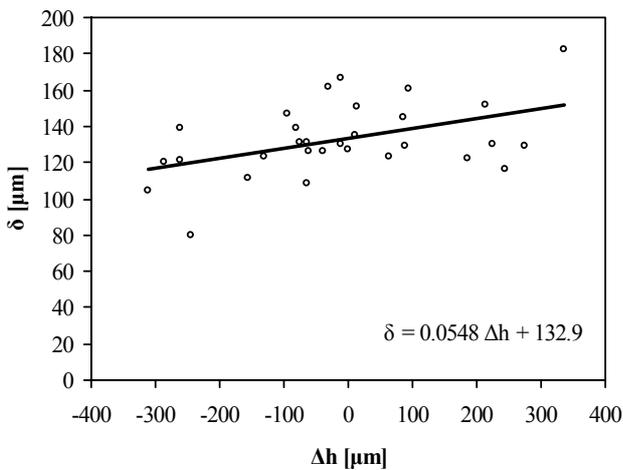


Fig. 2. Dependence of boride layer depth (δ) on sample dimension change (Δh) (Coefficient of correlation equal to 0.46)

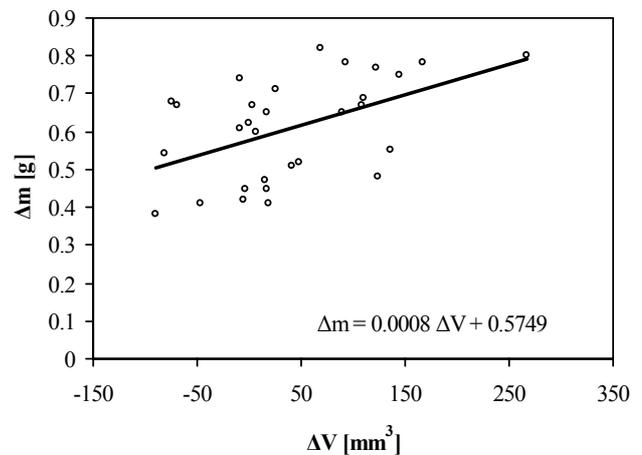


Fig. 3. Dependence of mass change (Δm) on volume change (ΔV) (Coefficient of correlation equal to 0.49)

Conclusion

The results of investigation and mathematical processing confirm that boride layers, obtained by boroning in solid mixtures with boron carbide (B_4C) in the presence of the activators, differ both in depth and quality (porosity, the bond with basic material).

It has been observed that, simultaneously with boroning, sintering occurred also, as a result of the process activation from saturation element side and activated medium, and that fact offers a possibility of chemical-thermal treatment application on sintered materials.

The composition of boroning mixture has influence on the volume change of pressed and boroned samples from iron powder. Depending on the amount and relation of activators, the volume change is obtained in the range from -0.099 to 4.449 %. It should be pointed out that noticed effect of activators (NH_4Cl , KBF_4 and NH_4HF_2) on volume change holds for used boroning regime. Simplex plan can be used for solving such chemical-thermal treatment problems – e.g. for optimization of mixture composition for chemical-thermal treatment. Suggested mathematical model (fourth degree polynomial) is adequate, and enables simple choice of the mixture composition for boroning, based on the volume change given in advance. Therefore, it is possible to avoid completely sizing process of products obtained by powder metallurgy.

References

- [1] L. S. Vorošnin, et al.: Chemical-Thermal Treatment of Cermet Materials (Nauka i tehnika, Minsk, 1977), p. 122-152, in Russian
- [2] A. Šalak, M. Selecka: Powder Metallurgy Progress Vol. 3 (12) (2002), p. 161
- [3] C. V. Robino, M. J. Cieslak: Metallurgical and Materials Transactions Vol. 7 (26A) (1995), p. 1673.
- [4] Ja. E. Geguzin: Physics of sintering (Nauka, Moskva, 1967), in Russian.
- [5] R. M. German: Sintering Theory and Practice (John Wiley and Sons, Inc, New York, 1996).
- [6] S. Ivanov, B. Stanojević: Science of Sintering Vol. 35 (2003), p.93-98
- [7] S. Ivanov and B. Stanojević, in: Science of Sintering: Current Problems and New Trends, (Serbian Academy of Sciences and Arts, Belgrade, 2003), p. 479-485.
- [8] H. H. Hausner: Progress in Powder Metallurgy (APMI, Detroit, 1970).
- [9] C. Martini, G. Palombarini, M. Carbuicchio: Journal of Materials Science Vol. 39 (2004), p.933
- [10] H. Silbereise, in: International Conf., I.P.N.Y., New York, (1960).
- [11] P. A. Kulu, O. D. Bussel, V. S. Puginuss: Powder Metallurgy Vol. 7 (1971), p.28, in Russian.
- [12] B. F. Shibryaev, Yu. N. Gribenyuk, T. A. Shuvalova: Russ. Powder Metallurgy, 6, 78. (1969), p. 40, in Russian.
- [13] I. V. Pohmurskij, V. G. Karpenko: FHMM. Vol. 3 (1967), p. 4, in Russian.
- [14] G. I. Krasovskii, G. F. Filaretov: Planed of Experiment, (Minsk, 1982), p.184, in Russian.
- [15] S. Chatterje, B. Price: Regression Analysis by Example, 2nd ed., (John Wiley and Sons, New York 1991).