MICROSTRUCTURE INVESTIGATION OF SINTERED IRON-BASED POWDERS WITH CARBON-BORON CONTAINING COATINGS

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Abstract

Experiments were carried out in order to develop a new carbon donor that will ensure close contact with iron particles and to be a boron carrier as well. For this purpose NC100.24 and Astaloy CrL powders were coated by products of simultaneous thermal decomposed polyvinyl-alcohol and boron acid. The coated powders were compacted and sintered at 1393 K in pure argon atmosphere. The microstructure of the specimens was investigated. A deeper penetration of carbon inside the particles and concentration of boron-containing structure elements, predominantly on the boundary surfaces, were established.

Keywords: powder metallurgy, coated powders, boron, microstructure formation

INTRODUCTION

The high performance requirements for powder metallurgy (PM) products necessitate the development of new alloys with improved properties. Special attention is paid to the application of boron in powder metallurgy. It is known that the introduction of $0.2 - 0.6\%$ boron helps the liquid phase generation during sintering, thus favouring the production of PM parts of increased density [1–7]. Since the liquid phase is composed of boron-containing eutectic usually the sintering is carried out at hypereutectic temperature (higher than 1452 K [8,9]).

Boron is added as elementary boron, ferroboron or as specially developed master alloys [10,11]. Regardless of the boron introduction method, its close contact with all iron particles is not accomplished, which could cause formation microstructure heterogeneity in the product. The introduction of carbon into iron based PM alloys generates similar problems. Carbon is commonly added as graphite to the ferrous powder. Due to the large density difference, problems of segregation arise, which at high C content can lead to undesirable local melting during sintering. Methods to minimize the segregation problem include incorporation of C into ferrous based powders e.g. coating the ferrous powder with hydrocarbon donor [12]. As the hydrocarbon dissociates, nascent carbon is deposited on all powder particles and is available for alloying and oxide reduction. The development of methods for improving the contact between carbon or boron-containing addition and the iron particles is of great interest.

The aim of this work is to use a new carbon-boron donor and to investigate its behaviour in the powder mixture.

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EXPERIMENTAL

For experiments were used two powders from Höganäs AB (Sweden) production: sponge iron powder NC100.24 and prealloyed powder Astaloy CrL with 1.5% Cr and 0.2% Mo.

Production of the carbon and boron carrier

The carbon-boron carrier was produced by the following procedure: Two separate 1.5% solutions of polyvinyl alcohol (PVA) and powdered boron acid in distilled water were prepared at 343 K. Both solutions were mixed into a homogenous mixture at room temperature followed by evaporation at 363-373 K [13]. The obtained dry residuum was thermally decomposed (in pure Ar or N_2) at 673 K for 35 min (heating rate was 10 K/min, cooling with the furnace to room temperature). The obtained product was grinded and dissolved in toluene ($C_6H_5CH_3$). The solution was filtered to remove the unsolved particles and the concentration of the dissolved substance ($C_xB_yH_z$) was determined. The metal powders NC100.24 and Astaloy CrL were mixed with a certain quantity solution of a 14.1 g/l concentration and then evaporated at continuous stirring of the mixture. In this way, every particle was coated by a carbon-boron-hydrogen containing layer thus resulting in a homogenous distribution of carbon and boron in the mixture.

Compaction and sintering

The coated powders were compacted under 600 MPa. The samples had a cylindrical shape (diameter of 11.3 mm, height 8 mm).

The specimens were sintered in a pure Ar (99.9) atmosphere (2 Ncm^3/min) at the following temperature regime: heating rate of 5 K/min till reaching 873 K, holding time 45 min; then heating rate of 10 K/min till reaching 1393 K, holding time 60 min. The hydrocarbon was fully decomposed at 1073 K ensuring in this way hydrogen-free reduction atmosphere and diffusion of carbon and boron in the metal particles.

After sintering the specimens with 3 different carbon concentrations, there were obtained and designated as NC 1, NC 2 and NC 3 (with 0.008, 0.04 and 0.111% C respectively) as well as Ast 1, Ast 2 and Ast 3 (with 0.015, 0.067 and 0.17%C respectively). The listed carbon quantities are a result of the carried out investigation of new carbon donor behaviour.

Their microstructure was investigated and the microhardness of every specimen was measured (load of 10 g, dwell time of 10 s). The microhardness values are the arithmetical mean value from 20 measurements at least.

RESULTS AND DISCUSSION

The microstructures of the investigated specimens are illustrated in Fig.1. The microstructural analysis does not establish any difference in the porosity grade of the NC100.24 specimens with different carbon content. The porosity in the core and in the periphery of every specimen was the same (Fig.1 a,b).

sample NC 1, periphery   sample NC 1, centre

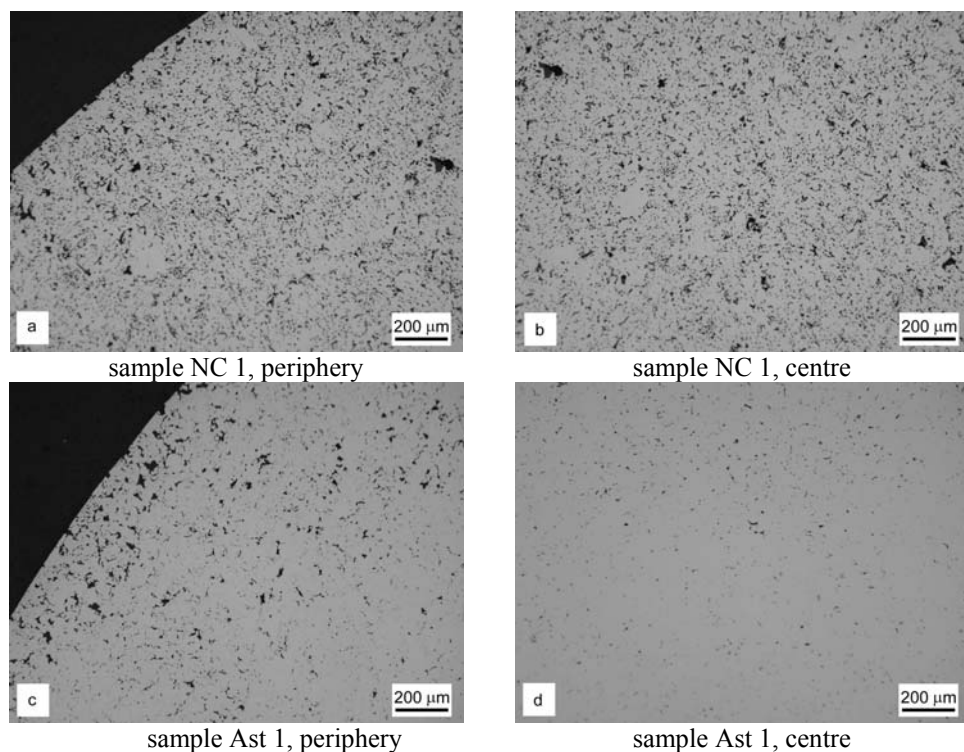sample Ast 1, periphery   sample Ast 1, centre

Fig.1. Porosity of the NC 1 and Ast 1 samples with carbon-boron addition.

The porosity of the Astaloy CrL specimens was not uniform – the porosity in the periphery was higher than in the core. The porosity difference was especially considerable in the Ast 1 specimen with the lowest C content, Figs.1c and d. Moreover, the porosity in the periphery was non-uniformly distributed.

Boundary boron-containing layers were observed in every NC 1, NC 2 and NC 3 specimen, Fig.2. The layers are more clearly visible and they are of larger quantity in NC 1 – the specimen with the lowest content of carbon-boron addition. There were globular inclusions with chemical composition probably similar to that of the layers in some grains. Close to the carbon-boron layers the formation of a fine carbide border began. The formation of troostite type grains was observed in specimens NC 2 and NC 3. According to the established carbon content, their number was insignificant in specimen 2 and a little higher in specimen NC 3. Regardless of the absence of visible microstructural alterations, especially in specimens NC 1 and NC 2, processes of diffusion saturation of the ferrite matrix with both alloying elements could be considered. Indirect evidence for this is the values of the measured matrix microhardness (Table 1).
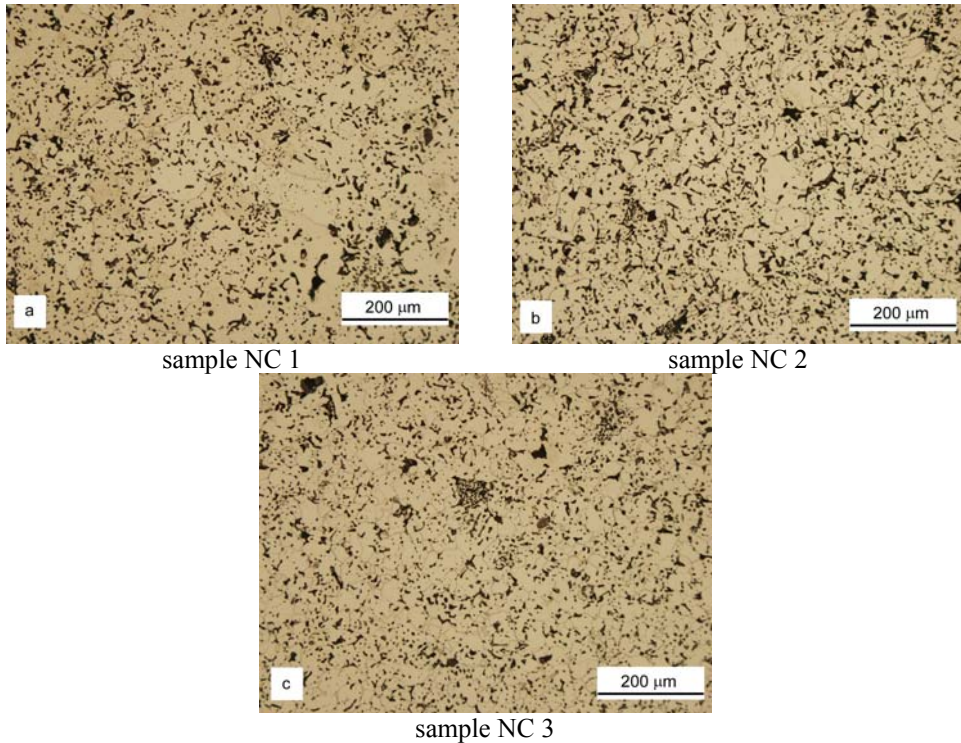
sample NC 1

sample NC 2

sample NC 3

Fig.2. Microstructure of the NC100.24 samples with carbon-boron addition.

Tab.1. Microhardness HV0.010 of ferrite and pearlite of the investigated specimens prepared from NC100.24 and Ast CrL powders.

	Base powder	NC100.24			AstCrL		
	specimen No.	NC 1	NC 2	NC 3	Ast 1	Ast 2	Ast 3
ferrite	HVaverage	127	115	114	137	108	124
	HVmin	72	87	80	80	84	101
	HVmax	154	154	133	164	125	142
	R*	82	67	53	84	41	41
pearlite	HVaverage	-	-	206	-	205	208
	HVmin	-	-	129	-	165	174
	HVmax	-	-	276	-	248	249
	R*	-	-	147	-	83	75

*R = HVmax – HVmin

The wide microhardness values alteration interval (from 72 to 154 HV0.010) in NC 1 specimen is evidence of the simultaneous existence of pure ferrite grains as well as alloyed to a different degree ferrite grains. The microhardness values interval is narrowed gradually in NC 2 and NC 3 specimens with a trend toward decreasing of the average microhardness value. This could be explained by the relatively equalized chemical composition of the matrix as well as by the process of troostite formation. The latter is accompanied on the one hand by the connecting of certain carbon quantities, and possibly

boron, for the formation of the chemical compound iron carbide or boron cementite. On the other hand, a carbide border was often formed on the ferrite-ferrite or troostite-ferrite boundaries (Fig.3) thus hindering carbon/boron diffusion in the iron matrix. Both factors contributed to the decreasing of the diffusion elements concentration in the α-solid solution. Moreover, the possibility of surface activity of boron when its content in the boron-containing addition is low has to be considered as well. In this case boron could replace carbon in the boundary surfaces, supplanting it toward the particle`s core which could cause an increase of the core`s microhardness [14-16]. This is especially valid for specimen NC 1 with minimal donor additions.
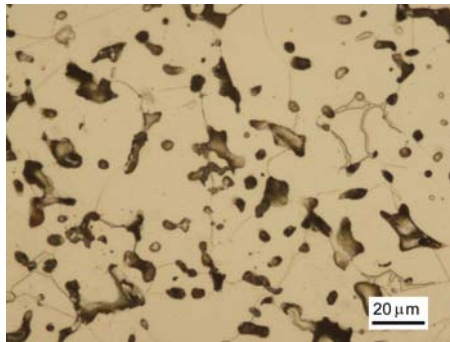

Fig.3. Microstructure of the NC 3 sample.

Boundary carbon-boron containing layers were also observed in the Ast 1, Ast 2 and Ast 3 specimens, Fig.4. They were concentrated mainly on the initial particles` periphery. A different pearlite portion was formed in the particles dependent on the carbon content: minimum in specimen Ast 1 and maximum in specimen Ast 3. The pearlite distribution was not uniform in the particle`s volume − its quantity was lower in the periphery than in the core. This difference was most pronounced in specimen Ast 1. The pearlite was formed predominantly in the boundary zones of the initial powder particles, forming well outlined troostite-sorbite type of grains.

Formation of boron containing carbides, possibly boron cementite $Fe_3(C, B)$, and probably certain amount of boron carbide $(Fe, Cr)_{23}(C, B)_6$ is possible. This is mere guesswork for formation of these types' carboborides. The assumption is based on the Fe-Cr-C-B equilibrium diagram and on probable enrichment of local areas by C and B during the sintering. Boron-rich boundary layers were clearly observed on the particles` periphery. The microstructures character proved that the alloying processes were more intensive in the boundary zones of the initial powder particles than on the grain boundaries (Figs.2a,b and Figs.4a,b). Nevertheless, alloying of the ferrite matrix was accomplished, which is obvious from the measured microhardness values (Table1). The established particularities of the microstructure formation in Astaloy CrL specimens were similar to these in the NC100.24 specimens and could be explained in the same way. The average microhardness values measured in both series of the specimens varied in the interval of 205 – 308 HV0.010.
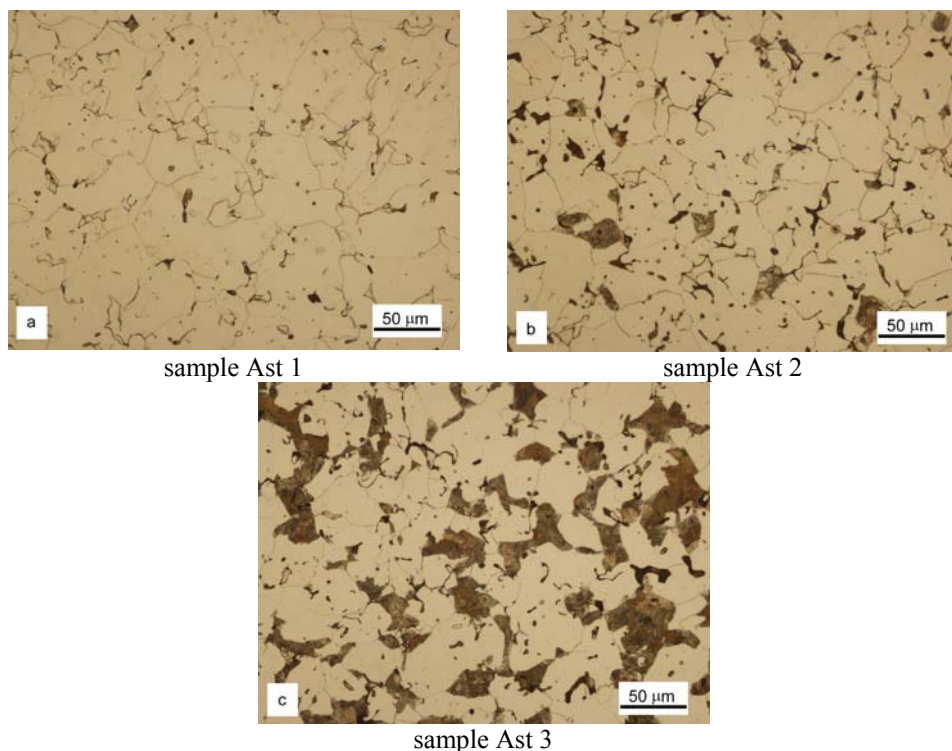
sample Ast 1

sample Ast 2

sample Ast 3

Fig.4. Microstructure of the Astaloy CrL samples with carbon-boron addition.

Metallographic analysis showed that the utilization of a combined carbon and boron donor contributed to microstructure formation according to the specific properties of both elements: deeper penetration of carbon inside the particles and concentration of boron-containing structure elements predominantly on the boundary surfaces. Their distribution in the specimen area was comparatively uniform.

CONCLUSION

The investigation carried out of the simultaneous alloying of PM alloys by carbon and boron using boron-containing hydrocarbons established that a close contact between the iron particles and the alloying elements carrier was achieved, thus accelerating the matrix diffusion saturation processes.

REFERENCES

[1] Houdremont, E.: Special Steels. Moscow : Metallurgia, 1966
[2] Dudrová, E., Selecká, M., Bureš, R., Kabátová, M.: ISIJ International, vol. 37, 1997, no. 1, p. 59
[3] Karwan-Baczewska, J., Pieczonka, T. In: Proc. of PM World Congress. Vol. 2. Granada, 1998, p. 282
[4] Molinari, A., Straffelini, G., Szewczyk, A., Tabor, A. In: Proc. of PM World Congress. Vol. 2. Granada, 1998, p. 584
[5] Selecká, M., Danninger, H., Šalak, A., Unami, S., Parilák, Ľ. In: DF PM´99. Deformation and Fracture in Structural PM Materials. Vol. 1. Piešťany, 19.-22.9.1999. Ed. Ľ. Parilák, H.Danninger. Košice : IMR SAS, 1999, p. 175

[6] Liu, J., Cardamone, A., Potter T., German, RM., Semel, FJ.: Powder Metallurgy, vol. 43, 2000, no. 1, p. 57

[7] Karwan-Baczewska, JA., Rosso, M. In: Deformation and Fracture in Structural PM Materials 2002. Vol. 1. Stará Lesná, 15.-18.9.2002. Ed. Ľ. Parilák, H. Danninger. Košice : IMR SAS, 2002, p. 100

[8] Equilibrium diagrams of two and multicompounds iron based systems. Reference book. Ed. O.A. Bannih, M.E. Drica. Moscow : Metallurgia, 1986, p. 439

[9] Yilmaz, R., Ekici, MR.: Journal of Achievements in Materials and Manufacturing Engineering, vol. 31, 2008, no. 1, p. 23

[10] Echude-Silva, JH., Martinelli, AE., de Lima, SJG.: Powder Metallurgy, vol. 41, 1998, no. 4, p. 255

[11] Sarasola, M., Sainz, S., Castro, F. In: Euro PM 2005 Congress & Exhibition. Vol. 1. Prague, October 2-5, 2005. EPMA, 2005, p. 349

[12] Mitchell, SC., Wronski, AS., Georgiev, J., Stoytchev, M. In: Powder Metallurgy World Congress and Exhibition. Vol. 3. Vienna, October 17-21, 2004. Ed. H. Danninger, R. Ratzi. EPMA, 2004, p. 313

[13] Shaulov, AYu., Lomakin, SM., Zarhina, TS., Rahimkulov, AD., Shilkina, NG., Muravlev, YuB., Berlin, AA: Papers of Academy of Sciences, vol. 403, 2005, no. 6, p. 772

[14] Pieczonka, T., Georgiev, J., Stoytchev, M., Mitchell, SC., Teodosiev, D., Gyurov, S.: Powder Metallurgy Progress, vol. 4, 2004, no. 4, p. 211

[15] Vinokur, BB., Pilyushinko, VL., Kasatkin, OG.: Structure of structural alloyed steel. Moscow : Metallurgia, 1983. 215 p.

[16] Krishtal, MA., Ivanov, LN., Grinberg, EM.: Metal Science and Heat Treatment, 1970, no. 8, p. 74