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THE PROPERTIES OF Fe-Ni-Mo-Cu-B MATERIALS PRODUCED VIA LIQUID PHASE SINTERING

WŁAŚCIWOŚCI STOPÓW Fe-Ni-Mo-Cu-B WYTWARZANYCH METODĄ SPIEKANIA W FAZIE CIEKŁEJ

Sintered materials base on pre-alloyed powders (Fe-Ni-Mo-Cu) are expansively applied in the automotive industry. However, their applications are limited by the particular porosity values of those materials. To reduce the porosity and, simultaneously, to increase the consolidation of sintered alloys, miscellaneous methods within powder metallurgy technologies are utilised, as well as an activated sintering process; for example some boron is added. The boron and iron built a system that is not soluble in any of the three allotropic forms of iron. While sintering at a temperature higher than 1433 K, a permanent liquid phase was generated as a result of a eutectic reaction between iron and Fe_2B. Owing to the limited boron solubility in iron, a liquid phase was continuously present during the sintering process, influence changes in the morphology of the porosity and the increase in density, also mechanical properties. In addition, boron showed a strong chemical affinity to oxygen; in sintering process it reacted with a chemically bound oxygen on the surface of powder particles and it simultaneously activated the sintering process. The paper presents the production of sintered materials based on Höganäs Distaloy SA (Fe-1.75% Ni-0.5% Mo-1.5% Cu) powder modified by boron powder in amounts of 0%, 0.2%, 0.4% and 0.6%. Alloys were manufactured using powder metallurgy technology through mixing of powders, compacting at 600 MPa pressure and sintering at 1473 K, during 30 minutes in hydrogen atmosphere. One of the phenomenon, which exists on the surface of sinters made from boron modified pre-alloyed powders (Fe-Ni-Mo-Cu) type Distaloy SA is creating a thickened layer. The similar thickened layer was observed also on the surface of another samples base on pre-alloyed powders with boron addition.

As well as the properties: density, hardness, tensile strength were examined and microstructure investigations were performed. Experimental results showed that if boron was added, while sintering, the shrinkage phenomena increased and properties were improved.

Keywords: pre-alloyed powders, boron, activated sintering, thickened layer, properties, microstructure

Materiały spiekane na osnowie stopowanego proszku Fe-Ni-Mo-Cu znajdują szerokie zastosowanie w przemyśle motoryzacyjnym. Jednakże ze względu na pewien stopień porowatości tych materiałów ich wykorzystanie jest ograniczone. Ażeby obniżyć porowatość i równocześnie podwyższyć zagęszczenie stopów spiekanych stosuje się różne warianty technologii metalurgii proszków oraz procesy aktywowanego spiekania, na przykład poprzez wprowadzenie dodatku boru. Bor tworzy z żelazem układ o prawie całkowitym braku rozpuszczalności w obu odmianach alotropowych Przy spiekaniu powyżej 1143 K w wyniku reakcji eutektycznej pomiędzy żelazem a Fe_2B tworzy się faza ciekła. Wskutek ograniczonej rozpuszczalności boru w żelazie proces spiekania przebiega przy ciągłej obecności fazy ciekłej, co w konsekwencji wpływa na zmiany w morfologii porowatości , wzrost zagęszczenia i podwyższenie właściwości mechanicznych. Ponadto bor posiada bardzo silne powinowactwo chemiczne do tlenu i podczas procesu spiekania reaguje z chemicznie związanym tlenem na powierzchni cząstek proszku i równocześnie aktywizuje proces spiekania. W artykule omówiono proces wytworzenia stopów na osnowie proszku Distaloy SA (Fe-1.75% Ni-0.5% Mo-1.5% Cu) produkcji firmy Höganäs, modyfikowanego borem w ilości 0%, 0.2%, 0.4%i 0.6%. Powyższe stopy były otrzymywane metodą metalurgii proszków w wyniku mieszania proszków, prasowania pod ciśnieniem 600 MPa i spiekania przy temperaturze 1473 K, podczas 30 minut, w atmosferze wodoru. Jednym z ciekawych zjawisk występujących podczas spiekania proszków Fe-Ni-Mo-Cu z gatunku Distaloy z dodatkiem boru jest występowanie zagęszczonej bezporowatej strefy, której grubość zmniejsza się wraz ze wzrostem zawartości boru. Podobne warstwy tworzą się na powierzchni spiekanych stopów na osnowie innych stopowanych proszków modyfikowanych borem.

W toku eksperymentów oznaczono gęstość, twardość i wytrzymałość analizowanych próbek oraz przeprowadzono badania strukturalne. Wykazano, że dodatek boru do proszków stopowanych podczas procesu spiekania odpowiada za zjawisko skurczu oraz wpływa na podwyższenie właściwości analizowanych próbek.

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1. Introduction

Sintered materials base on pre-alloyed powders (Fe-Ni-Mo-Cu) are expansively applied in the automotive industry. However, their applications are limited by the particular porosity values of those materials. To reduce the porosity and, simultaneously, to increase the consolidation of sintered alloys steels, miscellaneous methods within powder metallurgy technologies are utilised, as well as an activated sintering process; for example some boron is added. It was proved during the preliminary investigations and while studying the reference data that boron activated the sintering process and it consequence, it increased in the degree of densification and influenced the improvement of mechanical properties (Karwan-Baczewska 1996, 1997, 2000, 2008) and Karwan-Baczewska & Rosso 2001, Karwan-Baczewska and co-workers 2010).

One of the phenomenon, which exists on the surface of sinters made from boron modified pre-alloyed powders (Fe-Ni-Mo-Cu-) type Distaloy SA is creating a thickened layer. The similar thickened layer was observed also on the surface of another samples base on pre-alloyed powders with boron addition. The occurrence of an inspissated zone was already confirmed on the surface of Fe-Ni-Mo-B sample sinters in the atmosphere of dissociated ammonia (Selecka and co-workers 1995).

Fe-Ni-Mo-B samples, sintered in the atmosphere of dissociated ammonia ($75N_2$-$25H_2$), are characterized with a lower degree of densification against identical samples sintered in vacuum. As researchers have it, on the surface of Fe-Ni-Mo-B sinters is formed a pore-free layer, 80-280 μm thick related to the formation of BN (boron nitride) due to high affinity of boron to nitrogen. That pore-free layer came to exist without any liquid phase whose formation was unlikely to occur for low boron contents.

Another example of formation of a pore-free zone on the surface of samples was found upon investigating into austenitic stainless steels with boron addition (Molinari and others 1996; Kazior and others, 1998). A layer whose density is similar to the density of boron-free monolithic material occurs on the surface of sinters made from AISI 316 L powder with 0.2 - 0.8% boron, heated up to 1513 K, respectively, at a rate of 278 K/min and 293 K/min. The thickness of that layer diminishes from 0.8 mm for 0.2% B participation to 0 mm for 0.8% B participation. The work of Molinari and co-workers, 1996 presented a microstructure of sinters made from AISI 316 L powder with 0.8% B, heated up at a rate of 293K/min with a boron-free layer marked from the sample surface, and later on, from the eutectic layer with borides. The said results were corroborated with the analysis of boron decomposition (EDX and SIMS). Changes to the microstructure of sinters under investigation, the formation of boron-free thickened layer improves – first of all – the resistance to corrosion (Menapace and co-workers 2007).

2. Experimental and procedure

In the experiments a diffusion bonded powder type Distaloy SA (Fe-1.75%Ni-1.5%Cu-0.5%Mo) was used. It was alloyed by 0.2, 0.4 and 0.6 wt% elemental boron powder with the addition of 0.8 wt% lubricant in the form of zinc stearate. Powders were blended for 15 min. All the powder mixtures were compacted at 600 MPa, and then sintered for 60 min. in a hydrogen gaseous envelope at 1473 K.

For comparison purposes, the Astaloy Mo powder (Fe-1.5%Mo) and NC 100.24 iron powder sinters alloyed by 0.2, 0.4 and 0.6 wt% of boron were investigated.

The following properties of Distaloy SA, Astaloy Mo and NC 100.24 iron sintered alloys were examined: density, hardness and strength. The specimens' density value was determined by a water displacement method, their hardness by the Brinell method, and the tensile strength with use of an Instron machine. Next structural investigations by a light microscopy and SEM-EDX were made.

3. Results and discussion

On the basis of the investigations performed, it was stated that adding the boron stimulated the sintering process and, subsequently, increased densification and improved the mechanical properties of PM Distaloy SA, Astaloy Mo and NC 100.24 iron alloys.

The boron and iron built a system that is not soluble in any of the three allotropic forms of iron. (German 1986). While sintering at a temperature higher than 1433 K, a permanent liquid phase was generated as a result of a eutectic reaction between iron and Fe_2B. Owing to the limited boron solubility in iron, a liquid phase was continuously present during the sintering process, influence changes in the morphology of the porosity and the increase in density, also mechanical properties. In addition, boron showed a strong chemical affinity to oxygen; in sintering process it reacted with a chemically bound oxygen on the surface of powder particles and it simultaneously activated the sintering process (Karwan-Baczewska 1996).

With the increasing boron contents and the quantity of the liquid eutectic in Distaloy SA, a considerable increase in the density, hardness and tensile strength (Figs. 1-3) was seen.

The same effect was observed for Astaloy Mo and NC 100.24 iron samples but a highest values were obtained for Distaloy SA alloys.

In PM Distaloy SA samples containing 0.6 wt% boron, very high eutectic contents deposited at grain boundaries (Fig. 4d and Fig. 5).

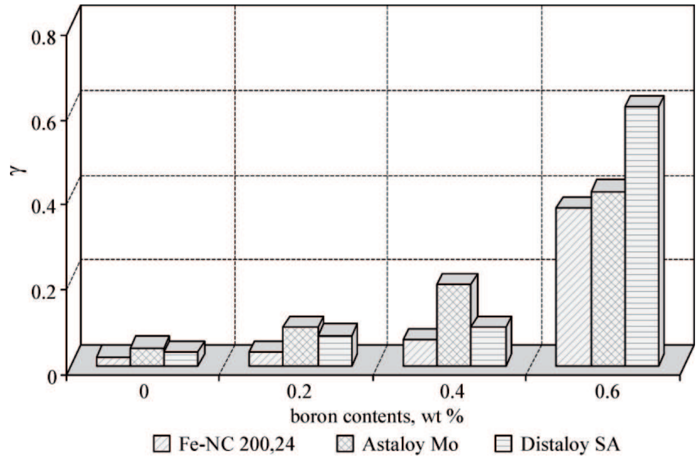


Fig. 1. Influence of boron on the compaction degree (γ) of sinters base on: iron NC 100.24, Astaloy Mo and Distaloy SA powders (1473 K/60'/hydrogen)

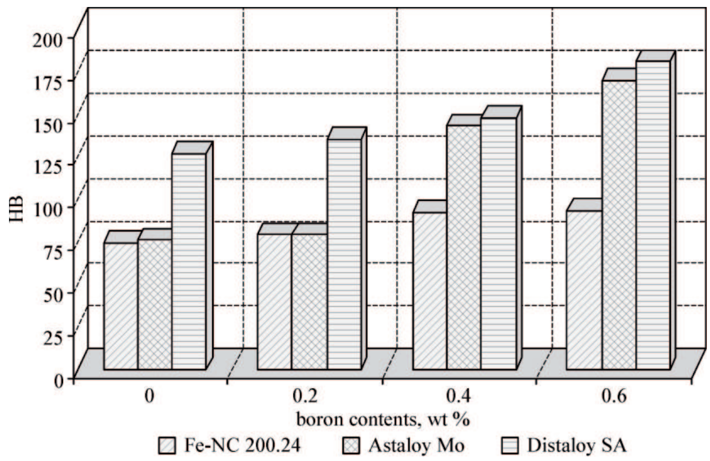


Fig. 2. Influence of boron on the hardness (HB) of sinters base on: iron NC 100.24, Astaloy Mo and Distaloy SA powders (1473 K/60'/hydrogen)

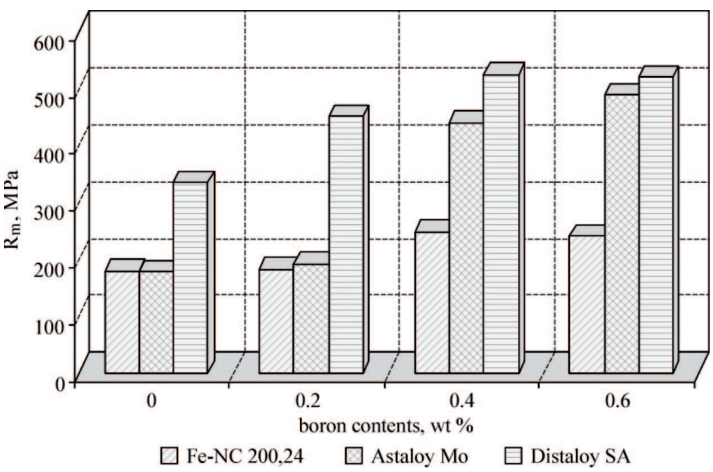
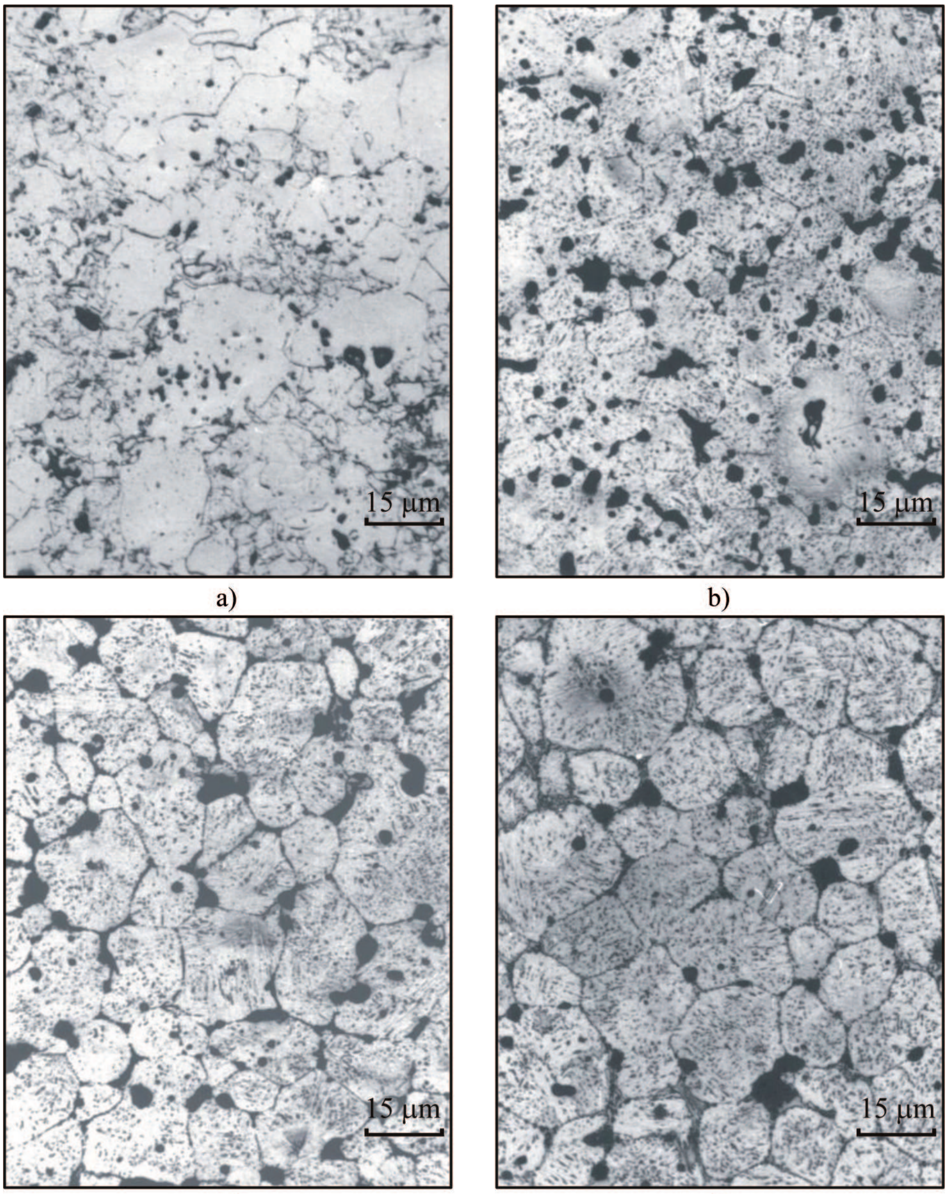


Fig. 3. Influence of boron on the tensile strength (R_m) of sinters base on: iron NC 100.24, Astaloy Mo and Distaloy SA powders (1473 K/60'/hydrogen)



a) b) c) d)

Fig. 4. Microstructures of Distaloy SA sinters with boron contents
a) 0 % B, b) 0.2% B; c) 0.4% B; d) 0.6% B. Sintering parameters: 1473 K/60'/hydrogen

The boride phase in the eutectic network blocked a further increase in tensile strength of examined specimens. While sintering Distaloy SA samples, boron most likely undergoes *in situ* chemical reaction with the surrounding alloyed powders to form a boride phase, possibly via diffusion of iron, molybdenum and nickel into boron particles. Iron, molybdenum and nickel are part of the boride phase which forms either as part of eutectic liquid phase solidification or precipitates formed at ferrite grain boundaries.

In previous research-work (Karwan-Baczewska 2008) it was stated that in Distaloy SA sintered samples modified by boron, an eutectic structure at grain boundaries containing ferrite plus complex borides type Fe_2B, $FeMo_2B_2$ and NiB. For comparison an eutectic structure at grain boundaries of Astaloy Mo sinters with boron containing ferrite plus complex borides of type Fe_2B and $FeMo_2B_2$. NC 100.24 iron sinters with boron are also characterized by an eutectic structure at grain boundaries containing ferrite and Fe_2B.

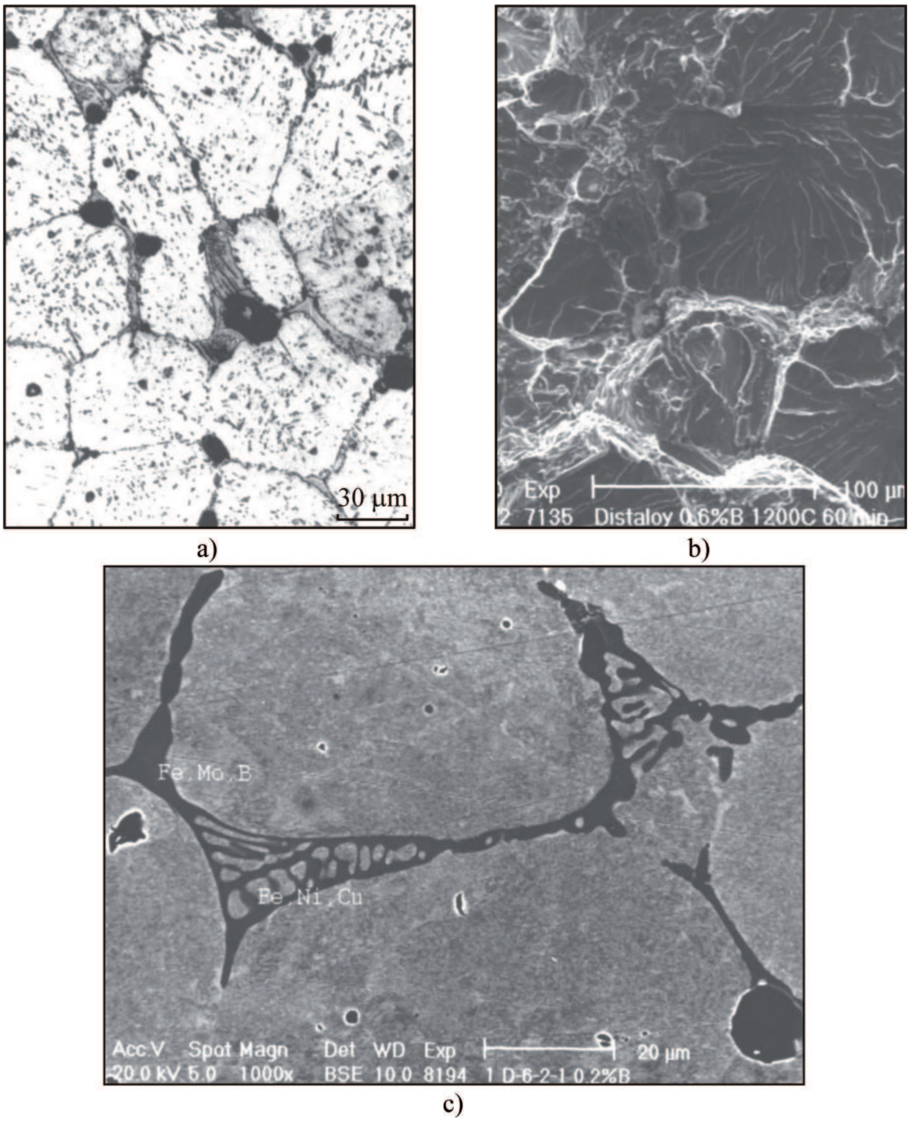


Fig. 5. Distaloy SA sinter with 0.6 % B
a) microstructure – a light microscopy, b) fracture – SEM, c) EDX. Sintering parameters: 1473 K/60'/hydrogen

3.1. The occurrence of a thickened layer on the surface of sinters made from boron-modified Distaloy SA powder

After sintering at 1473 K, a pore-free, thickened zone whose thickness diminishes as the boron content increases was found in the surface layer in boron-modified Distaloy materials. In that layer were present not pores but iron grains as well; neither were there detected any boron precipitations. The occurrence of a pore-free, thickened layer in Distaloy SA sinters with boron addition is a very interesting phenomenon and has a considerable effect, among other things, upon the heat and chemical treatment of sinters. Usually, problems are encountered while nitriding or carburizing sinters if joined pores are present in the structure of samples; then, it is possible to perform a 'thorough' nitriding, and a nitride coat on the surface of sinters is rather unlikely to occur.

Instead, the work of Szewczyk-Nykiel, 2001 presents the microstructure of the surface layer of sinter Astaloy Mo with 0.4% boron participation after having been sintered at 1473 K for a 60 minutes. It was also found that similar pore-free layers came to exist upon sinters made from iron powder ASC 100.29. A hypothesis was suggested that the mechanism governing the formation of that surface zone is related to the effect of boron upon the process of sintering iron powders ASC 100.29 and Astaloy Mo. Boron, for its high affinity to oxygen, reacts with the oxygen fixed on the surface of powder particles, which leads to a better metal-metal contact and favors the diffusion of iron atoms. The newly formed B_2O_3 which is generated upon the surface of particles of powders is molten at 723 K, which, in turn, favors the occurrence of liquid phase at a relatively low temperature.

On the one hand, the liquid phase under formation intensifies the sintering process; but on the other, as temperatures increase, the newly formed liquid phase evaporates, especially from the surface layer. At 1473 K, the liquid phase formed in consequence of an eutectic reaction shifts towards the core in line with the 'pore-filling' theory (Lee & Kang 1998).

Microstructures of surface layers of boron-modified Distaloy sinters SA are shown in Figs. 6.

According to the microscopic examinations performed, in the surface layers present are zones whose structures are different from the structure of the core of Distaloy SA samples with a boron addition. Moreover, as the boron contents in Distaloy SA sinters increase, the structure of zones is subject to changes and the thickness of zones is reduced. A fine-grained ferritic structure with a small number of pores was noticed in the surface layer of Distaloy SA sinters with 0.2 %B.

In the surface layers of Distaloy SA sinters with 0.4 and 0.6% B were observed zones with ferritic structures and precipitations of fine borides and pores, but the thickness of zone of Distaloy SA sinters with 0.6% B is smaller (Figs. 6 a-c).

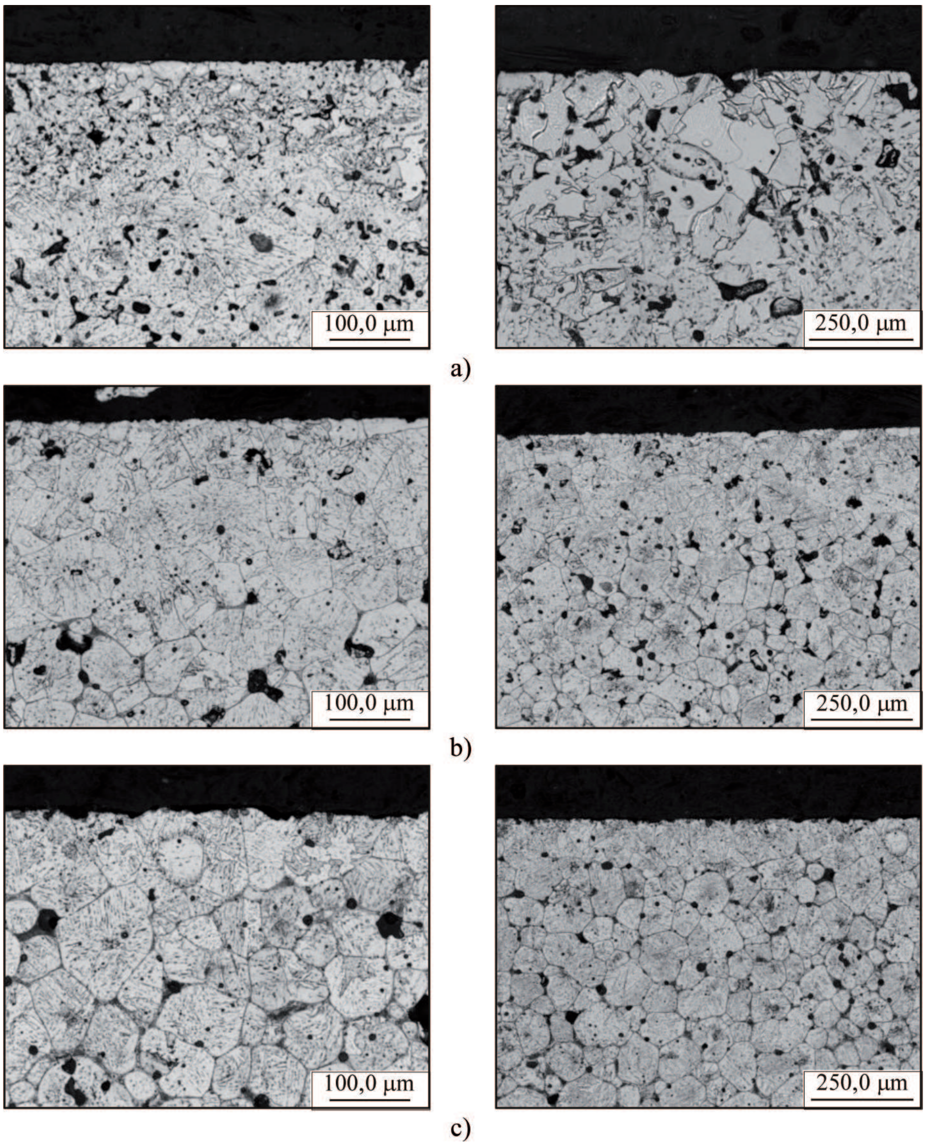


Fig. 6. Microstructures of surface layers of boron-modified Distaloy SA sinters, respectively:
a) 0.2% B; b) 0.4% B; c) 0.6% B. Sintering parameters: 1473 K/60'/hydrogen

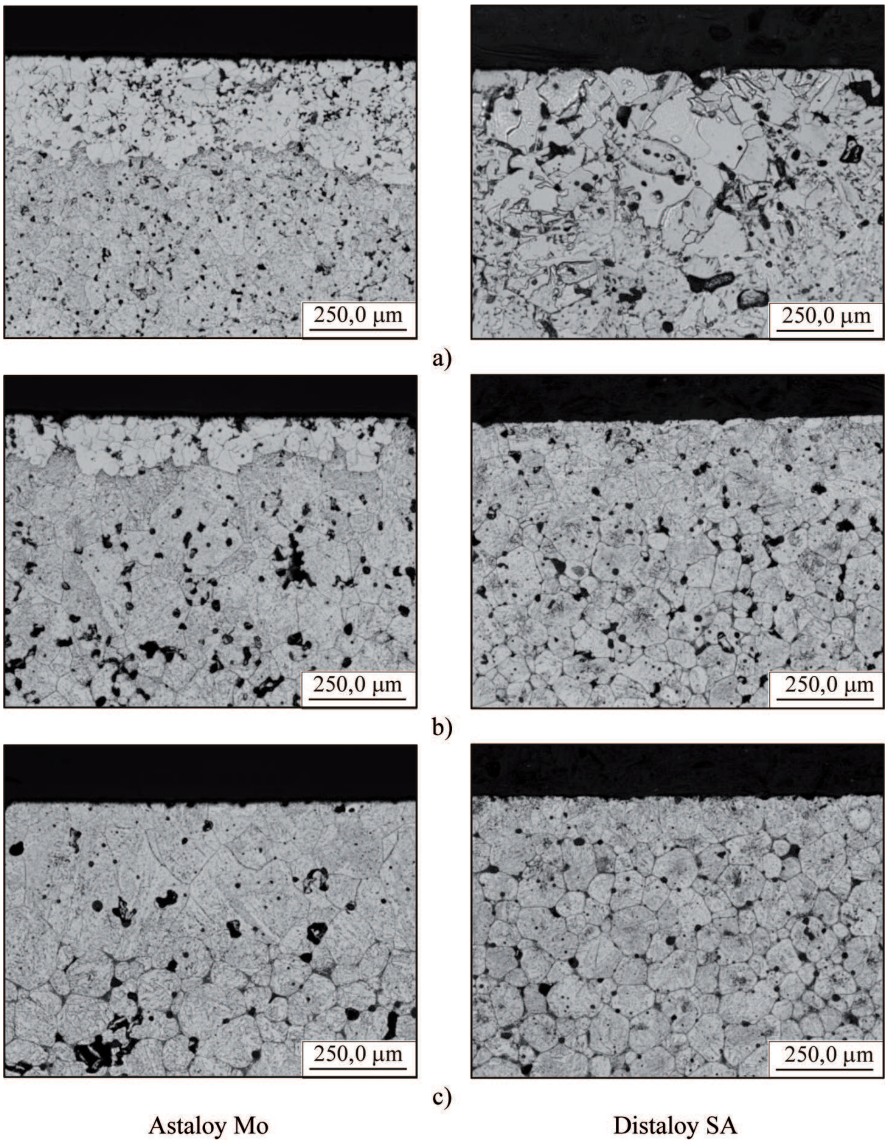


Fig. 7. Microstructures of inspissated surface layers of boron-modified Astaloy Mo and Distaloy SA sinters, respectively: a) 0.2% B; b) 0.4% B; c) 0.6% B Sintering parameters: 11473 K/60'/hydrogen

For comparison's sake, there were also illustrated microstructures of surface layers in boron-modified Astaloy Mo and Distaloy SA sinters (Fig. 7).

While comparing the structures of thickened zones in boron-modified Astaloy Mo and Distaloy SA sinters, it was found that at 0.2 % B, the structures of such sinters are ferritic with precipitations of fine pores (Fig. 7a). Differences in the zone structures can be noticed at boron contents as low as 0.4 %. In Astaloy Mo materials the zone structure is not altered, whereas in the zone structures in Distaloy SA materials some precipitations of fine borides and fine pores were observed in ferrite grains (Fig. 7b). The zones are similar in the surface layers in Astaloy Mo and Distaloy SA with 0.6% B (viz. fine borides and fine pores occur in ferrite grains), while the thickness of those zones is smaller if compared with the zones formed in samples with lower boron contents (Fig. 7c).

The differences noticed in the structure of inspissated surface zones in Astaloy SA Mo and Distaloy SA sinters arise from different analyses of input powders, sintering mechanisms with liquid phase and evaporation processes of B_2O_3.

While sintering samples of Astaloy SA and Distaloy SA with boron additions, boron oxide B_2O_3, which melts at 723 K, will come to exist; as temperature rises, the oxide is evaporated from the surface, and the remaining portion of liquid phase penetrates into the core, which is confirmed by the observed eutectic structure found exactly in the core of samples Fig. 8.

At higher boron contents (0.4% and 0.6%), less boron is evaporated from the surface as B_2O_3 (a smaller

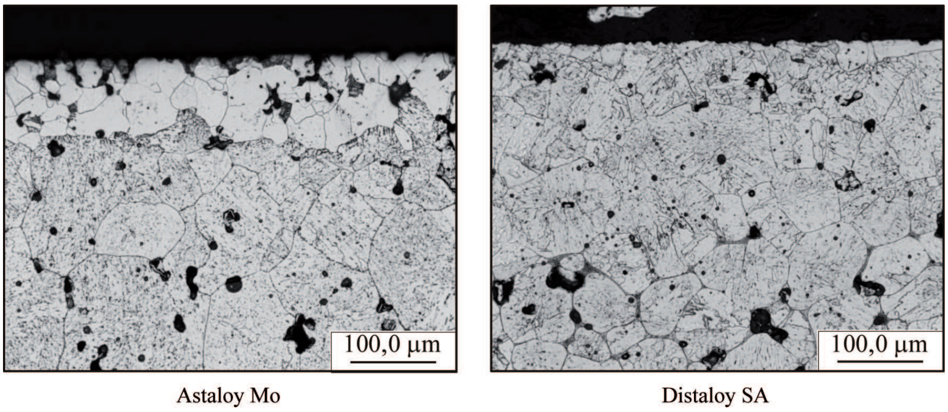


Fig. 8. Comparison of structures of inspissated zones formed in Astaloy Mo and Distaloy SA sinters modified with 0.4% B. Sintering parameters: 1473 K/60'/hydrogen

zone thickness is observed); a portion of it reacts with the matrix elements, which leads to the formation of borides, like in the case of Distaloy SA at 1473 K, a large portion of liquid phase is shifted towards the core of samples.

A similar phenomenon occurs in Astaloy Mo sinters, but only at 0.6% B (at which borides occur in the surface zone). It is likely to be connected with the analysis of input powders: apart from iron, Astaloy Mo contains only one alloy element (Mo), whereas Distaloy SA – apart from iron – contains three alloying elements, viz. Ni, Cu and Mo.

4. Conclusions

1. The sintering mechanism of Distaloy SA samples modified by boron is a liquid phase sintering , as a result of eutectic reaction between ferrite and complex borides.
2. The microstructures of Distaloy SA sinters with boron are characterized by an eutectic structure at grain boundaries with ferrite and complex borides.
3. With the increasing of boron (from 0.2 up to 0.6 wt%) the density, hardness and tensile strength values of Distaloy SA specimens improved. For comparison the same properties of Astaloy Mo and NC 100.24 sintered samples with boron were presented. It was stated that the highest values of properties were attained for Distaloy SA sinters modified by boron.
4. On the surface of sinters made from boron modified pre-alloyed powders (Fe-Ni-Mo-Cu) type Distaloy SA is creating a thickened layer. The similar thickened layer was observed also on the surface of Astaloy Mo samples with boron addition.

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