A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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ENHANCED SINTERING OF AUSTENITIC STAINLESS STEEL POWDER AISI 316L THROUGH BORON CONTAINIG MASTER ALLOY ADDITION

AKTYWOWANE SPIEKANIE PROSZKÓW AUSTENITYCZNEJ STALI NIERDZEWNEJ AISI 316L POPRZEZ DODATEK MIKROPROSZKÓW ZAPRAWY ZAWIERAJĄCEJ BOR

It is well known that boron is widely used in order to enhance sintering process for obtaining high density of sintered iron alloys. It was found that even a small amount of elemental boron added to iron based powder compacts, produces significant increase in densification rate upon formation of a liquid phase. Due to the attractive characteristic the use of boron has also been actively investigated for enhancing sintering stainless steels powders. In present research boron was added as a part of master alloy, which has been designed to provide the formation of wetting liquid phase, with accomplished characteristics for manufacturing controlled densification of sintered austenitic stainless steels powders AISI 316L. In this paper the influence of sintering atmosphere and the boron in 0,1; 0,2; 0,3 and 0,4 wt. % amount on the density, microstructure and selected properties of sintered austenitic stainless steels were reported. Green compacts obtained by cold compaction at 600 MPa reached densities around 6,2 g/cm^3. The sintering process was carried out both in pure dry hydrogen atmosphere and in vacuum at temperature 1240°C using dilatometer Netzsch DIL 402C. In order to interpret the influence of sintering atmosphere and boron content on the sintering behaviour of boron alloyed austenitic stainless steels powders during heating and isothermal holding, the evolution of the dilatometric curves have been discussed. The as-sintered microstructures were characterized under the SEM (EDS), while the pore morphology by the image analysis. In conclusion it could be affirmed that the addition of the master alloy containing boron to austenitic stainless steels powders, produces a permanent liquid phase that enhances densification compacts during sintering, in particular in hydrogen atmosphere. For this reason the results are promising from a technological point of view, because boron addition could extend applications of sintered stainless steel both with respect to lower sintering temperature and shorter time necessary to obtain well rounded pores which are desirable with respect to mechanical properties and corrosion resistance.

Keywords: Stainless steel, AISI 316L, boron, sintering, dilatometry

Bor jest skutecznym aktywatorem procesu spiekania proszków żelaza i proszków stopowych. Stwierdzono, że nawet niewielki dodatek boru aktywuje proces spiekania w wyniku pojawienia się cieczy zwilżającej powierzchnie cząstek proszków, przyczyniając się do wzrostu stopnia zagęszczenia spieku. Dzięki interesującym charakterystykom bor stosowany jest również do aktywowania spiekania proszków stali nierdzewnych. Celem przeprowadzonych badań było wyjaśnienie wpływu dodatku boru w ilości 0,1; 0,2; 0,3 i 0,4% cięż. wprowadzonego do mieszanki proszków w postaci mikroproszków zaprawy zawierającej bor, na kształtowanie się mikrostruktury i właściwości spiekanych austenitycznych stali nierdzewnych AISI 316L. Wypraski prasowano pod ciśnieniem 600 MPa uzyskując gęstość 6,2 g/cm^3. Spiekanie przeprowadzono w atmosferze suchego wodoru oraz w próżni, w temperaturze 1240°C, wykorzystując dylatometr Netzsch DIL 402C. W oparciu o przebieg krzywych dylatometrycznych analizowano wpływ dodatku boru oraz rodzaj zastosowanej atmosfery na przebieg procesu spiekania. Ponadto analizę mikrostruktury przeprowadzono w oparciu o obserwacje SEM (EDS), a morfologię porowatości w oparciu o analizę obrazu. Stwierdzono, że dodatek boru w postaci mikroproszków zaprawy przyczynia się do aktywacji procesu spiekania w szczególności w atmosferze wodoru. Uzyskane wyniki są bardzo interesujące nie tylko z naukowego punktu widzenia ale również z praktycznego, ponieważ mogą przyczynić się do zwiększenia zastosowań spiekanych austenitycznych stali nierdzewnych.

1. Introduction

Stainless steels owe their high position in modern industry, to their high corrosion resistance which is the critical feature in many applications, especially for parts exposed for contact with aggressive environments [1,2]. Powder metallurgy has been used in the manufacturing of stainless steels due to the low cost of production

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which eliminates any machining operations. Manufacturing through machining offers very high dimensional tolerance but the price for that is high cost, caused mainly by significant material loss. However, process of sintering stainless steels powders leaves in the sintering compacts an opened porosity which constitutes an effective way for corrosive factor to penetrate inner areas of the sintered component. Another stainless feature decrease is caused by the increased contact surface with environment also induced by opened porosity. Those problems are usually solved by forging or by other treatments which mechanically closes the opened pores, however such operations generates further costs and cannot be applied to every surface of a given part. Alternative way to solve the problem of opened porosity is to close it during the process of sintering by slight modification of chemical composition [3-10]. To achieve this goal the proper alloying system should intensify mass transport effectively and not to modify chemical composition significantly. Several researches indicate boron as an excellent activator for ferrous alloys sintering. Boron added to ferrous alloys creates during sintering liquid eutectic phase at the temperature of 1173°C which perfectly wets the base alloy particles' surfaces. This liquid induces several mechanisms of sinter densification, which mainly [11-13]:

1. Improved mass transport phenomena.
2. Particles rearrangements - liquid wets the base powder particles with their surfaces decreasing the friction between them what allows the particles start to translocate so that the higher density is being achieved.
3. Fragmentation. Liquid phase penetrates the grains boundaries and separate them from each other with the thin film of liquid which decreases the friction between them.
4. Its presence is directly linked up with an appearance of non-porous surface layer. When the boron amount is sufficient the non-porous surface layer thick for about $30 \div 40\mu m$ is being created. Curious thing is that, the former layer almost does not contain boron.

Even small mass boron addition in e.g. AISI 316L stainless steel is enough to intensify the sintering process. The boron addition beside the great positive changes in sintering stainless steels powders has also some negative influence on the sintered compacts properties, especially when almost continuous network of solidified brittle eutectic phase surrounding the grains appears. This solidified phase decreases mechanical properties of the sinter critically only when its' character is continuous. When network changes into dispersed precipitations the loss of mechanical properties is acceptable [14,15]. By optimization the sintering process, by design the proper temperature profile, sintering atmosphere and chemical composition the shape, amount and the size of precipitations changes. In the present work the results obtained after using a recently developed boron-containing master alloy for sintering the water atomized austenitic stainless steels powders is presented.

2. Experimental procedure

The possibility of eliminating continuous network of solidified eutectic phase accompanied with high densification level was investigated for two different atmospheres (hydrogen and vacuum) and four different additions of boron in the form of master alloy (Fe,Cr,Mn,Ni,Si,B).

All the mixtures of austenitic stainless steels AISI 316L powders were prepared by the calculated their chemical composition in order to obtain: 0,0; 0,1; 0,2; 0,3 and 0,4 wt. % of boron.

All tested mixtures were prepared in Turbula®mixer by 24h mixing. Rectangular dilatometric samples $4{\times}4{\times}15mm^3$ were manufactured by cold uniaxial pressing at 600 MPa. In order to minimize chemical composition changes, during pressing only matrix walls and punch walls were layered with lubricant: zinc stearate. After that, samples were sintered in Netzsch dilatometer DIL 402C in pure dry hydrogen atmosphere and under vacuum according to the following temperature profile:

- temperature stabilization to 30°C for 30min,
- heating up to 1240°C with a heating rate of 10°C/min,
- isothermal sintering at the temperature of 1240°C for 30min,
- cooling down to 30°C with a cooling rate of 20°C/min,
- temperature stabilization to 30°C for 60min,

For sintering in hydrogen the flow rate of the gas was 100 ml/min. Sintering was performed three times for each chemical composition to be sure of reproducibility of the obtained results.

Before and after sintering, samples were weighted to estimate material loss during sintering caused by vaporizing due to possibility of vaporization of boron and chromium, especially under vacuum at elevated temperature conditions. Density was measured by water displacement method.

Specimens for microstructural characterization were prepared by means of particular procedure in order to avoid modification of pore morphology. Evaluation of porosity quantity was performed using Aphelion^{TM}software. Five pictures were taken for analysis from the center of the samples. Standard deviation was calculated using these five values. The mi-

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crostructural characterization was also carried out with an optical microscope. After special grinding and polishing samples were chemically etched in temperature of 80°C÷90°C with Vilell's reagent:

- Grylerine 3cm^3
- Hydrochloric Acid 2cm^3
- Nitric Acid 1cm^3

In order to estimate differences in chemical composition of precipitations in sintered compacts the SEM EDS was used. The estimation of matrix chemical composition was performed by analyzing a fields of approx. 50-150 μm^2 while the same estimation made for precipitations was carried out only in a point. The interfaces between matrix and precipitations were under special attention.

3. Results and discussion

3.1. Dilatometry

Figure 1 shows the effect of sintering atmosphere on dimensional changes of boron free sintered austenitic stainless steel AISI 316L compacts. The total shrinkage after sintering in hydrogen is clearly higher than after sintering in vacuum what is directly connected with oxidized surfaces of stainless steel powder particles. Hydrogen as an atmosphere characterized with a much higher reductive potential is able to eliminate layer of Cr_2O_3 oxides and allow in this way diffusion to act. Removal of oxides layer lead to enhanced bonding between steel particles, what reflects as significant increased dynamic mechanical properties (elongation, impact strength).

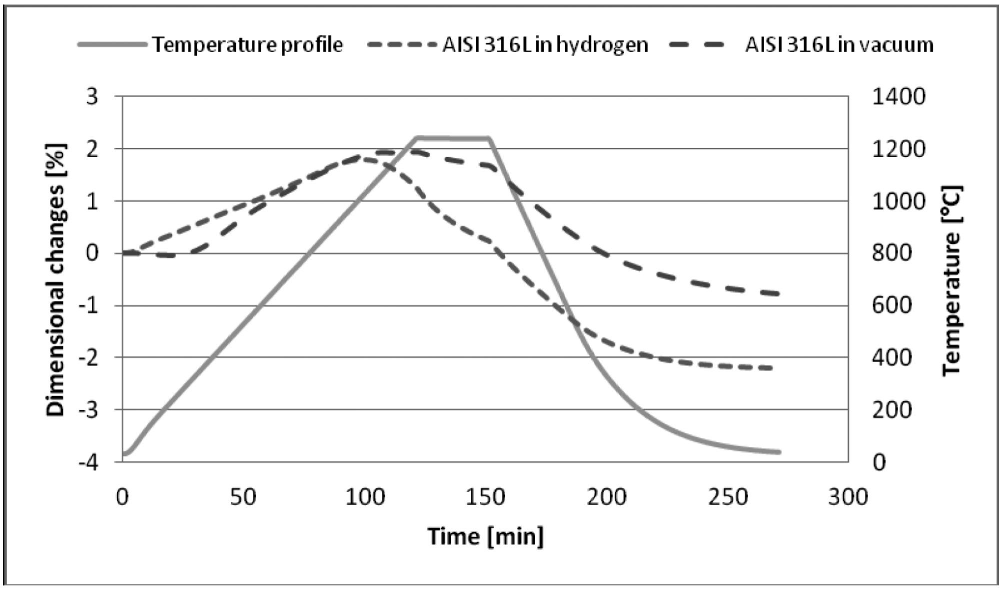

Fig. 1. Dimensional changes during sintering of boron free AISI 316L in pure hydrogen and in vacuum

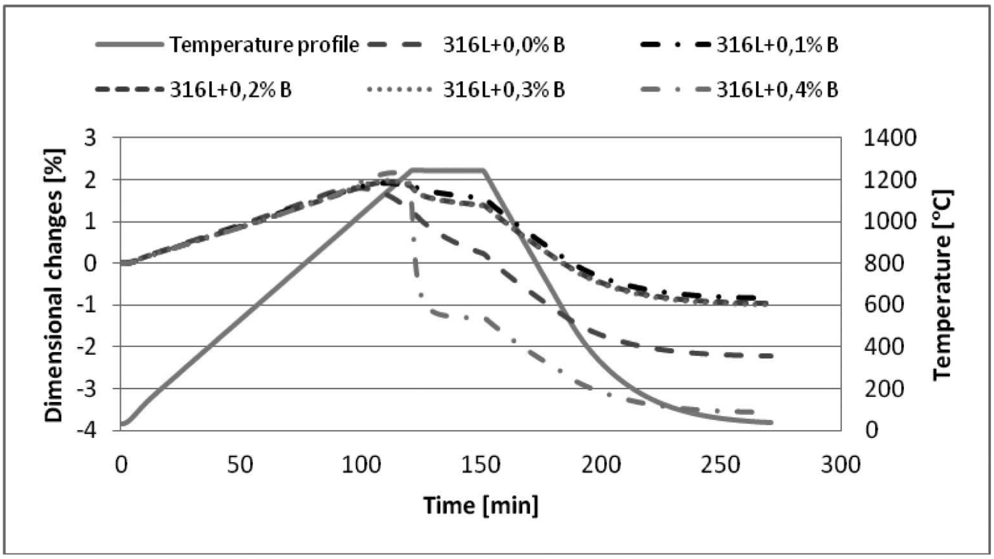

Fig. 2. Dimensional changes during sintering boron alloyed AISI 316L in pure dry hydrogen

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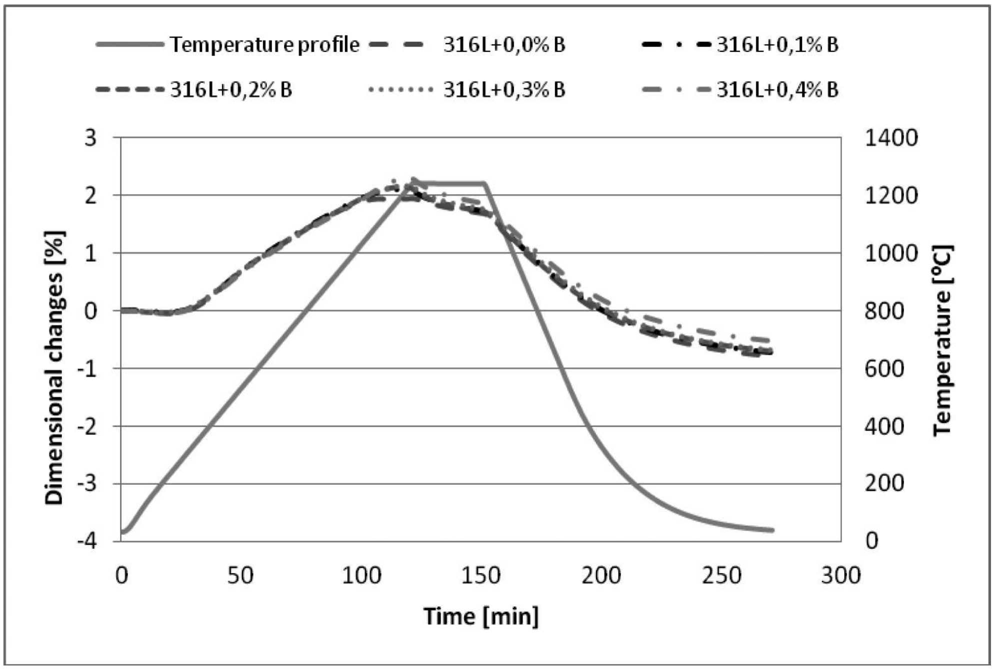

Fig. 3. Dimensional changes during sintering boron modified AISI 316L in vacuum

Figure 2 and 4 show the sintering behaviour of boron alloyed austenitic stainless steels powders sintered in pure dry hydrogen and vacuum. The significant shrinkage and though densification higher as compared with boron free sintered AISI 316L was obtained only for 0,4 wt. % of boron addition introduced in the form of MasterAlloy, during sintering in hydrogen. Furthermore, for 0,4 wt. % of boron addition, desired liquid phase was obtained what reflects as a slope's high angle of dilatometric curve which is defined as rate of dimensional changes. The greater is dimensional changes rate the grater is the angle of curve progress – especially in the moment of liquid appearance. For the other compositions not sufficient amount of liquid phase not only increases the friction on particles contact surfaces, but also in considerable extent blocks creation of liquid eutectic phase, what in consequences was revealed in dilatometric measurement by insufficient total shrinkage.

Figure 3 and 4 shows that sintering of boron alloyed austenitic stainless steel powder AISI 316L in vacuum does not brings any changes in shrinkage and in curve progress as well at all. These results suggest, that in spite of such reactive addition of boron in the form of MaterAlloy, the diffusion between master alloy powder and matrix in vacuum is not efficient what results in lack of dimensional changes of a compact during sintering.

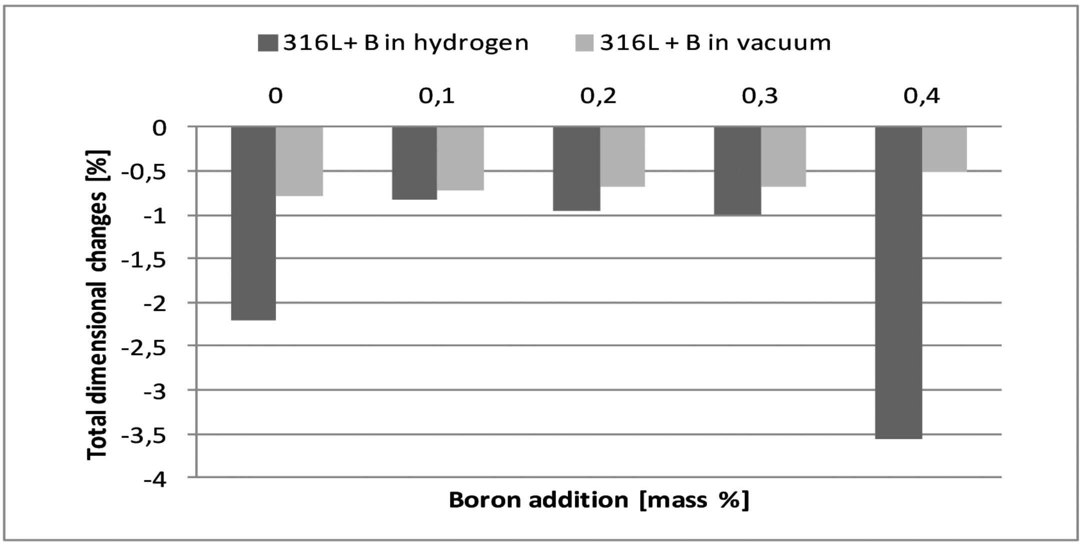

Fig. 4. Total shrinkage obtained after sintering of boron alloyed AISI 316L in pure hydrogen and in vacuum

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3.2. Density

Dilatometry shows in continuous way dimensional changes during whole process of sintering but does not provide the information about material dimensional behavior in directions perpendicular to axis of measurement. That is the main cause why the sample were measured and weighted after sintering. Results of density calculations are presented in the Figure 5.

Results obtained by weighting and measuring of samples confirms results of the dilatometric tests after taking into consideration the measurement uncertainty which was estimated on level of 0,5 mg. Only deviation for the 0.4 wt. % boron addition for compacts sintered in vacuum – weighting shows lower density than it comes out from dilatometry. Main cause was sample slight lateral deformation visible with an unarmed eye. In place of deformation additional measurements were made. In order to research mass loss caused by some elements (e.g. boron and chromium) vaporizing all samples were weighted on a precise laboratory balance before and after process of sintering. Results of weighting are presented in Figure 6.

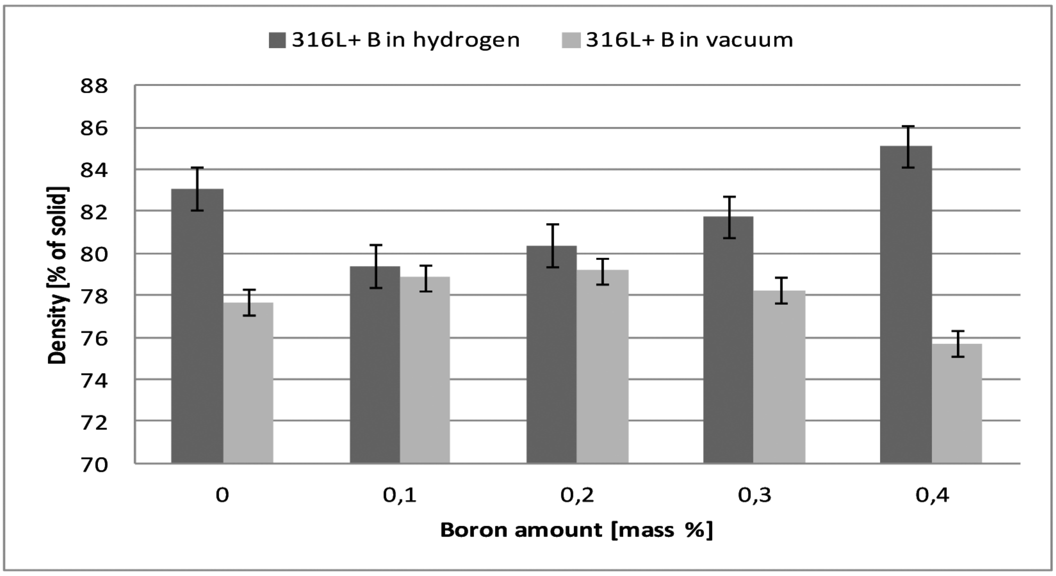

Fig. 5. Density of boron alloyed austenitic stainless steel AISI 316L after sintering in hydrogen and in vacuum

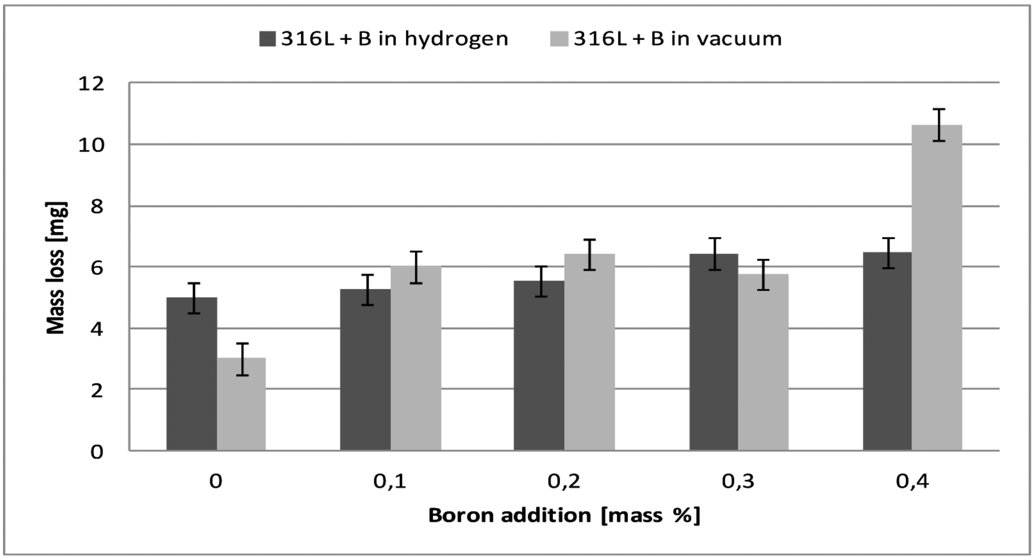

Fig. 6. Mass loss after sintering boron modified AISI 316L in pure hydrogen and in vacuum

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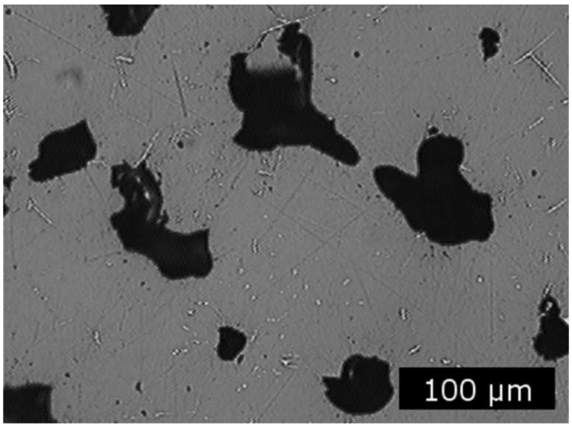

Fig. 7. Example of porosity morphology of sintered austenitic stainless steel alloyed with 0,4 wt.% boron sintered in hydrogen

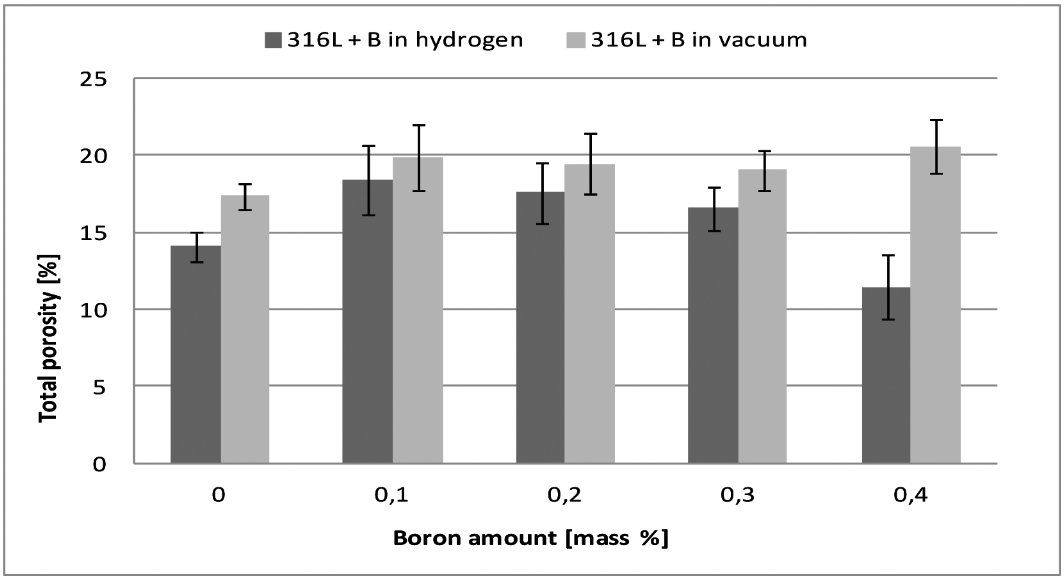

Fig. 8. Porosity estimated using Aphelion™software

3.3. Microstructural characterization

Metallographic cross sections were prepared according to particular procedures to avoid porosity morphology's deformation. What is more, software was calibrated in a way to count pores and to avoid counting precipitation or eventual scratches – Figure 7 is such an output image example.

Porosity estimation was performed using image analysis Aphelion™software. Five pictures were taken from places near the sample core. Average porosity value and standard deviation were calculated using those five values. Results presented in Figure 8 directly confirm the results from dilatometric tests.

For detailed microstructural characterization Villel's etchant was used in order to reveal the grain boundaries and precipitations in sintered materials. Microstructures of all the compacts sintered in hydrogen atmosphere (left column) and in vacuum as well (right column) are presented in Table 1. For both sintering atmospheres, typical microstructure obtained for stainless steels with addition of boron in the form of master alloy can be observed, which consists of the austenite matrix and the eutectic constituent at the grain boundaries and inside the grain, particularly for higher boron amount. Furthermore, as was observed in particular for the grain size, the microstructure and the eutectic formed in the sintered steel in vacuum are coarser than the corresponding ones in hydrogen. This phenomenon is probably due to the higher cooling rate in hydrogen than in vacuum. Beside the amount of eutectic constituent increases as boron and most particularly the master alloy added to the powder mixture increases.

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TABLE 1

Microstructures of boron alloyed AISI 316L sintered in hydrogen and in vacuum

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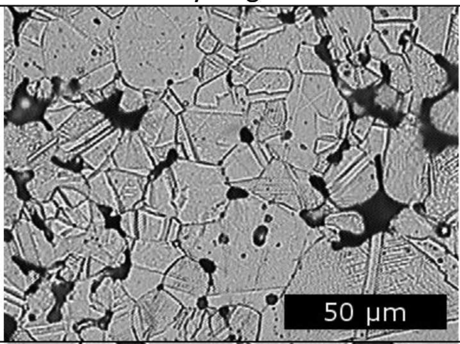
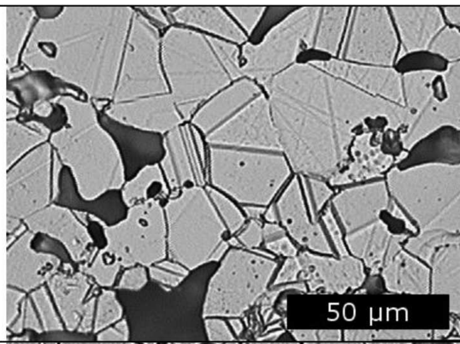
<tr><td>316L + 0,0%B</td><td>
</td><td>
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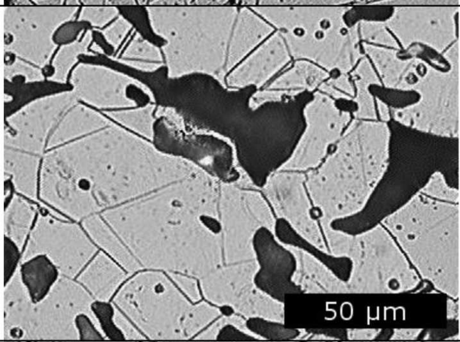
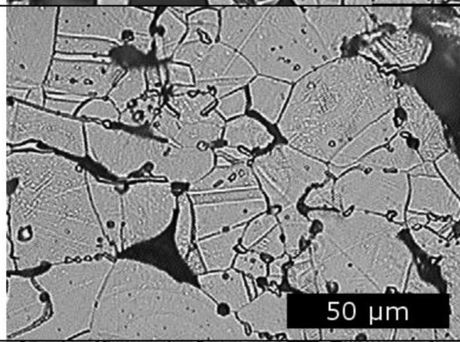
<tr><td>316L + 0,1%B</td><td>
</td><td>
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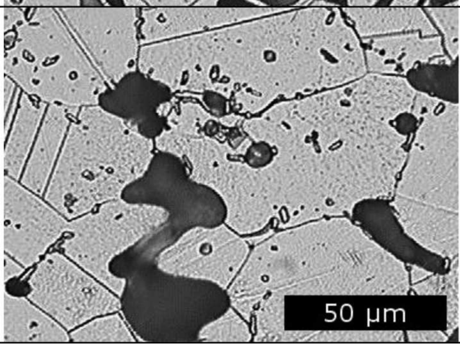
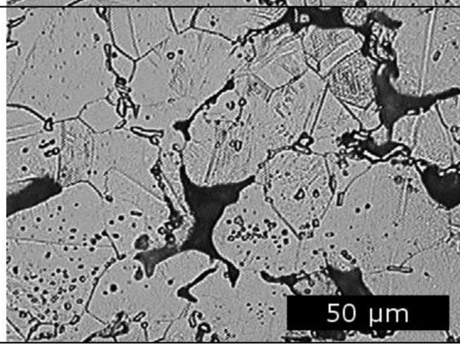
<tr><td>316L + 0,2%B</td><td>
</td><td>
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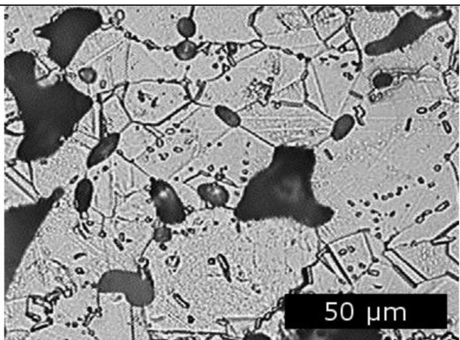
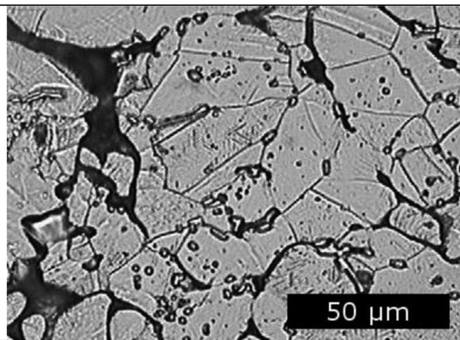
<tr><td>316L + 0,3%B</td><td>
</td><td>
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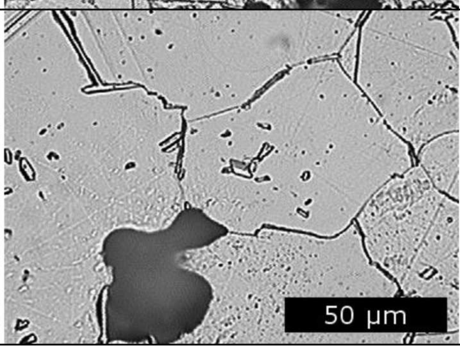
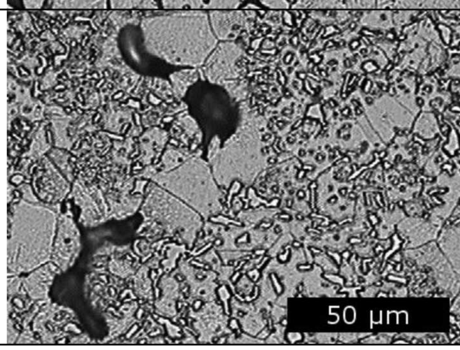
<tr><td>316L + 0,4%B</td><td>
</td><td>
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In order to distinguish the difference in chemical composition in eutectic constituent and in matrix after sintering in both sintering atmospheres, a detailed EDS analyses was performed. In figures 9 and 10 SEM images of boron alloyed austenitic stainless steel AISI 316L after sintering in hydrogen and in vacuum were presented respectively. EDS analysis done by linear mode included the matrix and the precipitation as well, point analysis of precipitation and surface analysis of the matrix.

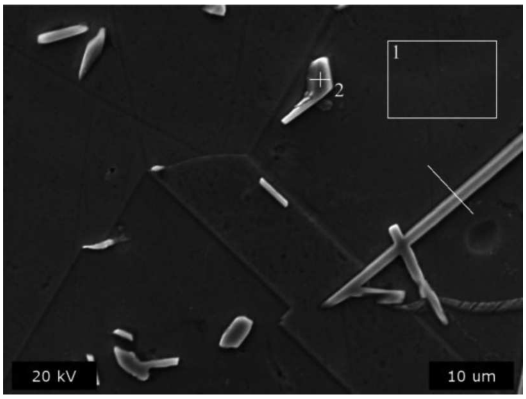

Fig. 9. SEM image of AISI 316L modified with 0,4 wt. % of boron introduced as MasterAlloy, after sintering in hydrogen. 1) point analysis, 2) surface analysis, 3) linear analysis

The analysis of EDS results shows clearly that upon solidification the liquid phase decomposes in a combination of Cr-borides, Mo-borides and austenite. Furthermore, during sintering some diffusion Mn, Si and Ni from master alloy to the matrix occurred. However sintering atmosphere doesn't influence chemical composition of matrix and eutectic constituent.

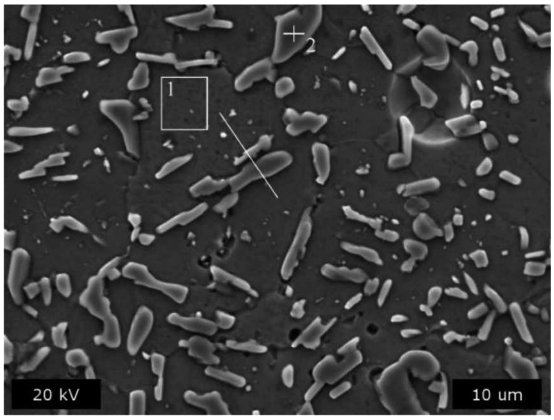

Fig. 10. SEM image of AISI 316L modified with 0,4 wt. % of boron introduced as MasterAlloy, after sintering in vacuum. 1) point analysis, 2) surface analysis, 3) line analysis

TABLE 2

Summary of EDS results from various phases in sintered microstructure as shown in Fig. 9

Elements (wt%)	Point analysis	Surface analysis
Fe	31,01	61,88
Cr	54,25	18,31
Ni	1,35	13,22
Mo	9,60	2,85
Mn	3,54	1,91
Si	0,2	1,84

Linear analysis of Mr, Mn, Fe, Ni in Fig.9.

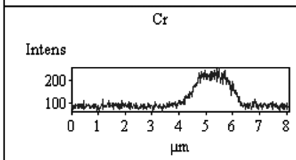	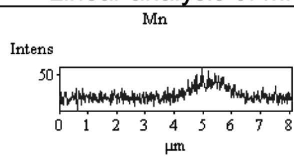	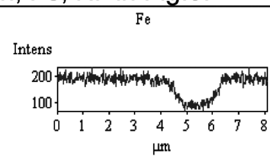	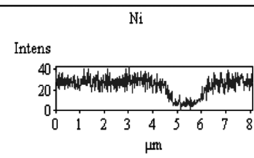

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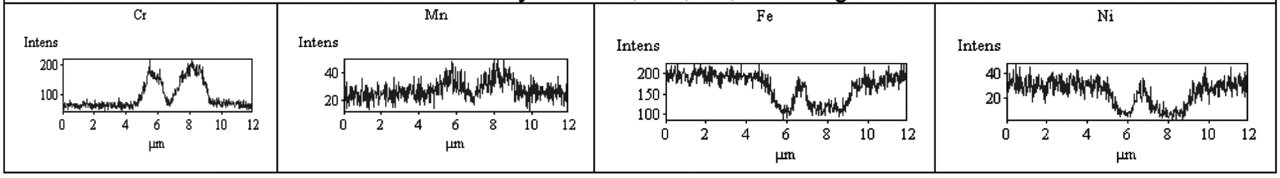
TABLE 3

Summary of EDS results from various phases in sintered microstructure as shown in Fig. 9

Elements (wt%)	Point analysis	Surface analysis
Fe	35,31	61,73
Cr	52,12	16,71
Ni	1,39	12,74
Mo	6,31	4,33
Mn	4,83	2,69
Si	0,04	1,8
Linear analysis of Mr, Mn, Fe, Ni in Fig.10.		



4. Conclusions

The addition of the master alloy containing boron produces a permanent liquid phase especially for 0,4 wt.% addition of boron that enhances densification of the compacts during sintering, in particular in hydrogen atmosphere. Sintered in vacuum doesn't allow to exploit beneficial effect of boron on densification of sintered materials. On the basis of EDS analysis it could be concluded that persistent liquid phase was formed as a result of eutectic reaction between the alloy matrix and a complex boride (Cr,Mo,Fe). Furthermore, from the microstructural observation of specimens it was evidenced that when introduced boron in the form of master alloy, solidified eutectic network of grain boundary can be avoided, what is important because it would be possible to maintain good mechanical properties of sintered steels.

For this reason the results are promising from technological point of view, because boron addition could extend applications of sintered stainless steel both with respect to lower the sintering temperature and shorter time necessary to obtain well rounded pores which are desirable with respect to mechanical properties and corrosion resistance.

Acknowledgements

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