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EFFECT OF BORON SINTER-AID ON THE MICROSTRUCTURE AND PROPERTIES OF AUSTENITIC STAINLESS STEEL-TIB$_2$ COMPOSITES

WPŁYW DODATKU BORU NA MIKROSTRUKTURĘ I WŁAŚCIWOSCI KOMPOZYTÓW STAL AUSTENITYCZNA-TIB$_2$

In the work, the effect the boron addition on the microstructure and properties of the composites with austenitic steel of matrix was investigated. The composites were consolidated using the high pressure-high temperature (HP-HT) method. Two composite types were fabricated, i.e. steel with 8 vol.% TiB$_2$ and steel with 8 vol.% TiB$_2$ and 1 vol.% boron. Density of sintered materials was measured according to the Archimedes principle. Mechanical properties were determined by Vickers microhardness and compression test. The wear resistance was investigeted using ball-on-disc method. The microstructure of composites was analyzed using a scanning electron microscope.

The results show that the boron addition and sintering parameters have influence on the mechanical and tribological properties of the composites. Materials are characterized by very high density. The composites with boron exhibited higher Young's modulus and microhardness in comparison with the properties of composites without boron addition.

Keywords: HP-HT sintering, boron, AISI316L matrix composite, TiB$_2$, physico-mechanical properties

W pracy przedstawiono wyniki badań dotyczące wpływu dodatku boru na mikrostrukturę oraz właściwości kompozytów o osnowie stali austenitycznej. Do wytworzenia kompozytów zastosowano spiekanie wysokociśnieniowe. Wytworzono dwa wartianty kompozytu: stal z 8%obj. TiB$_2$ oraz stal z 8%obj. TiB$_2$ +1% obj. boru. Po procesie spiekaniu określono gęstość pozorną, moduł Younga, mikrotwardość Vickersa oraz wytrzymałość na ściskanie spiekanych kompozytów. Odporność na ścieranie określono stosując metodę ball-on–disc. Badania mikrostruktury przeprowadzono za pomocą skaningowej mikroskopii elektronowej (SEM).

Otrzymane wyniki wykazały, że dodatek boru oraz warunki spiekania mają wpływ na właściwości mechaniczne oraz tribologiczne kompozytów. Wszystkie spiekane materiały charakteryzowały się bardzo wysoką gestością. Kompozyty modyfikowane borem wykazują wyższy moduł Younga oraz mikrotwardość.

1. Introduction

Powder metallurgy has been widely used in the production of metal matrix composites. The main advantages of powder-based technologies include energy and material savings, high productivity and dimensional accuracy of sintered parts. The properties of sintered composites depend on the sintering method and sintering conditions and on parameters such as the grain size and roughness of its surface, the type of the reinforcing phase (particles or fibres), its distribution in the matrix, etc. Steel matrix composites are very attractive materials in terms of both economy and application. Composite materials with steel matrix and ceramic particles are potential materials dedicated for structural applications because of their attractive physical and mechanical properties [1-3]. Currently, austenitic steels are increasingly used as a composite matrix [4-6].

In recent years, studies have been conducted [7-12] on the effect of various activators, such as copper, phosphorus, and boron, on the sintering process and on the properties and microstructure of sintered austenitic stainless steels. It has been demonstrated that the addition of a few thousandths of a percent of boron affects the strength and elongation of the austenitic steel during creep tests. This is a result of the boron tendency to segregate at grain boundaries and reduce in this way their energy. Boron in these steels forms the complex borides of iron, nickel and chromium. As established in the studies, the addition of boron to the mixture of iron powder effectively activates the process of free sintering. At the sintering temperature higher than the temperature of the eutectic transformation, a liquid phase appears and it greatly contributes to the densification of sinter, changing also its structure and consequently improving the mechanical properties [13,14]. The authors of the research works [7-9,15,16] have explained the mechanism of the

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sintering process of the austenitic stainless steel modified with boron. According to studies described in [10,11], the sintering process carried out on steel containing 0.4 wt.% boron leads to significant densification of the material. In this case, sintering takes place in the liquid phase which is formed by a eutectic reaction between the matrix and the boride phase (Fe, Cr, Mo)$_2$B. The mechanical properties of steel modified with boron depend not only on the density of this steel but also on its microstructure. To obtain the required microstructure and best properties, an optimum amount of boron should be added. It has been shown that, depending on the content of boron and the heating rate to a temperature of 1240°C, some changes take place in the microstructure of materials tested. At a cooling rate of 20°C/min and the boron content of 0.2 wt.%, an austenitic matrix was obtained in the sintered products, while at the boron content of 0.8 wt.%, fine precipitates of borides were traced in the matrix. On the other hand, Kazior et al. [9,17] determined the effect of various sintering parameters on the properties and microstructure of AISI 316L steel. In terms of the performance properties, the best results were obtained by sintering boron-containing steel in an atmosphere of hydrogen. It has been shown that sintering at 1240°C in pure hydrogen at a suitable rate of heating and with an appropriate addition of boron gives the degree of compaction close to the theoretical density.

This article attempts to clarify the effect of the addition of boron on the microstructure and properties of sintered AISI 316L steel reinforced with TiB$_2$ particles, produced by the HP-HT method.

2. Materials and experimental procedures

The initial materials were powders (Fig. 1):

- TiB$_2$ (average grain size below 2.5-3.5 μm, purity of 99.9%, H.C. Starck)
- AISI 316L austenitic stainless steel (average grain size of about 25 μm, Hoganas)
- boron (average grain size below 5-7 μm, purity of 99.9%, Goodfellows).

Initial phase compositions of mixtures for the samples preparation were as follow (Fig. 2):

- AISI 316L steel + 8 vol.% TiB$_2$ mixtures,
- AISI 316L steel + 8 vol.% TiB$_2$ +1 vol.% B.

The mixtures were produced by mixing the powders in a TURBULA mixer for 8 hours.

Aditionally, the AISI 316L austenitic stainless steel was sintered.

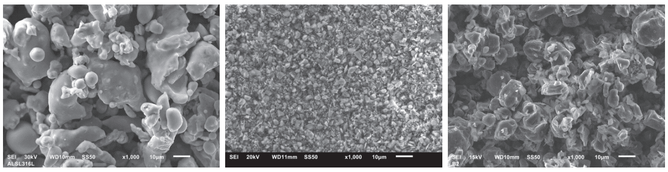

a) b) c)

Fig.1. SEM micrographs of: (a) AISI 316L steel, (b) TiB$_2$ and (c) boron powders

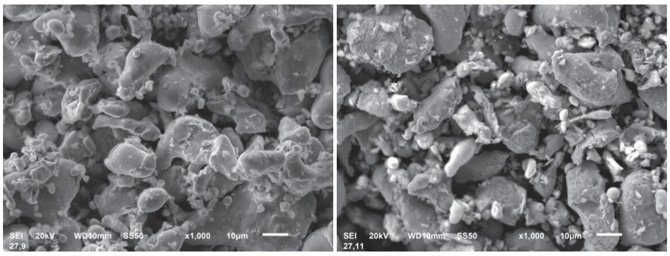

a) b)

Fig. 2. SEM micrographs of powders mixtures: (a) steel +8 vol.% TiB$_2$, (b) steel + 8 vol.% TiB$_2$+1 vol.% boron

A special gasket assembly for high pressure-high temperature (HP–HT) apparatus was used. The experiment was carried out using high pressure apparatus of the Bridgman type at temperature of 1100°C and 1300°C and pressure of 5 and 7±0.2 GPa for 60 seconds. Samples were heated in an internal graphite heater of an inside diameter of 15 mm.

The density was determined by the Archimedes method. Young's modulus of the composites was measured basing on the velocity of the ultrasonic waves transition through the sample using ultrasonic flaw detector Panametrics Epoch III. The accuracy of the calculated Young's modulus was estimated at 2 %. The microstructure of the sintered materials was evaluated by scanning electron microscopy (SEM; Hitachi SU-70) with Wavelength Dispersive Spectroscopy (WDS). The X-ray diffraction (XRD) analysis was used to determine the phase compositions.

The microhardness of the specimens was measured by Vickers method using a microhardness tester (NEXUS 4000) with a load of 2.942 N. The compression tests were carried out using a universal testing machine with (INSTRON TT-DM) with strain rate of 10^{-3} s.

Tribological tests were performed using a ball-on-disc wear machine UMT-2T (producer CETR, USA). Tests were carried out without lubricant according to the ISO 20808:2004(E [18]. The friction force was measured continuously during the test using the extensometer. For each test a new ball was used. Specimens were washed in high purity acetone and dried. After the ball (Al$_2$O$_3$) and sample were mounted, materials were washed in ethyl alcohol and then dried. Table 1 presents the wear test conditions. Following the wear test, the specific wear rate was calculated. The cross-sectional microstructure of worn surface was observed using a scanning electron microscope (SEM).

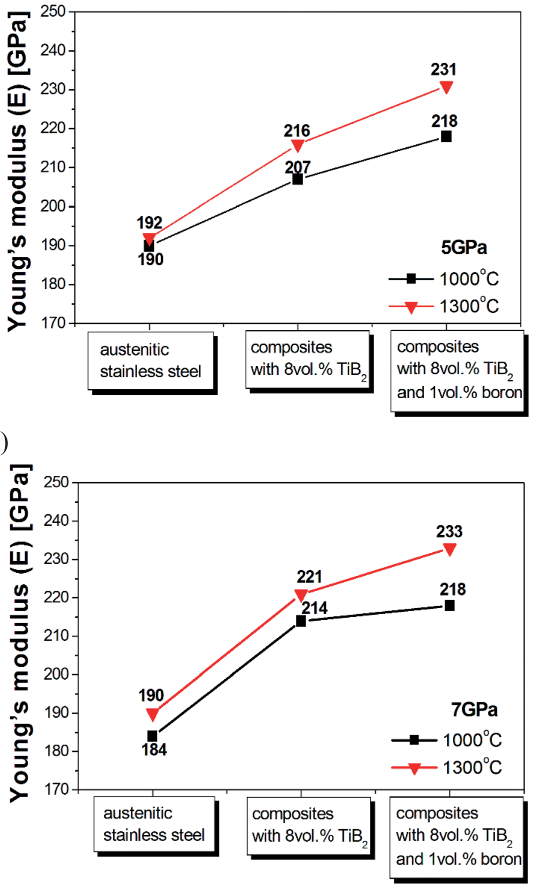
TABLE1

The wear test conditions which were applied in tribcological tests

Wear test conditions	
ball material	Al$_2$O$_3$
diameter of ball	3.175 mm
friction track diameter	4mm
sliding speed	0.1 m/s
total sliding distance	200 m
test duration	2000 s
load applied	4 N
temperature	23°C

3. Results and discussion

Table 2 gives the results of studies of the physical and mechanical properties of sintered materials allowing for the effect of boron addition. The results showed that, in all the examined materials, a very high degree of compaction was achieved in a very short time of sintering, i.e. 60 seconds. The combination in HP-HT method of high pressure and high temperature allowed carrying out a very effective sintering, yielding materials with very high density confirmed by the density measurements. For all the sintered composites and for the austenitic stainless steel, a very high relative density of the order of 99-100% of the theoretical density was obtained. In contrast, the porosity of the sintered composites was at a level of 0.003-0.015%. The results obtained (Fig. 3, Table 2) clearly show an improvement in Young's modulus and an insignificant decrease in Poisson's ratio as a result of the reinforcing TiB_2 phase and boron addition introduced to the composite matrix. Higher temperature of 1300°C yielded the highest value of Young's modulus. In the case of composite modified with boron, further improvement in Young's modulus was obtained. Based on these results, it has been concluded that the addition of boron introduced to the composite matrix allows for an improvement of Young's modulus compared to the results obtained for the boron-free composite (Fig. 3). Young's modulus for the composite with 8% TiB_2 is 216 GPa (1300°C-5GPa), while in the same composite modified with boron it amounts to 231 GPa (1300°C-5GPa).



a)

b)

Fig. 3. Effect of the boron addition on the Young's modulus of the composites

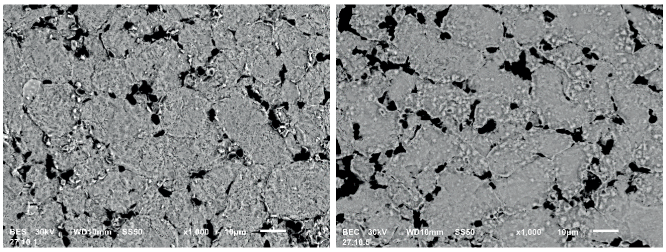
Figures 4 and 5 show examples of microstructures obtained in the composites sintered by HP-HT under different conditions. Microstructural observations by scanning electron

TABLE2

The physical and mechanical properties of sintered composites

Tested materials	Sintering parametres		Apparent density ρ_0 [g/cm³]	$\frac{\rho_0}{\rho_{teor}}$ [%]	Porosity [%]	Poisson's ratio η [-]	Young's modulus E [GPa]	$\frac{E}{E_{teor}}$ [%]
	Temperature [°C]	Pressure [GPa]						
AISI316L steel	1000	5	7.94	100	0.005	0.30	190±3.8	91
	1300	5	7.91	100	0.004	0.31	192±3.8	94
	1000	7	7.54	100	0.005	0,29	184±3.7	91
	1300	7	7.52	100	0.005	0.30	190±3.8	93
AISI316L steel+ 8 vol.% TiB_2	1000	5	7.66	100	0.007	0.29	207±4.1	88
	1300	5	7.77	100	0.004	0.29	216±4.3	93
	1000	7	7.57	99	0.011	0.29	214±4.3	88
	1300	7	7.59	100	0.005	0.29	221±4.4	94
AISI316L steel+ 8 vol.% TiB_2 +1 vol.% B	1000	5	7.89	99	0.010	0.29	218±4.4	92
	1300	5	7.87	99	0.013	0.28	231±4.6	97
	1000	7	7.93	100	0.005	0.29	218±4.4	92
	1300	7	7.93	100	0.003	0.28	233±4.7	98

microscopy revealed a uniform distribution of the reinforcing TiB_2 phase in the steel matrix obtained in both sintered composite types. Microscopic examinations showed that the tested composites were almost completely free from porosity. Analysis of the chemical composition (WDS) in microregions of the sintered composites revealed the presence of precipitates containing nickel (Fig. 6). Additionally, in the composites modified with 1 vol.% boron, the presence of characteristic boron-rich but titanium-free areas of about 20-40 μm size was evidenced (Fig. 7). The areas were surrounded by a diffusion zone, shown in Figure 7. This may prove the fact that the very short time of HP-HT sintering (60 seconds) is not sufficient to complete boron diffusion in the steel matrix. The results of X-ray examinations (Figs. 8 and 9) have indicated the presence of TiB_2 and of an iron-nickel-chromium phase in the matrix of both composite types.



a) b)

Fig.4. SEM micrographs of the sintered composites with 8 vol.% TiB_2: a) 1000°C-7GPa and b) 1300°C-7 GPa

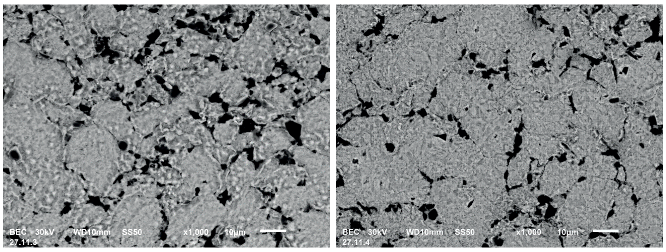


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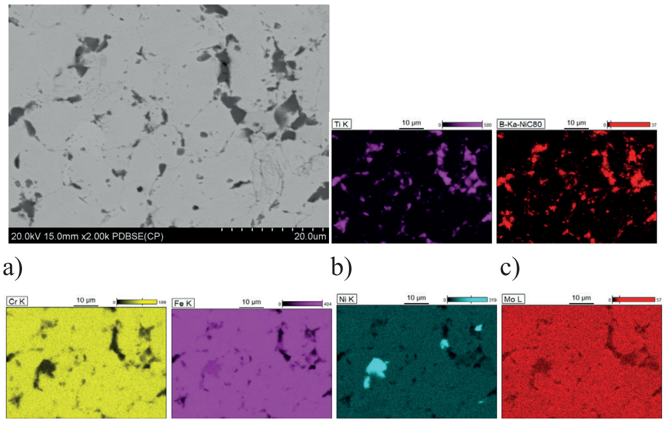
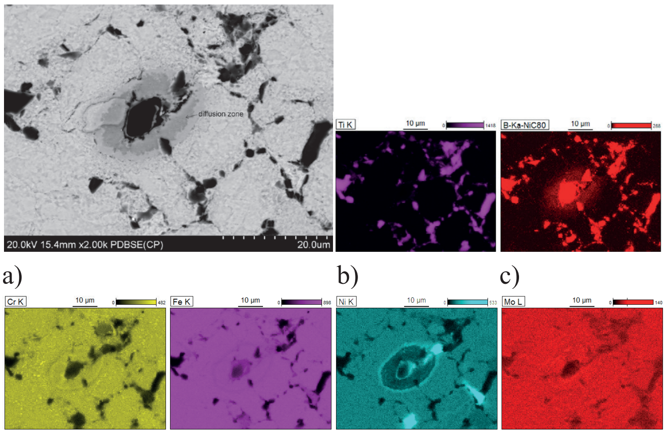
Fig. 5. SEM micrographs of the sintered composites with 8 vol.% TiB_2 and 1 vol.% boron: a) 1000°C-7GPa and b) 1300°C-7GPa



a) b) c)

d) e) f) g)

Fig. 6. (a) Microstructure (SEM) of the composite with 8 vol.% TiB_2 and (b-g) the element distribution maps by WDS analysis for titanium, boron, chromium, iron, nikel and molibdenium



a) b) c)

d) e) f) g)

Fig.7 . (a) Microstructure (SEM) of the composite with 8 vol.% TiB_2 and 1 vol.% boron and (b-g) the element distribution maps by WDS analysis for titanium, boron, chromium, iron, nikel and molibdenium

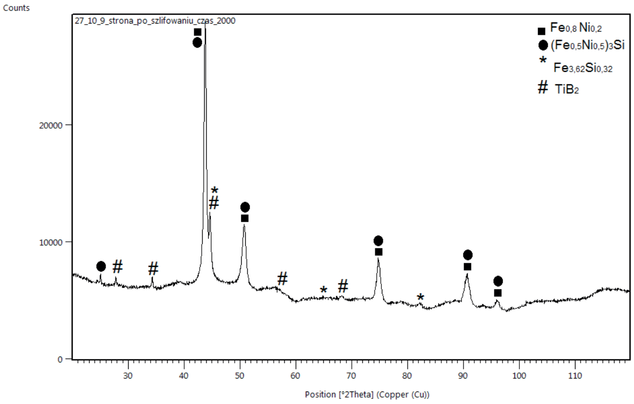


Fig. 8. XRD patterns of the composite with 8 vol.% TiB_2 (1300°C-7 GPa)

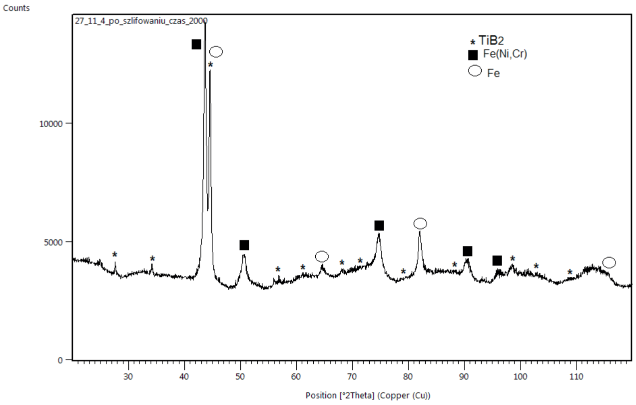
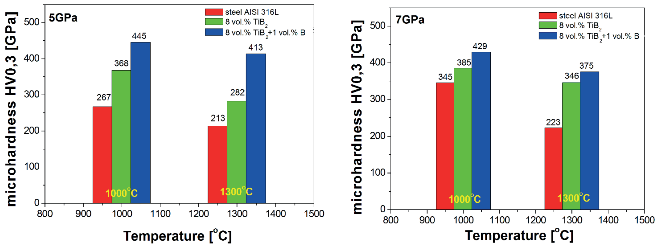


Fig. 9. XRD patterns of the composite with 8 vol.% TiB_2 + 1 vol.% boron (1300°C-7 GPa)

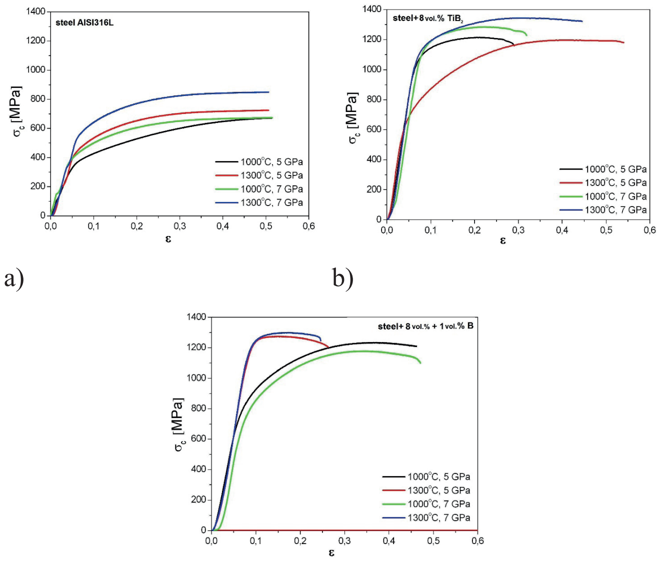
The results of microhardness measurements taken on the sintered materials are shown in Figure 10. Studies proved that the addition of 1 vol.% boron to the matrix of the austenitic steel improves microhardness, especially in the composites sintered at low pressure. The comparison shows that in the steel sintered at a pressure of 5 GPa at a temperature of 1000°C and 1300°C, the microhardness values are 267 HV0.3 and 213 HV0.3, respectively, while in the composite with 8 vol.% TiB_2, microhardness increases to 368 HV0.3 and 282 HV0.3, respectively. Adding 1 vol.% boron to the composite raises the microhardness to 445 HV0.3 and 413 HV0.3 for the temperature of 1000°C and 1300°C, respectively (5 GPa).



a) b)

Fig. 10. Results of microhardness as a function of sintering temperature for sintered materials

The performed compression tests (Fig. 11) have demonstrated that the use of TiB_2 as a reinforcing phase improves mechanical properties of the tested composites as compared to the steel without reinforcement. Considering the sintering conditions, for composites with 8 vol.% TiB_2, a compressive strength in the range of 1170-1320 MPa was obtained, while for the AISI 316L steel without reinforcement, the compressive strength was in the range of 600-800 MPa. Adding 1 vol.% boron to the matrix slightly improved the compressive strength of the composites. In all boron-modified composites, the obtained compressive strength exceeded 1250 MPa.



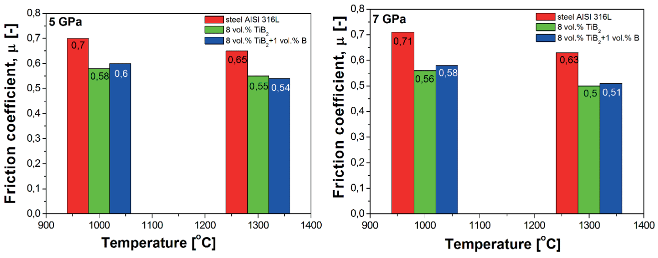
a) b)

c)

Fig. 11. Compressive strength as a function of strain for: a) steel AISI316L, b) steel+8 vol.% TiB_2 and c) steel+8 vol.% TiB_2 +1 vol.% B

Figures 12 and 13 show the results of tribological tests, which were carried out by the ball-on-disc method. For composites containing 8 vol.% TiB_2, the obtained friction coefficient (μ) was in the range of 0.5-0.58. For comparison, the coefficient of friction (μ) obtained in the sintered AISI 316L steel was in the range of 0.63-0.70. The addition of TiB_2 improved the wear resistance of the composite due to the high hardness of TiB_2 ceramics, amounting to 3400 HV [19]. TiB_2 particles protect the steel matrix during the process of friction, reducing its wear. This is confirmed by the values of the specific wear rate ($W_{v(disc)}$, Fig. 13). Introducing TiB_2 ceramics to the matrix reduced the value of the specific wear rate ($W_{v(disc)}$) by about 25-30%, compared to the value obtained for the AISI 316L steel without reinforcement. The test results have indicated that the coefficient of friction also depends on the sintering pressure, particularly at the sintering temperature of 1300°C. Boron, on the other hand, was observed to have no significant effect on the tribological properties of sintered composites. The coefficients of friction (μ) and wear rates ($W_{v(disc)}$) of the composite with 8 vol.% TiB_2 and of the composite with 8 vol.% TiB_2 + 1 vol.% B were very similar (within the measurement uncertainty), assuming the values of $\mu = 0.5$ and 0.51 and $W_{v\,(disc)} = 348$ and $364 * 10^{-6}\ mm^3 / N \bullet m$, respectively.

After tribological tests, the wipe traces formed on the sample surfaces were examined microscopically. Figure 14 shows examples of wipe traces formed on the sintered composite materials. It is easy to notice visible signs of wear in the form of grooves present in the friction areas. Uniform furrowing visible on the whole friction surface proves that in this case it is the abrasive mechanism that is responsible for the wear process. No major differences in the nature of abrasion were observed in either of the examined composites.



a) b)

Fig. 12. Coefficient of friction vs. sintering temperature of the composites for sintering pressure of: a) 5 and b) 7 GPa

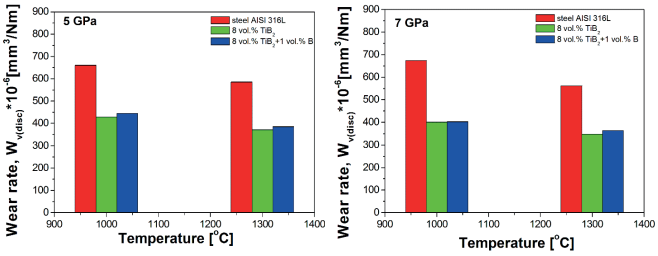


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Fig. 13. Wear rate vs. sintering temperature of the composites for sintering pressure of: a) 5 and b) 7 GPa

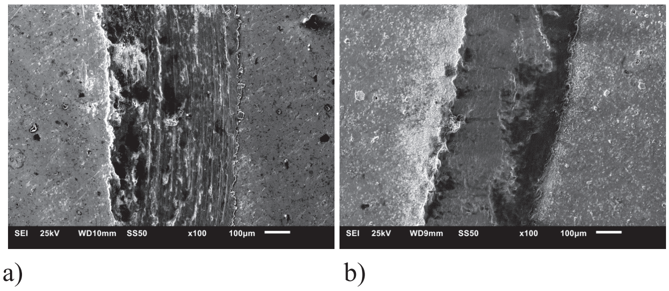

Fig. 14. The selected micrograph (SEM) of the worn surface of composites: a) steel+8 vol.% TiB_2 and b) steel+8 vol.% TiB_2 +1 vol.% boron (1300°C-7GPa).

4. Conclusions

1. The addition of boron in an amount of 1 vol.% improves some mechanical properties of composites sintered by HP-HT, in particular the Young's modulus and microhardness.
2. The results show that the properties of sintered composites depend on the sintering conditions (temperature and pressure).
3. All sintered composites have reached nearly 100% apparent density with very low porosity.
4. The formation of boron-rich areas was observed in the microstructure of composites modified with this element.

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