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COMPOSITES THEORY AND PRACTICE

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AUSTENITIC STAINLESS STEEL-TiB_2 COMPOSITES OBTAINED BY HP-HT METHOD

Titanium diboride has many advantages such as a high melting point, high Young's modulus, low density, good thermal conductivity and high Vickers hardness. Therefore, the addition of TiB_2 to metal matrices has also been observed to greatly increase stiffness, hardness and wear resistance. The aim of the studies was to determine the influence of different contents of TiB_2 ceramics on selected properties of AISI 316L austenitic stainless steel. Metal matrix composites containing TiB_2 as a particulate phase were produced by high pressure-high temperature (HP-HT) sintering. Next, the apparent density (ρ_o) was measured using the hydrostatic method. The hardness was determined by the Vickers method. Young's modulus measurements of the sintered composites were also taken using the ultrasonic method of measuring the transition speed of transverse and longitudinal waves. This paper also presents the microstructure analysis of composites with different contents of TiB_2 particles. The composite was analyzed by observations with an optical microscope, scanning electron microscope (SEM) and energy dispersive spectrometry (EDS). It was shown that the properties of the composites significantly depend on the sintering conditions. Generally, the application of a larger participation of strengthening phase improves the properties of the sintered composite materials. The microstructure of the composites with different contents of TiB_2 consisted of a fine and uniform TiB_2 particle distribution along the grain boundaries.

Keywords: **metal matrix composites, TiB_2 ceramic, HP-HT sintering**

KOMPOZYTY STAL AUSTENITYCZNA AiSi316L -TiB_2 OTRZYMYWANE METODĄ SPIEKANIA HP-HT

Dwuborek tytanu charakteryzuje wysoka temperatura topnienia, wysoki moduł Younga, stosunkowo niewielka gęstość, dobra przewodność cieplna oraz wysoka twardość. Czyni to z ceramiki TiB_2 materiał nadający się na umocnienie kompozytu o osnowie metalowej, ponieważ wpływa on na podwyższenie m.in. sztywności, twardości oraz odporności na ścieranie. Celem przeprowadzonych badań było określenie wpływu różnej zawartości dwuborku tytanu na wybrane właściwości stali austenitycznej AISI316L. Kompozyty metalowe zawierające cząstki TiB_2 otrzymano, stosując metodę wysokociśnieniowego--wysokotemperaturowego (HP-HT) spiekania. Po procesie spiekaniu określono gęstość pozorną (ρ_o) poszczególnych kompozytów, twardość Vickersa przy obciążeniu 2,942 N oraz wartość modułu Younga, stosując metodę ultradźwiękową pomiaru prędkości przechodzenia fali poprzecznej i podłużnej. W artykule przedstawiono wyniki badań mikrostrukturalnych kompozytów z różną zawartością cząstek TiB_2. Analiza mikrostruktury obejmowała badania przy zastosowaniu mikroskopu optycznego oraz skaningowego mikroskopu elektronowego wraz z analizą składu chemicznego (EDS). Wykazano, że właściwości kompozytów istotnie zależą od warunków spiekania. Generalnie, zastosowanie większego udziału fazy umacniającej wpływa na poprawę właściwości spiekanych materiałów kompozytowych. Badania mikrostruktury wykazały jednorodne rozmieszczenie cząstek TiB_2 wzdłuż granic ziaren osnowy.

Słowa kluczowe: **kompozyty o osnowie metalowej, ceramika TiB2, spiekanie HP-HT**

INTRODUCTION

Sintering is one of the techniques giving the possibility to receive materials with better properties in comparison to regular alloys. Classic methods of sintering require the application of a high temperature and long time, which very often causes the growth of grains and, as a consequence, loss of properties due to the grain-refined microstructure of the material [1, 2]. A sintering process under high pressure is one of the techniques which restrains grain growth and accelerates densification processes. So far, a few special processes have been developed: Hot Pressing (HP), Hot Isostatic Pressing (HIP), High Pressure-High Temperature (HP-HT).

The main advantage of HP-HT sintering is the possibility of reaching simultaneously an extremely high pressure (hundreds of GPa) and high temperatures during the process. Therefore, due to the concurrent operation of both pressure and temperature, the sintering process proceeds much faster (usually in several minutes) than free sintering which usually takes a few to several hours. The obtained sinters are characterized by a degree of densification reaching almost 100%. This allows for a fine microstructure of the sintered materials. The high-pressure devices are constructed with hydraulic presses and special chambers for the sintering process. The basic types of high-pressure chambers utlitized in industry are spherical chambers of the Bridgman type, chambers of the 'Belt' type and multi-anvil chambers of type [3, 4].

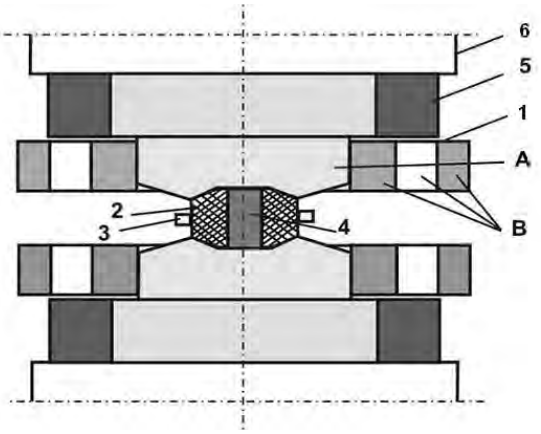


Fig. 1. Scheme of Bridgman-type, toroidal HP-HT apparatus: 1 - anvil (A - central part made of sintered carbides, B - supporting steel rings), 2 - pyrophyllite container, 3 - pyrophyllite gasket, 4 - material for sintering, 5 - punch, 6 - supporting plate [5]

Rys. 1. Schemat komory do spiekania wysokociśnieniowego z kowadłami sferycznymi typu Bridgamana; 1 - matryca (A - kowadło węglikowe, B - pierścienie ściskające), 2 - osłona pirofyllitowa, 3 - pierścień uszczelniający z pirofyllitu, 4 - wkład reakcyjny, 5 - stempel, 6 - płyty prasy [5]

Such a structural solution of the synthesis chamber guarantees a relatively large volume of reactive charge, optimal distribution of pressure and possibility of obtaining high temperatures. Their characteristic feature is attaining a quasihydrostatic state of stress through a solid medium transmitting the pressure, usually through various types of rocks. The temperature allowed for the sintering process can be as high as 2000ºC or even higher depending on the duration of the sintering. Such features make the HP-HT method a promising technique for the densification of materials. Figure 1 presents a scheme of the chamber for high-pressure sintering with spherical anvils of the Bridgman type. The HP-HT method was applied for the sintering of a large group of materials: diamond [5, 6], regular boron nitride (cBN) [7], TiB_2 ceramics [8], gradient materials [9, 10] and composite materials [11-14].

The aim of the research was to determine the influence of different contents of TiB_2 ceramics on the properties and microstructure of composites obtained by HP-HT sintering.

EXPERIMENT

The starting materials used in this study were commercial diboride titanium powders (H.C. Starck, 2.5-3.5 μm grade, purity 99.9%) and AISI 316L austenitic stainless steel (KAMB Import-Export, 25 μm grade). The chemical compositions of the AISI 316L steel powder and TiB_2 ceramic powder under study are given in Table 1. Figure 1 presents the morphology of the AISI 316L steel powder and TiB_2 powder.

TABLE 1. **Chemical composition of AISI 316L stainless steel powder**

TABELA 1. **Skład chemiczny proszku stali AISI 316L**

Chemical composition [wt.%]								
C	Cr	Ni	Mo	Mn	Si	S	P	Fe
0.027	17.20	12.32	2.02	0.43	0.89	0.030	0.028	balance

TABLE 2. **Chemical composition of TiB_2 powder**

TABELA 2. **Skład chemiczny proszku TiB_2**

Chemical composition [wt.%]					
B	O	C	N	Fe	Ti
30.1	1.6	0.36	0.32	0.06	balance

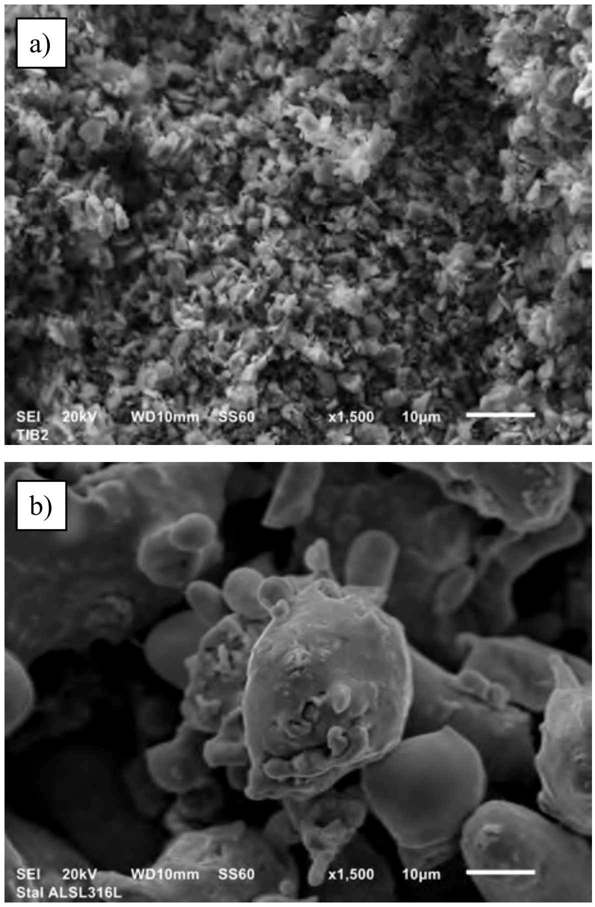


Fig. 2. Morphology of: a) TiB_2 powder and b) AISI 316L steel powder used in current study

Rys. 2. Morfologia proszków: a) TiB_2 oraz b) stali AISI316L zastosowanych w badaniach

The composites were produced by mixing the powders in a TURBULA® mixer for 8 hours. The initial phase compositions of the mixtures for the sample preparation were as follow:

- 98 vol.% AISI 316L + 2 vol.% TiB_2
- 96 vol.% AISI 316L + 4 vol.% TiB_2

The resulting mixtures were formed into discs (15 mm in diameter, 5 mm high) by pressing in a steel matrix under the pressure of 200 MPa. The sintering process was carried out using a high temperature-high pressure (HT-HP) Bridgman type apparatus. Figure 3 presents the scheme of the reactive charge. The samples were sintered at temperatures of 1000 and 1300°C and the pressure of 5 ± 0.2 GPa and 7 ± 0.2 GPa. The samples were sintered for 60 seconds.

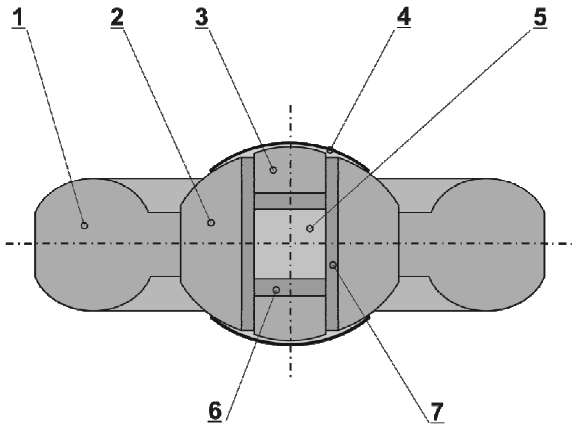


Fig. 3. Assembly for high pressure-high temperature sintering: 1 - pyrophyllite external gasket, 2 - internal gasket, 3 - ceramic plate, 4 - molybdenium plate, 5 - sintered sample, 6, 7 - graphite heater [7, 15]

Fig. 3. Schemat wsadu reakcyjnego stosowanego w procesie wysokociśnieniowego spiekania: 1 - kształtka zewnętrzna, 2 - kształtka wewnętrzna, 3 - zatyczka, 4 - blaszka molibdenowa, 5 - spiekana próbka, 6, 7 - grafitowe elementy grzewcze [7, 15]

The density was determined by weighing in air and water using the Archimedes method. The uncertainty of the measurements was 0.02 g/cm^3. The Young's modulus of the composites was measured based on the velocity of ultrasonic waves transition through the sample using the ultrasonic flaw detector Panametrics Epoch III. The velocities of the transverse and longitudinal waves were determined as the ratio of sample thickness and relevant transition time. The accuracy of the calculated Young's modulus is estimated at 2%. Calculations were made using the following formula:

$$E = \rho C_T^2 \frac{3C_L^2 - 4C_T^2}{C_L^2 - C_T^2}$$

where: E - Young's modulus, C_L - longitudinal wave velocity, C_T - transversal wave velocity, ρ - material density.

Vickers indentation tests were performed on the polished surface of the samples using an FM-7 microhardness tester. Five hardness measurements, with indentation loads of 2.94, were carried out for each sample. The standard deviations of the HV values were no more than 4% of the average values. For the morphological characterization of the composites, an Olympus GX-51 optical light microscope and a JEOL JSM 6610LV scanning electron microscope (SEM) were used. The EDS technique (AZtec) was applied to determine the chemical composition of the sintered materials.

RESULTS AND DISCUSSION

The results of the measurements of the selected properties of the composites obtained by HP-HT sintering are given in Table 3 and Figures 4 and 5. For the applied conditions of sintering, composites with a very high level of consolidation were obtained. The density values are 99 and 98% of theoretical density. It was observed that the Young's modulus of the composites increases with the increasing content of TiB_2 phase (Fig. 4). The highest values of Young's modulus were obtained for the samples with 4% vol. TiB_2, namely: 205 GPa and 204 GPa at the temperature of 1300°C and pressure of 5 ±0.2 GPa and 7 ±0.2 GPa, respectively. The application of various pressures at the same temperature do not essentially affect the Young's modulus values. Moreover, the Young's modulus of the sintered composites increased with a rise in sintering temperature. An increase in microhardness with an increase in titanium diboride content was observed. It is interesting that the composites which were obtained at the lower temperature of 1000°C have a higher hardness value. In the case of the composites with 2% vol. TiB_2, the hardness is 336 HV0.3 and 354 HV0.3 at the pressure of 5 ±0.2 GPa and 7 ±0.2 GPa, respectively. However, the composites with 4% vol. TiB_2 reached the hardness of 350 GPa and 370 GPa, at the pressure of 5 ±0.2 GPa and 7 ±0.2 GPa, respectively. The application of the highest temperature of 1300°C at the same pressures caused a reduction in the hardness of about 28÷35%. In these conditions, the hardness of the investigated composites was in the range of 223÷254 GPa.

TABLE 3. **Effect of temperature, pressure and different TiB_2 content on composite density**

TABELA 3. **Wpływ temperatury, ciśnienia oraz różnej zawartości TiB_2 na gęstość kompozytów**

Composite	Temperature [°C]	Pressure [GPa]	Density ρ_o [g/cm^3]	ρ_o/ρ_{Teor} [%]
AISI 316L+ 2% vol.TiB_2	1000	5	7.86	100
	1000	7	7.85	99
	1300	5	7.86	100
	1300	7	7.74	99
AISI 316L + 4% vol. TiB_2	1000	5	7.80	100
	1000	7	7.87	100
	1300	5	7.75	99
	1300	7	7.75	99

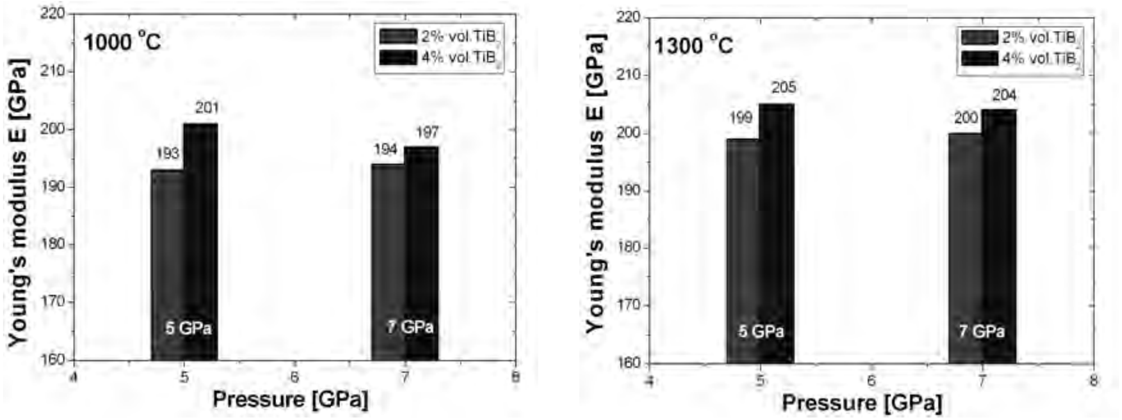


Fig. 4. Effect of TiB_2 particle content and sintering conditions on Young's modulus values

Rys. 4. Wpływ zawartości ceramiki TiB_2 oraz warunków spiekania na wielkość modułu Younga

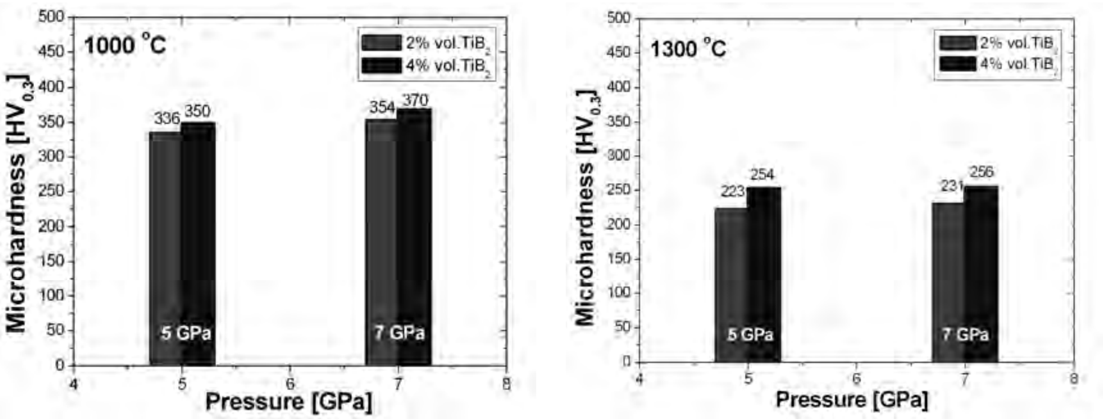


Fig. 5. Effect of TiB_2 particle content in matrix and sintering conditions on composites microhardness

Rys. 5. Wpływ zawartości ceramiki TiB_2 w osnowie oraz warunków spiekania na mikrotwardość kompozytów

Figures 6-8 present the microstructure of the composites reinforced with 2 and 4% vol. TiB_2 which were sintered in different conditions. The uniform distribution of titanium diboride in the micro-structure of the composites was observed (Fig. 6). The EDS analyses indicated the presence of TiB_2 along the grain boundaries in all the sintered materials. The TiB_2 particles that appear in dark contrast present an average grain size of about a few μm. Additionally, the mapping of the element distribution (Fig. 8) confirmed the occurrence of TiB_2 ceramic along the grain boundaries.

a)

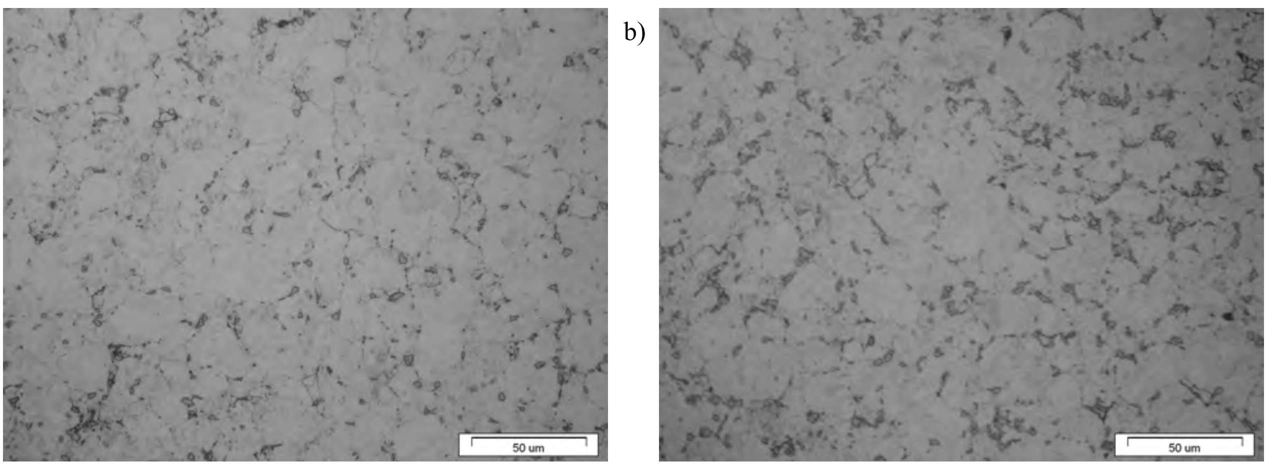
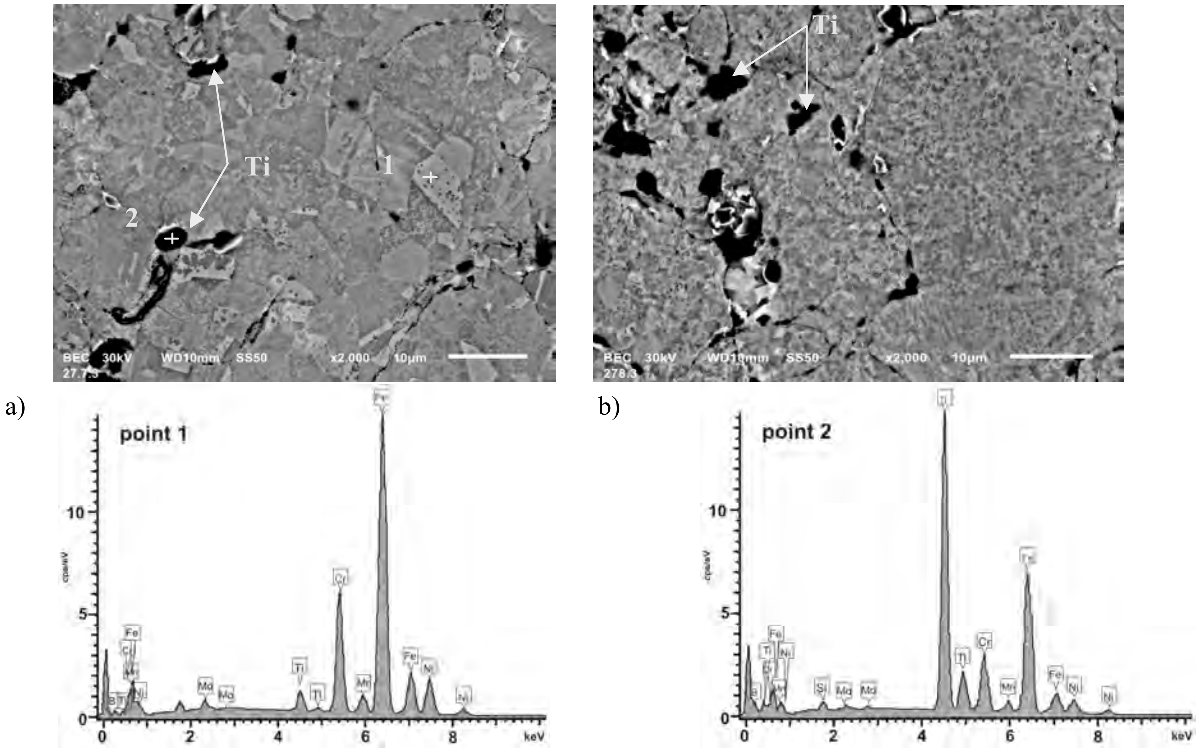


Fig. 6. Selected composite microstructures with different of TiB_2 particle content (sintered at temperature of 1000°C and pressure of 7±0.2 GPa): a) 2% vol. TiB_2 and b) 4% vol. TiB_2

Rys. 6. Mikrostruktura kompozytów z różną zawartością cząstek TiB_2 (spiekanych w temperaturze 1000°C oraz przy ciśnieniu 7±0.2 GPa): a) 2% vol.TiB_2 and b) 4% vol. TiB_2



c)

EDS analyses	Fe [wt.%]	Cr [wt.%]	Ni [wt.%]	Mo [wt.%]	Si [wt.%]	Ti [wt.%]	Mn [wt.%]	B [wt.%]
Point 1	67.0	17.7	11.8	1.9	1.3	---	0.3	---
Point 2	25.9	7.9	4.4	0.6	0.4	30.7	0.1	30.0

Fig. 7. Typical composite microstructure with different of TiB_2 particle content (sintered at temperature of 1000°C and pressure of 7±0.2 GPa): a) 2% vol. TiB_2 and b) 4% vol. TiB_2 and c) corresponding EDS point analyses

Rys. 7. Typowa mikrostruktura kompozytów z różną zawartością cząstek TiB_2 (spiekanych w temperaturze 1000°C oraz przy ciśnieniu 7±0.2 GPa) a) 2% vol.TiB_2 i b) 4% vol. TiB_2 oraz c) wyniki analizy punktowej EDS

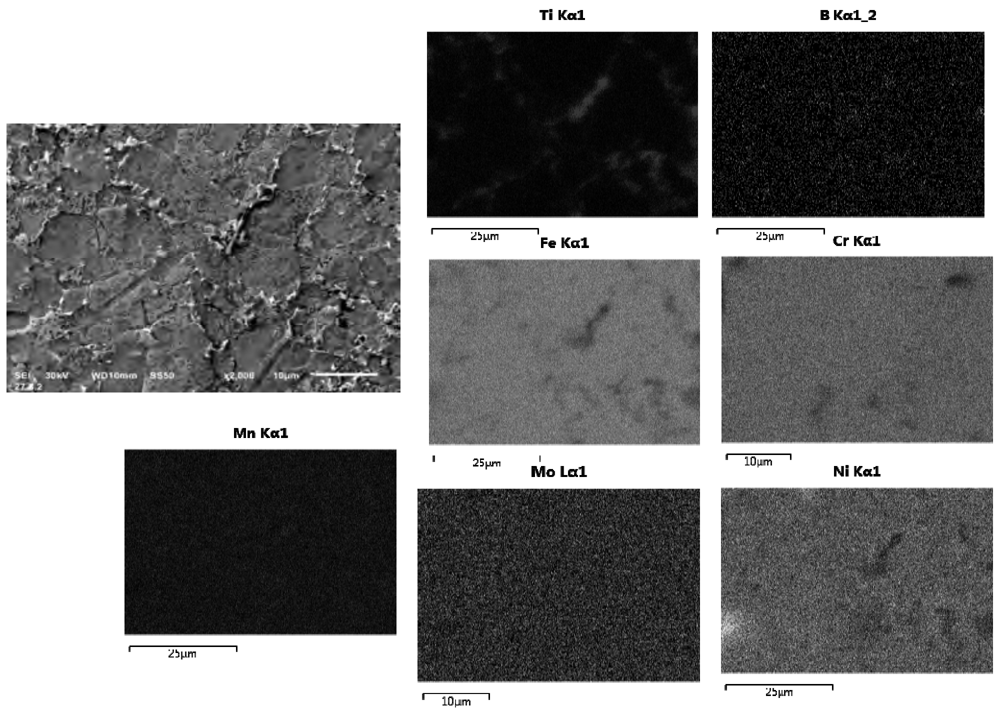


Fig. 8. Selected SEM microstructures of composites with 4% vol. TiB_2 particles and corresponding maps of Ti, B, Mo, Fe, Cr, Mn and Ni (sintered at temperature of 1300°C and pressure of 5 ±0.2 GPa)

Rys. 8. Wybrana mikrostruktura SEM kompozytów z udziałem 4% obj. cząstek TiB_2 wraz z powierzchniową analizą składu chemicznego (spiekanych w temperaturze 1300°C oraz przy ciśnieniu 5 ±0.2GPa)

CONCLUSIONS

In this work, AISI316L stainless steel-diboride titanium composites were successfully fabricated using HP-HT sintering. It was shown that the composites properties significantly depend on the sintering conditions. The density, Young's modulus, hardness and microstructure of the composites sintered at different temperatures and different pressures suggest that the lower temperature of 1000°C is sufficient for good quality HP-HT sintering of these materials. Moreover, the influence of the different volume fraction of TiB_2 ceramic phase on the mechanical and physical properties was analyzed. The increase in TiB_2 content improves the properties of the sintered composites. The microstructure of the composite materials was characterized by uniform distribution of fine TiB_2 particles along the grain boundaries.

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