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SINTERING OF TiB_2-TiN NANO- AND MICROPOWDERS

The TiN-TiB_2 ceramic composite (CC) could be attractive for applications in jet engine parts, armour plates, cutting tools and dies as well as high performance electrical systems. Because of the high melting points of TiB_2-TiN, consolidation of these powders requires extremely high temperatures and long duration of the sintering process for conventional sintering methods. The main causes of this problem are strong covalent bonding, a low self-diffusion coefficient and the existence of an oxygen rich surface layer on the particle surface. The compaction and sintering of nanocrystalline powders are accompanied by intensive growth of particles. The Spark Plasma Sintering (SPS) process and High Pressure-High Temperature (HP-HT) method of sintering have been applied to the formation of composites consisting of TiB_2 and TiN nano- and micropowders. Commercial TiB_2-TiN nanopowders, obtained using Self Propagating High Temperature Synthesis (SHS) were used for the studies. The influence of the method of sintering on the densification, grain growth, microstructure, some physical and mechanical properties of TiN-TiB_2 ceramic composites were investigated. Microstructural observations revealed that both TiN and TiB_2 crystal grains had micrometer sizes in the composites obtained from nanopowders for both SPS and HP-HT methods of sintering. In the materials obtained using the HP-HT method of sintering, there are numerous cracks in the compact and stresses build up during the high pressure sintering process. The TiB_2-TiN material obtained utilizing the HP-HT method from nanopowders is characterized by lower porosity. In XRD experiments, TiB_2, TiN and hBN phases were detected. TiB_2-TiN commercial SHS nanopowders are more reactive than the mixture of TiB_2 and TiN micropowders. For the composites prepared from nanopowders there is about 14% of hBN content. The amount of hBN in the composites for micropowder sintering using the SPS method is about 1.3%.

Keywords: composites, nanopowders, Spark Plasma Sintering, HP-HT method, grain growth, phase composition, porosity

SPIEKANIE NANO- ORAZ MIKROPROSZKÓW TiB_2-TiN

Kompozyty ceramiczne TiN-TiB_2 mogą znaleźć powszechne zastosowanie w przemyśle jako części do silników odrzutowych, płyty pancerne, narzędzia skrawające, matryce, a także w wysokiej klasy systemach elektronicznych. Ze względu na wysoką temperaturę topnienia składników kompozytów TiB_2-TiN tradycyjne spiekanie tych proszków wymaga zastosowania bardzo wysokiej temperatury i długiego czasu spiekania. Przyczynami tego są silne wiązania kowalencyjne występujące w przedstawianym kompozycie, niski współczynnik samodyfuzji oraz obecność bogatej w tlen warstwy na powierzchni cząstek. Zagęszczaniu i spiekaniu nanokrystalicznych proszków towarzyszył intensywny rozrost ziaren. Do wytworzenia spieków kompozytowych TiB_2-TiN z wykorzystaniem nano- oraz mikrometrycznych proszków zastosowano metodę Spark Plasma Sintering (plazmowe spiekanie iskrą elektryczną- SPS) oraz spiekanie wysokociśnieniowe HP-HT. Do badań zastosowano komercyjny nanoproszek TiB_2-TiN, otrzymany metodą samorozwijającej się wysokotemperaturowej syntezy (SHS). W przeprowadzonych badaniach przedstawiono wpływ zastosowanych metod spiekania na zagęszczenie, rozrost ziaren, mikrostrukturę oraz wybrane właściwości fizyczne i mechaniczne spieków TiB_2-TiN. Badania mikrostruktury materiałów kompozytowych otrzymanych z proszków nanometrycznych metodą HP-HT i SPS wykazały mikrometryczną wielkość kryształów ziaren zarówno TiN, jaki i TiB_2. W spiekach otrzymanych metodą HP-HT widoczne są liczne pęknięcia. Wynikają one z naprężeń towarzyszących procesowi spiekania wysokociśnieniowego. Kompozyty TiB_2-TiN uzyskane metodą HP-HT charakteryzują się mniejszą porowatością w porównaniu do spiekanych metodą SPS. Badania XRD wykazały w otrzymanych materiałach udział takich faz, jak TiB_2, TiN i hBN. Okazało się również, że komercyjny nanoproszek TiB_2-TiN otrzymany metodą SHS charakteryzował się większą reaktywnością niż mieszanka mikrometrycznych proszków TiB_2 oraz TiN. W kompozytach wykonanych z nanoproszków udział hBN wyniósł około 14%, natomiast w przypadku materiałów z mikroproszków, spiekanych metodą SPS, wynosi on około 1,3%.

Słowa kluczowe: kompozyty, nanoproszki, plazmowe spiekanie iskrą elektryczną (SPS), spiekanie wysokociśnieniowe, rozrost ziarna, skład fazowy, porowatość

INTRODUCTION

The use of TiB_2-TiN ceramic offers the advantages of high fracture toughness and a non catastrophic failure mode. The TiN-TiB_2 ceramic composite (CC) could be attractive for applications in jet engine parts, armour plates, cutting tools and dies as well as high performance electrical systems. Titanium nitride has a high melting point (2950°C), high hardness (HV 18÷ ÷21 GPa), low electrical resistivity (20÷10 μΩ·cm) as

well as high corrosion resistance to acid and alkaline solutions. Titanium diboride also exhibits high hardness (HV 33 GPa), high melting point (2980°C) in addition to high thermal conductivity (24.3 W/K·m) [1]. Because of their high melting points, consolidation of these powders requires an extremely high temperature and long duration of the sintering process for conventional sintering methods. The main reasons for this problem are strong covalent bonding, low self-diffusion coefficient and the existence of an oxygen rich surface layer on the particle surface [2]. The elimination of the influence of oxide layers on the TiB_2 particle surface could be executed by two methods: by using additives ($MoSi_2$, SiC, TaC, TaN) or high temperature sintering to evaporate oxygen compounds (for example TiO_2) [2, 3]. A number of new sintering methods have been investigated to overcome the problem of TiB_2-TiN composite consolidation. The self-propagating high-temperature synthesis (SHS) process has been applied to obtain composites consisting of TiB_2 and TiN ceramics synthesized simultaneously [4]. The synthesis and densification of TiN-TiB_2 ceramic composites via reactive spark plasma sintering (RSPS) was also investigated. Spark Plasma Sintering (SPS) shows some advantages, such as thermo-efficiency, rapid heating, self-cleaning, fast densification under relatively low temperatures [5]. Manufacturing bulk material from nanopowders is still a problem. One of the main reasons for the difficulties is that the compaction and sintering of nanocrystalline powders are accompanied by intensive growth of particles. The standard methods for manufacturing bulk material from powders are: cold compaction with sintering, hot pressing, sintering under high pressure and shock-wave sintering. To prevent the processes of grain growth, the duration of the sintering processes should be limited to a certain extent [6]. Limiting sintering time is possible for the SPS method and for the High Temperature-High Pressure (HP-HT) method as well. In the present studies, some physical and mechanical properties of the composites obtained from TiB_2-TiN nano- and micropowder mixtures were investigated in order to examine the difference between the SPS and HT-HP processes. X-ray diffraction was applied to determine the phase composition of the samples.

MATERIALS AND RESEARCH METHODOLOGY

The characteristics of the powders for sintering are shown in Table 1.

TABLE 1. **Characteristics of powders for sintering**
TABELA 1. **Charakterystyka proszków przeznaczonych do spiekania**

No.	Powder	Median grain size μm	Manufacturer
1	TiB_2-TiN	~45 nm	NEOMAT CO. Latvia
2	TiB_2	2.5-3.5	H.C. STARCK
3	TiN	0.8-1.2	H.C. STARCK

The nanocomposite powders TiB_2-TiN (SHS synthesis method NEOMAT CO., Latvia; N 11.6±0.1%; B 15,9±0.1%, ssa 31±2 m^2/g) were granulated in the Planetary PULVERISETTE 6 mill. For this process, grinding bowls and grinding Si_3N_4 balls were used. The suspension mixture of the TiN-TiB_2 nanopowders was granulated at a speed of 200 rpm during 1 hour. The mixture of TiN and TiB_2 micropowders was milled in isopropyl alcohol using a colloid mill for 30 hours.

The composites were properly consolidated using two methods of sintering. For the High Pressure-High Temperature method of sintering, samples were preformed in steel dies under a pressure of 200 MPa. The samples were heated using an assembly provided with an internal graphite heater of 15 mm inner diameter. The compacts were sintered under the conditions presented in Table 2, in a Bridgman type high pressure apparatus.

The samples for SPS sintering consisted of mixtures of powders placed directly in the graphite die, which is a heater.

In Table 2, the HP-HT sintering parameters for TiB_2-TiN nanopowders are presented. In Table 3, the conditions of the nano- and micropowder SPS sintering of TiB_2-TiN are shown.

TABLE 2. **Parameters of TiB_2-TiN nanopowder mixture sintering using HP-HT method**
TABELA 2. **Parametry spiekania mieszanki nanoproszków TiB_2-TiN metodą HP-HT**

Sample	Sintering parameters				
	Sintering temperature °C	Pressure GPa	Heating and cooling time ↑ s	→ s	↓ s
TiB_2+TiN nano (SHS, NEOMAT Lotwa)					
TiNB(1).1	2147	7.5	120	180	240
TiNB(1).2	1883	7.5	5	60	5

TABLE 3. **Parameters of TiB_2-TiN nano- and micropowder mixture sintering using SPS method**
TABELA 3. **Parametry spiekania mieszanek mikro- oraz nanoproszków TiB_2-TiN metodą SPS**

Sample	Atm.	Press. kN	Heating	Hold time
			˚C/min	min
TiB_2-TiN(1)	Argon	11	173	3
TiB_2-TiN(2)	Argon	15	183	3
TiB_2-TiN(3)	Argon	11	173	3
TiB_2-TiN(4)	Argon	11	165	3

An example of the sintering curve for the SPS sintering of TiB_2-TiN nanopowders is presented in Figure 1.

The samples for Vickers hardness measurements were prepared using an automatic precision cut-off and grinding machine, Accutom-50. The samples for studies were prepared with Struers polishing agents.

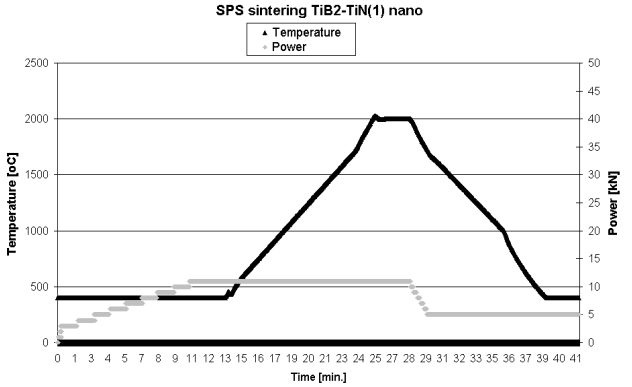


Fig. 1. Example of SPS sintering curve for sample TiB_2-TiN(1), in Table 3

Rys. 1. Przykładowa krzywa spiekania metodą SPS dla próbki TiB_2-TiN(1), z tabeli 3

The density and porosity were determined utilizing the hydrostatic method. Young's modulus measurements of the sintered samples were also taken employing the ultrasonic method of measuring of the transition speed of transverse and longitudinal waves, using a Panametrics Epoch III flaw detector.

The hardness was determined by the Vickers method at a load of 2942 mN using a digital hardness tester (Future Tech. Corp. FM-7). The phase composition of the composites were identified by X-ray diffraction analysis based on the ICDD data base. XRD measurements were executed using the X'Pert Pro system (Panalytical) with monochromatic Cu $K_{\alpha 1}$ radiation. The microstructure investigations were performed using a scanning microscope (Jeol JSM-6460LV with EDS and WDS spectometers).

RESULTS AND DISCUSSION

The results of the measurements of density, Young's modulus and Vickers hardness are contained in Table 4.

TABLE 4. **Density, Young's modulus and hardness of TiB_2-TiN samples, sintered using HP-HT and SPS methods**
TABELA 4. **Gęstość, moduł Younga i twardość próbek TiB_2-TiN spieczonych metodami HP-HT i SPS**

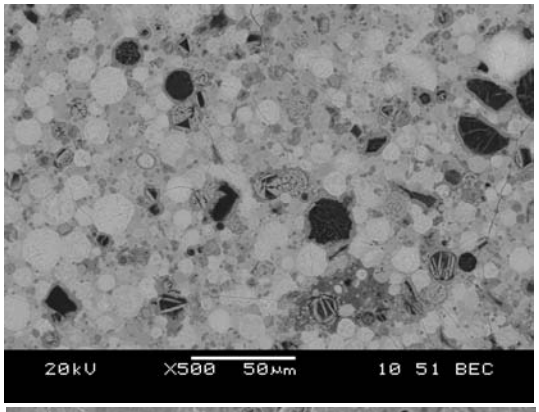
Sample	Density g/m^3	Porosity %	Young modulus, GPa	Hardness HV0.3*
TiB_2+TiN nano(HP-HT)				
TiNB (1).1				1568
TiNB (1).2	4,28		390	1896
TiB_2+TiN nano(SPS)				
TiB_2-TiN(1)	4.44	0.06	352	1792
TiB_2-TiN(2)	4.32	0.04	343	1800
TiB_2+TiN micro(SPS)				
TiB_2-TiN(3)	4.74	0.03	445	1786
TiB_2-TiN(4)	4.70	0.01	442	1886

* load of 2942 mN

For the HP-HT method, high pressure sintering at 7.5 GPa generates stresses in the sintered TiB_2-TiN material. Stresses cause the presence of microcracks, inside the composites. Because of the cracks, there were difficulties in measuring Young's modulus and the densities for the samples obtained using the HP-HT method.

The HP-HT composites were characterized by SEM microscopy (Fig. 2 a, b).

a)



b)

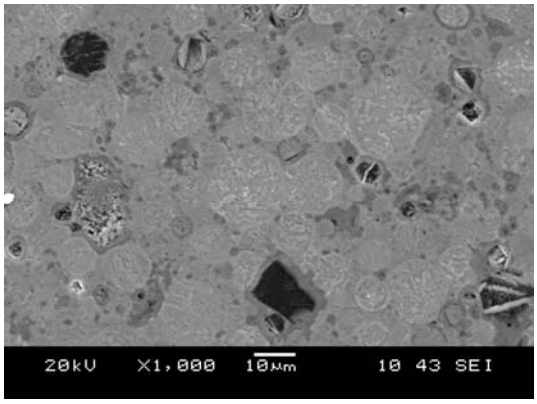


Fig. 2. SEM image of TiB_2-TiN composite obtained with HP-HT method from nanopowders: a) magnification of 500x BEC, b) magnification of 1000x, SEI

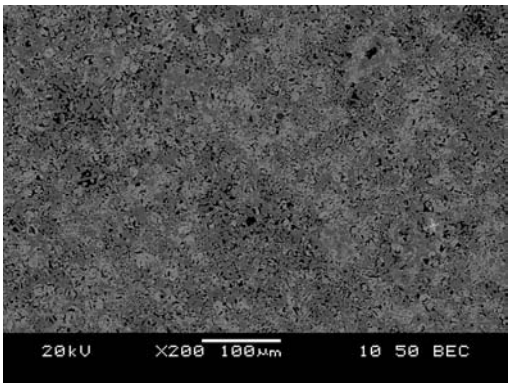
Rys. 2. Obraz SEM dla kompozytu TiB_2-TiN otrzymanego z nanoproszków metodą HP-HT: a) powiększenie 500x BEC, b) powiększenie 1000x, SEI

Despite the microcracks, the HP-HT material is characterized by a non-porous microstructure and lower grain growth than that of the SPS samples. The average size of grains for the HP-HT samples is 8.85 μm, however, this material has a more complicated structure since inside a large grain there are smaller nanosize particles. During the high pressure process of sintering, the powder particles (size ~45 μm) are cumulated within large spherical areas (Fig. 2b).

The microstructures confirmed the grain growth during the SPS process (Fig. 3 a, b). The average size of the grains for this material is 6 μm, nevertheless, the grains are monolithic.

In the SPS samples from the TiB_2-TiN nanopowders, the porosity amounts to 0.06%. For the TiB_2-TiN micropowder mixtures which were sintered using the SPS method (Fig. 4 a, b), the porosity is lower than the SPS samples obtained from nanopowders reaching 0.01÷0.03%. The grain growth is not as intensive as in nanopowders (about 3 times, only).

a)



b)

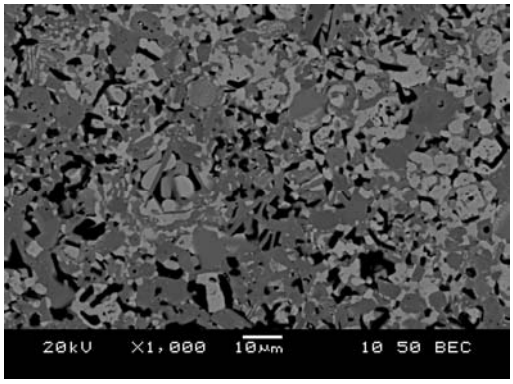
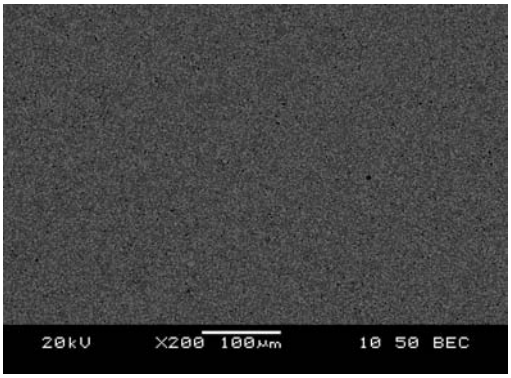


Fig. 3. SEM image of TiB2-TiN composite obtained using SPS method from nanopowders: a) magnification of 200x, BEC, b) magnification of 1000x, BEC

Rys. 3. Obraz SEM dla kompozytu TiB2-TiN otrzymanego z nanoproszków, metodą SPS: a) powiększenie 200x, BEC, b) powiększenie 1000x, BEC

a)



b)

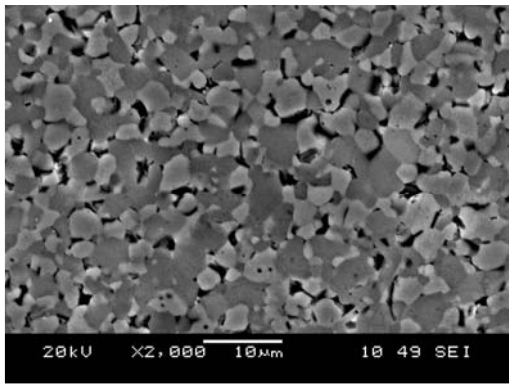


Fig. 4. SEM image of TiB2-TiN composite obtained using SPS method from micropowders: a) magnification of 200x, BEC, b) magnification of 2000x, SEI

Rys. 4. Obraz SEM dla kompozytu TiB_2-TiN otrzymanego z mikroproszków metodą SPS: a) powiększenie 200x, BEC, b) powiększenie 2000x, SEI

The phase composition of the SPS composites was identified by X-ray diffraction analysis (Figs. 5 and 6).

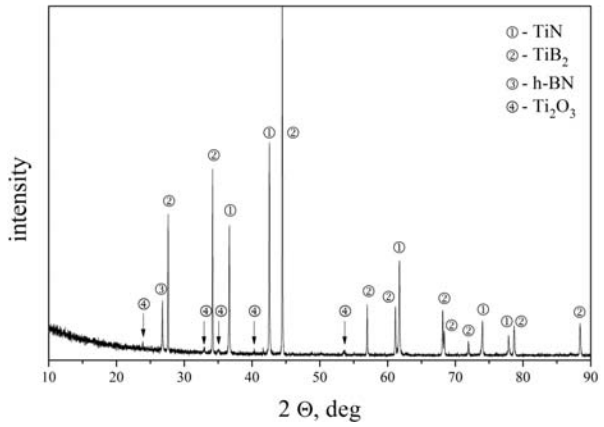


Fig. 5. X-ray diffraction diagram of TiB_2-TiN(2) composite obtained using SPS method from nanopowders

Rys. 5. Dyfraktogram próbki kompozytowej TiB_2-TiN (2) otrzymanej metodą SPS z wykorzystaniem nanoproszków

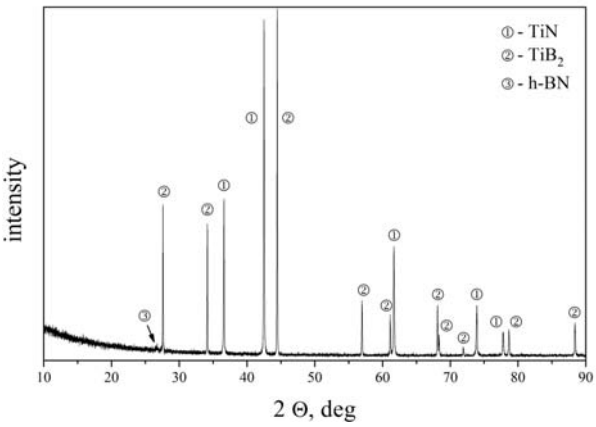


Fig. 6. X-ray diffraction diagram of TiB_2-TiN(3) composite obtained using SPS method from micropowders

Rys. 6. Dyfraktogram próbki kompozytowej TiB_2-TiN (3) otrzymanej metodą SPS z wykorzystaniem mikroproszków

During the sintering of the micropowders in the phase composition there is a small amount of 1.3% hBN. For nanopowders, the content of hBN is about 14%. SHS TiB_2-TiN nanopowders are more reactive during the SPS sintering process.

CONCLUSIONS

The materials sintered utilizing the SPS and HP-HT methods are characterized by grain growth of TiB_2-TiN nanoparticles. However, in the materials obtained employing the HP-HT method of sintering, there are numerous cracks in the compact, probably resulting from the occurrence of high stresses during the sintering process. The TiB_2-TiN material obtained using the HP-HT method is characterized by lower porosity. TiB_2-TiN commercial SHS (Self Propagating High Temperature Synthesis) nanopowders are more reactive

than a mixture of TiB_2 and TiN micropowders. For the composites prepared from nanopowders there is about 14% of hBN. The content of hBN for micropowders sintered employing SPS is about 1.3%.

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