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## SYNTHESIS OF THE TiN-TiB<sub>2</sub> CERAMIC COMPOSITES UNDER VARIOUS SPARK PLASMA SINTERING CONDITIONS

## SYNTEZA KOMPOZYTÓW CERAMICZNYCH TiN-TiB<sub>2</sub> W RÓŻNYCH WARUNKACH ISKROWEGO SPIEKANIA PLAZMOWEGO

The TiN-TiB<sub>2</sub> ceramic composites with different ratios of components have been obtained via spark plasma sintering (SPS) by varying such process parameters as temperature, duration, protective atmosphere and current load. The sintering was performed by means of two Methods and TiN – TiB<sub>2</sub> composites with the relative density of 64-99 % were obtained. The samples sintered with the use of superposition of direct and alternative currents had a higher level of properties (HV=19.7-25.4 GPa (load 100 g), fracture strength  $K_{Ic}=5.4-5.8 \text{ MPa}\times\text{m}^{1/2}$  (load 20 kg )) in the TiB<sub>2</sub> content range 36-60 wt %, as compared with the sintering by a pulsating current.

Ceramiczne kompozyty TiN-TiB<sub>2</sub> o różnych proporcjach komponentów otrzymano w wyniku iskrowego spiekania plazmowego (SPS) poprzez różnicowanie takich parametrów procesowych jak temperatura, czas trwania, atmosfera ochronna i obciążenie prądu. Spiekanie zostało przeprowadzone z wykorzystaniem dwóch metod i otrzymano kompozyty TiN-TiB<sub>2</sub> o gęstości względnej 64-99 %. Próbki spiekane z wykorzystaniem superpozycji prądu stałego i zmiennego odznaczały się wyższym poziomem właściwości (HV=19.7-25.4 GPa (obciążenie 100 g), odporność na pękanie  $K_{Ic}=5.4-5.8 \text{ MPa}\times\text{m}^{1/2}$  (obciążenie 20 kg) w zakresie zawartości TiB<sub>2</sub> 36-60 wt %, w porównaniu ze spiekaniem przy pomocy prądu tętniącego.

### 1. Introduction

Recently, researchers and developers in the sphere of cutting and abrasive tools have shown great interest in the composition TiN – TiB<sub>2</sub> – above of all due to the successful combination of the mechanical and thermochemical properties [1, 2]. This composition can be obtained mainly by the combustion synthesis (self-propagating high-temperature synthesis (SHS)) [3], sintering under high pressure and high temperature (HPHT) [4], electric field activation or spark plasma sintering (SPS) [1, 2] and reactive hot pressing (exchange reaction under pressure) (RHP) [5, 6]. The disadvantages of these methods are: the introduction of the additional dehydrogenation operation [5]; long ball milling (about 25-70 h) of the starting powder mixtures with plastic Ti as a metallic component [1, 4]; the necessity of a protective atmosphere application during the high-temperature synthesis and the composite consolidation [3]; use of a high pressure nitrogen atmosphere [2, 6].

The obtaining of the ceramic composite material TiN-TiB<sub>2</sub> by SPS of TiH<sub>2</sub>-BN powder mixture in a

graphite die is promising [7]. The advantages of this route are: using brittle, well milled TiH<sub>2</sub>, which leads to a decrease in the time of the ball milling operation to 1 min.; a combination of the dehydrogenation and initial sintering stage (TiN-TiB<sub>2</sub> synthesis), and, as a result, the interaction of active atomic hydrogen with BN, which leads to an intensification of the formation of TiN – TiB<sub>2</sub> composition [8]; the obtaining of active metallic Ti (dehydrogenation product) as an intermediate reagent; the use of the processes of atomic hydrogen recombination and molecular hydrogen burning as an additional heat source; the use of H<sub>2</sub> as a protective atmosphere at the initial sintering stage and gas mixture CO + N<sub>2</sub> (the result of the oxidation of the graphite die surface by atmospheric oxygen) at the intermediate and final stages of the sintering.

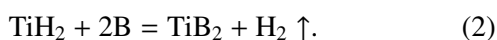
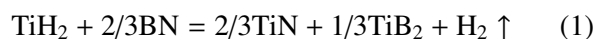
The aim of this study was to examine the synthesis of the dense TiN-TiB<sub>2</sub> composite with different component ratio by SPS, by varying the process parameters (temperature, sintering time, protective atmosphere, heating rate and a presence/absence of the dehydrogenation stage).

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## 2. Experimental procedure

As raw materials, the powder mixtures  $\text{TiH}_2+\text{BN}$ ,  $\text{TiH}_2+\text{BN}+\text{TiN}$  and  $\text{TiH}_2+\text{BN}+\text{B}$  were used. The initial component ratio corresponded to the  $\text{TiB}_2$  content of 20-80 wt% in the sintered samples and the stoichiometric ratio, in accordance with the following reactions:



The  $\text{TiH}_2$  powder was obtained on the basis of iodide titanium. The tetragonal structure of  $\text{TiH}_2$  indicates a higher content of hydrogen, compared to that of a cubic one.

The initial powder mixtures 1-3 (Table 1) were obtained by a 60 s-milling in an oxygen atmosphere using a planetary-centrifugal ball mill. The ratio of the balls: mixture = 10 : 1 and the rotation speed of the cylinders was 1630 rpm. The milled powders were subjected to further mixing by hand with TiN and B powders in ethanol. The characteristic parameters of the powders are given in Table 1 and Table 2.

The synthesis and the sintering were carried out by means of two methods.

Method 1 consisted of sintering in a graphite die in air using the equipment ERAN-2/1 (IPMS of NASU) [7] and a superposition of electric currents: a direct current with a density of  $J=5 \times 10^6 \text{ A/m}^2$  and an alternative current with a density of  $J=2.0-2.5 \times 10^6 \text{ A/m}^2$  and a frequency of  $f = 5 \text{ kHz}$ . The total sintering time was 180 s. During the sintering the pressure of 60-80 MPa was applied to the powder mixtures. The pressure is necessary for the powder compaction as well as for supporting proper electric contacts between the powder particles

and the graphite die. The heating rate was 28-42 °C/s. The dehydrogenation, the synthesis and the initial stage of consolidation proceeded simultaneously.

Method 2 included sintering by a pulsating current using the equipment "Sumitomo" SPS-1050 (NIMS of Japan) in a graphite die in an argon atmosphere, with previous dehydrogenation in a vacuum of  $10^{-3} \text{ mm Hg}$ . The total sintering time was 480-670 s, the pressure was 40 MPa, and the heating rate was 2-4 °C/s.

The relative density of the sintered samples was determined by the hydrostatic method, the hardness – by the Vickers method (load 100 g) and the fracture toughness – by the indentation method (load 20 kg). The microscopical analysis of the sintered samples was carried out by SEM in a secondary electron regime.

## 3. Results and discussion

The properties of the initial and the milled powders and mixtures are summarized in Table 1. It is clearly seen that the initial powders of BN, B and TiN have higher specific surface areas as well as oxygen content than the  $\text{TiH}_2$  powder. The boron powder consists mainly of a fine-dispersed phase of boron and a more coarse phase of  $\text{B}_2\text{O}_3$ . The milled mixtures contained 2.0-4.0 wt% of oxygen, 0.09-0.16 wt% of iron and had a specific surface area of 5.2-10.8  $\text{m}^2/\text{g}$ . The increase in the  $\text{TiH}_2:\text{BN}$  weight ratio from 3.2 to 4.9-9.6 leads to an increasing of the specific surface area from 5.2 to 10.8-12.7  $\text{m}^2/\text{g}$ , as a result of the increase in the relative amount of the brittle component (titanium hydride). Yet it does not result in an increasing of the oxygen amount, due to the decrease in the relative content of the more oxidized component (BN).

TABLE 1

Properties of the initial and the milled powders and mixtures

Powder	XRD	$S_{\text{specific}}, \text{ m}^2/\text{g}$	$d_{\text{cp}}, \mu\text{m}$	[O], wt%	[Fe], wt%
$\text{TiH}_2$	$\text{TiH}_2$ (tetragonal)	0.233	8.31	0.13	0.04
BN	$\text{BN}+\text{B}_2\text{O}_3$	2.820	0.93	5.40	0.03
B	$\text{B}_{\text{rhom}}+\text{B}_2\text{O}_3+\text{B}_{\text{tetr.}}+\beta\text{-B}$	5.9	0.429	3.71	0.04
TiN	TiN	16.06	0.069	3.68	0.06
Mixture 1	75.9wt.% $\text{TiH}_2$ +24.1wt.%BN $\text{TiH}_2 : \text{BN} = 3.2$	5.19	0.410	2.63	0.16
Mixture 2	83.1wt.% $\text{TiH}_2$ +16.9wt.%BN $\text{TiH}_2 : \text{BN} = 4.9$	12.73	0.161	4.03	0.09
Mixture 3	90.6wt.% $\text{TiH}_2$ +9.4wt.%BN $\text{TiH}_2 : \text{BN} = 9.6$	10.77	0.186	2.06	0.10

TABLE 2

Component ratios in the prepared mixtures

Mixing components	Composition of powder mixture, wt%	TiB <sub>2</sub> content in sintered samples, wt%
Mixture 1 + TiN	41.21%TiH <sub>2</sub> + 13.09%BN + 45.7%TiN	20
Mixture 1	75.9%TiH <sub>2</sub> + 24.1%BN	36
Mixture 2 + B	73.47%TiH <sub>2</sub> + 14.93%BN + 11.6%B	60
Mixture 3 + B	71.56%TiH <sub>2</sub> + 7.44%BN + 21%B	80

In order to determine the total thermal effect in the sintering reaction of the investigated mixtures the thermochemical calculation [9] of the specific thermal effects for the corresponding chemical reactions was performed. The results are shown in Table 3 and Table 4. In accordance with [10], the range of the evolving heat amount for the self-propagating high-temperature synthesis (SHS) equals 0,42-4,2 kJ/g. As can be seen from Table 3, during reaction 1 the heat evolution is significantly smaller than that for reactions 2-4. The use of TiH<sub>2</sub> and BN as the initial reagents decreases the thermal effect, as a considerable amount of energy is spent on the decomposition of these compounds. However, the heat evolution during the recombination of hydrogen atoms (1304 kJ/mol) in the reaction zone can improve the conditions for the SHS proceeding.

The properties of the sintered samples and the specific thermal effects of the chemical reactions of the sintered powder mixtures are presented in Table 4. The carried out investigations show that the TiN-TiB<sub>2</sub> ceramic composites can be synthesized by the spark plasma sintering (SPS) method, with a 64-99% relative density and a small amount of unreacted reagents and additional impurities. The samples that were sintered by Method 1 had higher properties compared to Method 2 at 36-60 wt% TiB<sub>2</sub>: HV=19.7-25.4 GPa (the load was P=100 g), fracture strength K<sub>1c</sub>=5.4-5.8 MPa×m<sup>1/2</sup> (P=20 kg). This may be related to the improvement of the structure formation condition of the composite when the heating rate was increased. Herein, the sintering time is of no importance.

TABLE 3

Thermal effects of reactions (T=298 K)

No.	Reaction	Q <sub>1</sub> , kJ/mol	Q <sub>2</sub> , kJ/g
1.	TiH <sub>2</sub> + 2/3BN = 2/3TiN + 1/3TiB <sub>2</sub> + H <sub>2</sub> ↑	4.58	0.07
2.	TiH <sub>2</sub> + 2B = TiB <sub>2</sub> + H <sub>2</sub> ↑	135.1	1.89
3.	Ti + 2/3BN = 2/3TiN + 1/3TiB <sub>2</sub>	152.3	2.36
4.	Ti + 2B = TiB <sub>2</sub>	279.5	4.02

TABLE 4

Properties of sintered samples

Method	TiB <sub>2</sub> wt%	XRD	Relative density, %	Hardness HV, GPa	K <sub>1c</sub> , MPa×m <sup>1/2</sup>	Temperature of sintering T, °C	Sintering time τ, sec	Specific thermal effect of chemical reaction Q <sub>3</sub> , kJ/g
1	20	TiN+TiB <sub>2</sub> +Ti <sub>v.sm.</sub>	85.2	18.6	2.9	1500	180	0.04
	36	TiN+TiB <sub>2</sub>	99.4	19.7	5.4	1400	180	0.07
	60	TiN+TiB <sub>2</sub> + (Ti+TiO <sub>2v.sm.</sub> )	97.2	25.4	5.8	1450	180	0.76
	80	—	—	—	—	≈900	Destr. in 12 sec.	1.31
2	20	TiN+TiB <sub>2</sub>	91.8	18.2	2.3	1400	670	1.26
	20	TiN+TiB <sub>2</sub>	94.8	16.2	3.8	1500	480	1.26
	36	TiN+TiB <sub>2</sub>	84.7	9.2	3.7	1400	480	2.36
	36	TiN+TiB <sub>2</sub>	95.9	20.6	2.3	1500	480	2.36
	60	TiN+TiB <sub>2</sub>	80.2	6.2	3.1	1400	600	3.06
	80	TiN+TiB <sub>2</sub>	63.7	3.6	absence of cracks	1400	600	3.54

The use of a high heating rate (28-42°C/s) and a simultaneous dehydrogenation, synthesis and the initial stage of consolidation (Method 1) leads to the improving of the sample properties, when the boron content in the initial powder mixtures was increased and consequently in the  $\text{TiB}_2$  in the sintered samples. This is related to the increasing contribution of reaction 2 to the thermal balance of the total chemical reaction. However, owing to the dehydrogenation, a considerable part of the reaction product may be synthesized via reactions 3, 4 with a much stronger thermal effect. A particular role is performed by the active atomic hydrogen that is a decomposition product of  $\text{TiH}_2$ . It enhances the BN decomposition and the reduces of the boron and titanium oxide phases under sintering by Method 1. An increase in the  $\text{TiB}_2$  content up to 80 wt% results in an excessive heat evolution at the beginning of the sintering process, as well as a heating and a destruction of the graphite die, which is related to a considerable intensification of the SHS reaction, due to the interaction between Ti and B at such a high heating rate and a sufficient partial pressure of hydrogen. Synthesis by Method 2 yields a composite with a spongy structure (Table 4).

A preliminary dehydrogenation at the synthesis carried out by Method 2 leads to the obtaining of the composite through reactions 3 and 4. A relatively low heating rate (2-4°C/sec) leads to a formation of a structural skeleton at the early stage of sintering and consequently to the inhomogeneity of the final structure as a result of the skin effect. This does not result in an improving of the obtained composite properties, in spite of the considerable densification due to the sintering temperature increase by Method 2 (Table 4). The proceeding of reaction 4, which has a higher rate, causes a primary formation of the  $\text{TiB}_2$  crystal lattice. The higher hardness of  $\text{TiB}_2$  (34 GPa) in comparison with that of TiN (25 GPa) at approximately equal melting points (about 3123 and 3220 K respectively [9]) leads to an increase in the formed skeleton hardness, owing to the increasing  $\text{TiB}_2$  content, and consequently to the decreasing of the density and the mechanical properties of the sintered composites. An increase in the specific thermal effect of the chemical reactions in the corresponding initial powders mixtures does not exert an appreciable influence on the product properties.

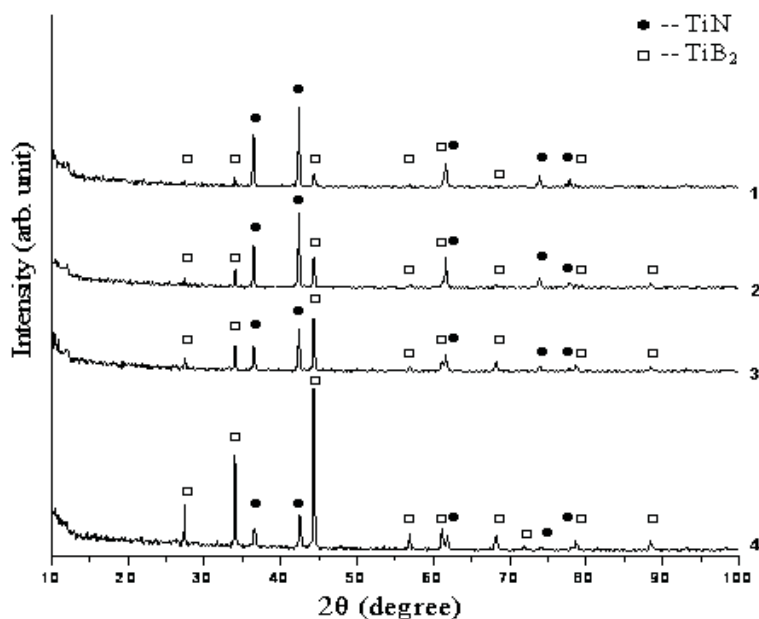


Fig. 1. XRD patterns of sintered samples for (1) 20% $\text{TiB}_2$ +80%TiN; (2) 36% $\text{TiB}_2$ +64%TiN; (3) 60% $\text{TiB}_2$ +40%TiN; (4) 80% $\text{TiB}_2$ +20%TiN

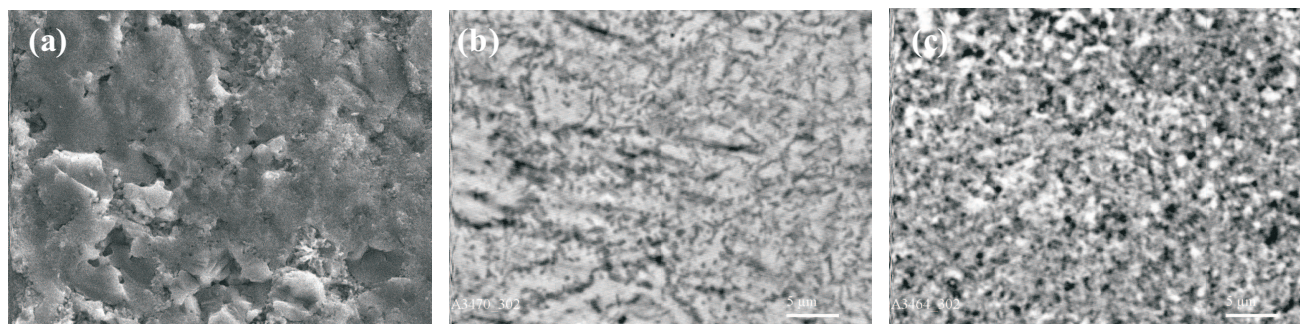


Fig. 2. SEM micrographs of samples sintered by Method 1 for (a) 20% TiB<sub>2</sub>; (b) 36% TiB<sub>2</sub>; (c) 60% TiB<sub>2</sub>

In Fig. 1 the XRD data for the obtained samples is presented. As can be seen, as a result of all the performed sintering processes the corresponding TiN-TiB<sub>2</sub> composites were obtained.

The SEM micrographs of the sintered samples are given in Figs 2 and 3. It is evident that the composites with 36-60 wt% TiB<sub>2</sub> content which were obtained by Method 1 have a homogeneous micro-grained structure.

The mean grain size of the composite with 60 wt% TiB<sub>2</sub> content does not exceed 0.5-0.7 μm. The composites that were obtained by Method 2 generally have a porous and heterogeneous structure with a mean grain size of about 1 μm. Increasing the sintering temperature leads to a certain grain growth. With the increasing of the TiB<sub>2</sub> content the porosity and the structure heterogeneity increase.

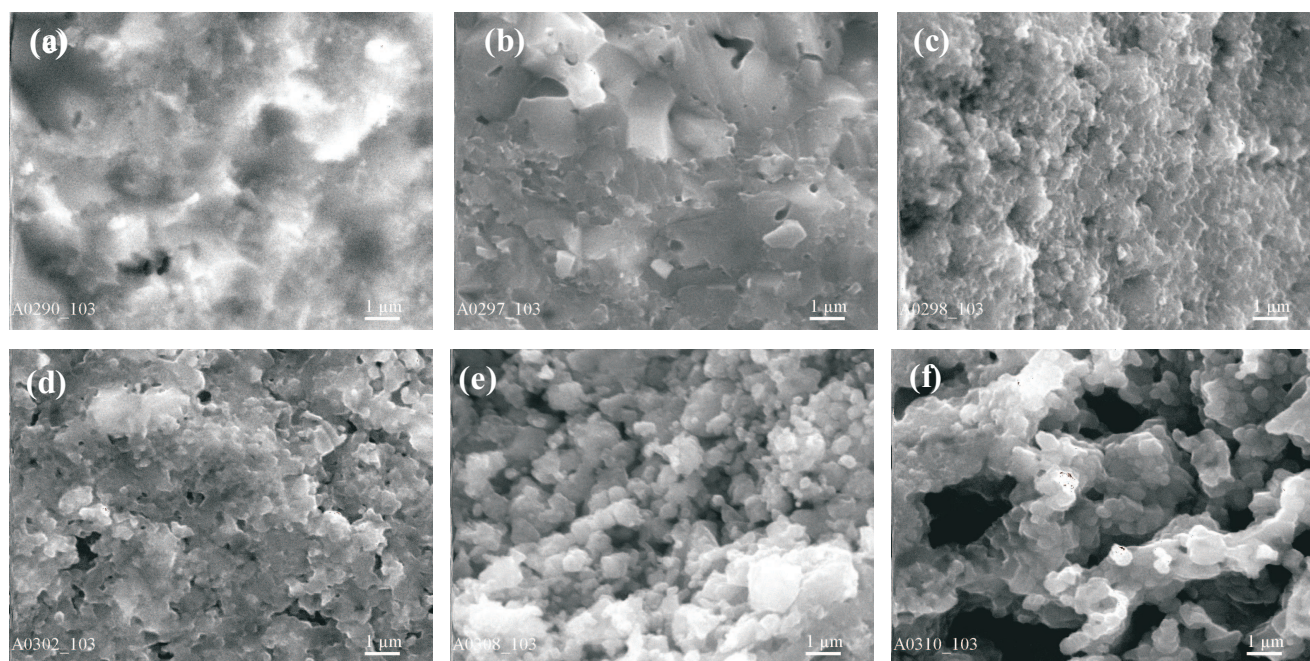


Fig. 3. SEM micrographs of samples sintered by Method 2 for (a) 20% TiB<sub>2</sub>, T<sub>sint.</sub>=1400°C; (b) 20% TiB<sub>2</sub>, T<sub>sint.</sub>=1500°C; (c) 36% TiB<sub>2</sub>, T<sub>sint.</sub>=1400°C; (d) 36% TiB<sub>2</sub>, T<sub>sint.</sub>=1500°C; (e) 60% TiB<sub>2</sub>, T<sub>sint.</sub>=1400°C; (f) 80% TiB<sub>2</sub>, T<sub>sint.</sub>=1400°C

#### 4. Conclusion

Practically pure TiN – TiB<sub>2</sub> composites with the relative density of 64-99 % have been synthesized. A possibility of obtaining the TiN-TiB<sub>2</sub> composite (40-60 wt% TiB<sub>2</sub>) with high mechanical properties ((HV=19.7-25.4 GPa (load P=100 g), fracture strength K<sub>1c</sub>=5.4-5.8 MPa×m<sup>1/2</sup> (P=20 kg )) has been shown. On the basis of

the carried out investigations, it has been established that the samples sintered by Method 1 have better properties (compared to Method 2) at 36-60 wt. % TiB<sub>2</sub> content, which may be related to the improvement of the structure formation conditions with an increasing heating rate. Herein, the sintering time is of no importance. A particular role is performed by the active atomic hydrogen that



is a decomposition product of  $\text{TiH}_2$ . It enhances the BN decomposition and reduces the boron and titanium oxide phases under the sintering carried out by Method 1. An increase in the  $\text{TiB}_2$  content up to 80 wt% leads to an extreme heat generation, heating-up and destruction of the graphite die, as a result of the intensification of the SHS reaction between Ti and B at high heating rate and a sufficient partial pressure of hydrogen. Via a synthesis by Method 2 the composite with a spongy structure was obtained. An increase in the sintering temperature by Method 2 leads to a considerable densification but the properties of the obtained composites do not improve. The composites with 36-60 wt%  $\text{TiB}_2$  content obtained by Method 1 have a homogeneous micro-grained structure. The mean grain size of the composite with 60 wt%  $\text{TiB}_2$  content does not exceed 0.5-0.7  $\mu\text{m}$ . The composites obtained by Method 2 have generally a porous and heterogeneous structure with a mean grain size of about 1  $\mu\text{m}$ . A rise of the sintering temperature leads to a certain grain growth. With increasing of the  $\text{TiB}_2$  content the porosity and the structure heterogeneity increases.

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