



## Selected properties of ZrB<sub>2</sub> composites obtained by SPS method for parts of electro-erosion shaping machines

Wybrane właściwości kompozytów na bazie ZrB<sub>2</sub>, otrzymanych metodą SPS i przeznaczonych na części maszyn do kształtowania elektroerozyjnego

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DOI: <https://doi.org/10.17814/mechanik.2018.2.32>

The effect of the addition of silicon carbide and boron carbide powders on the properties of ZrB<sub>2</sub> ceramic composites constituting UHTC materials (ultra high temperature ceramics) was investigated. Polycrystalline zirconium boride samples as well as matrix composites of this phase with addition of 2 and 10 wt.% SiC and B<sub>4</sub>C were obtained by pressure-assisted sintering using SPS/FAST (spark plasma sintering/field assisted sintering technique) in the temperature range of 1800÷2000°C. Samples were characterized by X-ray diffraction, scanning electron microscopy, hardness and fracture toughness. The obtained materials are characterized by a high relative density in the range of 97÷98%. Higher hardness and fracture toughness were observed for the composite obtained in temperature 1900°C.

KEYWORDS: UHTC ceramics materials, fracture toughness, SPS/FAST

*Badano wpływ dodatku proszków węglik krzemu i węglik boru na właściwości kompozytów ceramicznych na bazie ZrB<sub>2</sub>, stanowiących materiały UHTC (ultra high temperature ceramics). Próbki z polikrystalicznego dwuborku cyrkonu oraz kompozyty na osnowie z tej fazy z dodatkiem 2 i 10% wag. SiC oraz B<sub>4</sub>C otrzymano na drodze spiekania wspomaganego ciśnieniowo, z użyciem metody SPS/FAST (spark plasma sintering/field assisted sintering technique) w temperaturze w zakresie 1800÷2000°C. Otrzymane kompozyty scharakteryzowano pod kątem składu fazowego, mikrostruktury, właściwości mechanicznych i odporności na pękanie. Materiały cechują się wysoką gęstością względną – w zakresie 97÷98%. Wykazano wyższą twardość oraz odporność na pękanie kompozytów o osnowie z dwuborku cyrkonu z dodatkiem faz ceramicznych, otrzymanych w temperaturze 1900°C.*

SŁOWA KLUCZOWE: ceramika UHTC, odporność na pękanie, SPS/FAST

There is a growing interest in ceramics and ceramic composites based on transition metals (Zr, Hf, etc.) mainly diborides but also carbides, often referred to as ultra high temperature ceramics (UHTCs), due to the unique combination of physical, thermal and mechanical properties, such as high refractoriness (melting points above 2500°C), high electrical and thermal conductivity, chemical inertness against molten metals and slags, good thermal shock resistance, low density and high resistance to ablation in oxidizing environments [1–3]. ZrB<sub>2</sub>-based composites are attractive because of the excellent electrical conductivities of their matrices, which make these materials amenable to electro-discharge machining for the purpose of near-net shaping [4].

The characteristic properties of these materials determine their potential application on: military and thermonuclear reactor, parts of machines and devices, components of thermal protection, edges of attack in airplanes, as well as cutting tools. The high melting point and oxidation resistance allows their use in the space industry, e.g. on jet engine nozzles [5–7]. The manufacturing processes and physico-mechanical properties of ceramics based on ZrB<sub>2</sub> have been extensively described in [8–10]. Compaction of ZrB<sub>2</sub> powders without additives is difficult due to its low sinterability resulting from a strong covalent ZrB<sub>2</sub> bond.

In order to improve the sinterability of ZrB<sub>2</sub> and increase the resistance to cracking, whether the bending resistance is introduced by additives that reduce the sintering temperature, which has a positive effect on limiting the grain growth. Pressure sintering technologies for powder materials developed in the last decade, including the SPS/FAST method, HP-HT, expand the possibilities of sintering and research on materials with a high melting point. The heating process in the SPS method is carried out as a result of the current flow through the stamps and the graphite matrix or by the compressed powder grains. During the current flow through the powder, a spark discharge occurs at the powder grain contact points, which removes adsorbed gases and oxides from the surface of

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the particles. This facilitates the formation of active contacts between the sintered powder particles and allows the process to be carried out at a lower temperature than for classical methods and in a much shorter time [11]. The obtained materials are characterized by a density close to the theoretical density.

The aim of the present contribution was to investigate the influence of the SiC and B<sub>4</sub>C addition on the microstructure development, hardness, fracture toughness and fracture characteristics of ZrB<sub>2</sub> based ceramics prepared by SPS.

### Experimental procedure

This study used commercially available ZrB<sub>2</sub> powder (Grade B) with an average particle size of 1.5±3 μm. Likewise, the SiC powder (Grade UF 15) with an average particle size of 0.4±0.6 μm and B<sub>4</sub>C powder (Grade HS) with an average particle size of 0.6±1.2 μm. Zirconium dioxide, silicon carbide and boron carbides were provided by producer H.C. Starck. The morphology of the starting powders are shown in fig. 1.

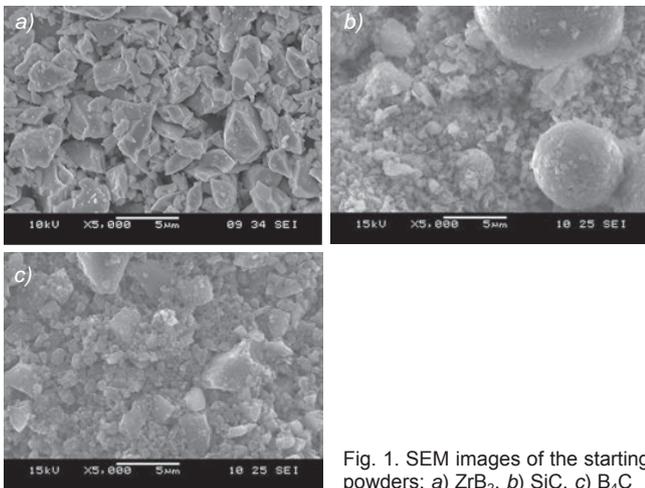


Fig. 1. SEM images of the starting powders: a) ZrB<sub>2</sub>, b) SiC, c) B<sub>4</sub>C

### Ball milling

Three types of zirconium boride based systems monolithic ZrB<sub>2</sub>, ZrB<sub>2</sub> with 2 and 10 wt.% of SiC and 2 and 10 wt.% of B<sub>4</sub>C were prepared using Fritsch Pulverisette 6 planetary ball mill equipped with WC-Co grinding vessel and balls. The powders were homogenised with rotation speed of 200 rpm for 2 h in acetone. The ball-to-powder weight ratio was 10:1. After milling the particle shape were examined by SEM. The results are presented in fig. 2.

### Spark plasma sintering (SPS)

The ball-milled powders were sintered using the HPD 5 type SPS system. Each powder was placed in a graphite die, 20 mm in diameter, axially pressed under 35 MPa and heated up to sintering temperature with a heating rate of 100°C/min (fig. 3). A graphite sheet with 0.5 mm in thickness was inserted between the raw material powder and the graphite die to prevent punch scuffing and to lighten the sintered sample extraction from the matrix. The graphite die was also wrapped with carbon blankets in order to minimize the heat loss during the sintering process. The samples were sintered in the temperature range from 1800 to 2000°C for 10 min in argon. SPS curves are presented in fig. 4.

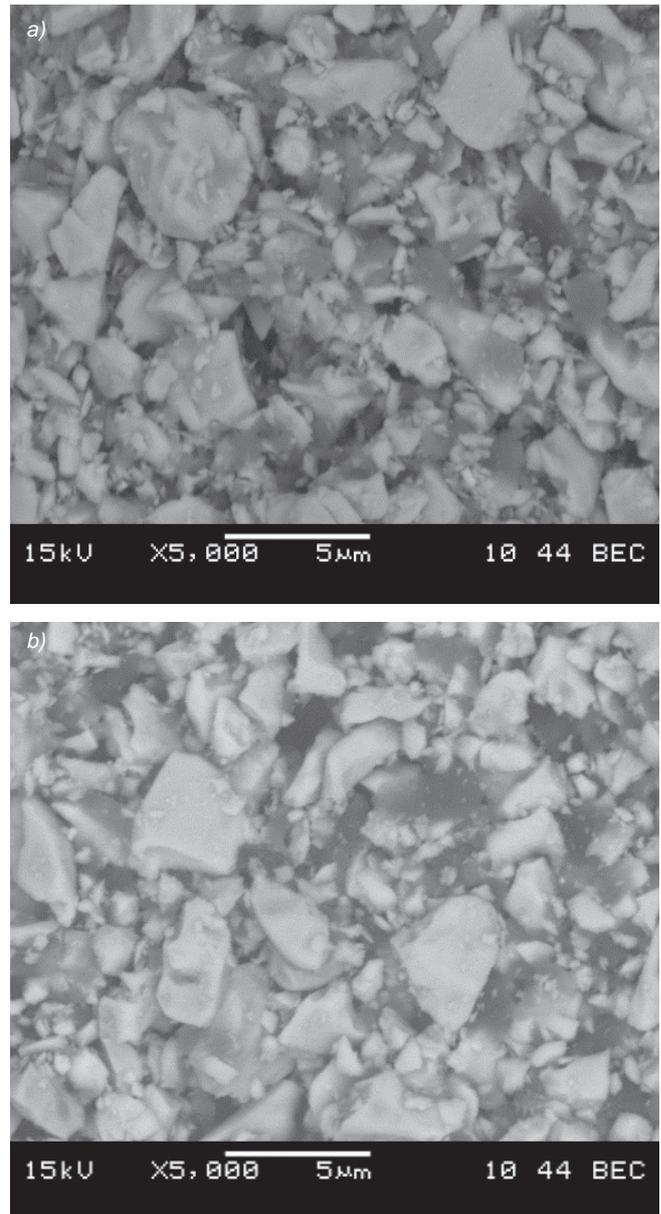


Fig. 2. ZrB<sub>2</sub>-based ball milled powders with additives: a) SiC, b) B<sub>4</sub>C

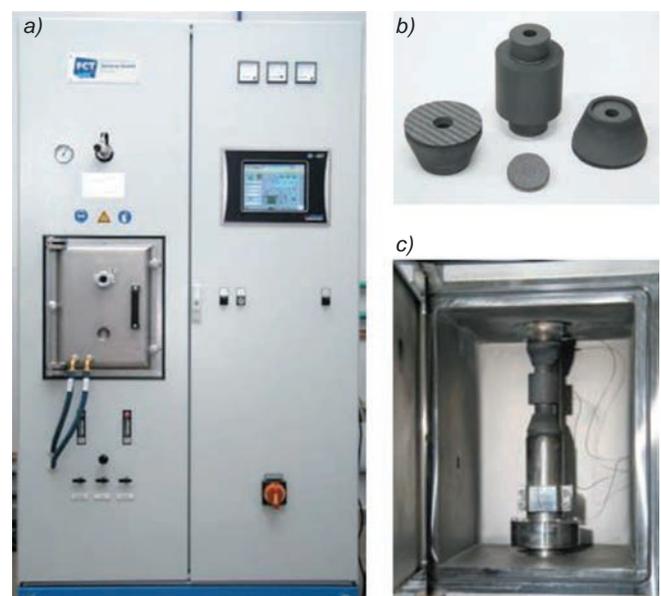


Fig. 3. Sintering furnace (a), graphite elements (b), oven chamber (c)

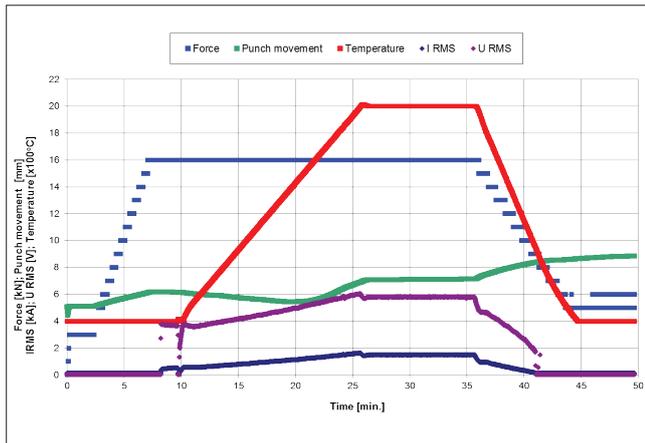


Fig. 4. Temperature and punch movement SPS curves recorded during densification of  $ZrB_2 + 10 \text{ wt.}\% B_4C$

## Investigations methods

Bulk density of specimens was measured by Archimedes' method using distilled water as the immersing medium according to ASTM C373-88. XRD patterns were obtained using the PANalytical Empyrean diffractometer with the copper radiation ( $\lambda_{Cu} = 1.5406 \text{ \AA}$ ). The quantitative phase analysis of the studied material was carried out using Rietveld refinement and High Score PANalytical software. Microstructure of the materials was studied with a scanning electron microscope (JEOL JSM-6460LV). Young's modulus of the composites was determined by ultrasonic wave transition method measuring the velocity of ultrasonic sound waves passing through the material using an ultrasonic flaw detector (Panametrics Epoch III). The velocities of transversal and longitudinal waves were determined as a ratio of the sample thickness and the relevant transition time. The hardness and the fracture toughness were determined by the Vickers indentation method applying load of 9.81 N (1 KG) and 98 N (10 KG), by a Future Tech FLC-50VX hardness tester. For each sample five indentations were made and the stress intensity factor  $K_{Ic}$  was calculated from the length of cracks which developed during a Vickers indentation test using Niihara's equation [12]. Fractographic analysis was used for the characterization of toughening mechanisms on the fracture lines after the IF test.

## Results

The analysis of the microstructure was made for sintered constituting the  $ZrB_2$  as starting material and with additions: SiC and  $B_4C$ , obtained by SPS method at  $1900^\circ\text{C}$ . An example of the microstructure of the surface of one of the materials ( $ZrB_2 + 10 \text{ wt}\% B_4C$ ) is shown in

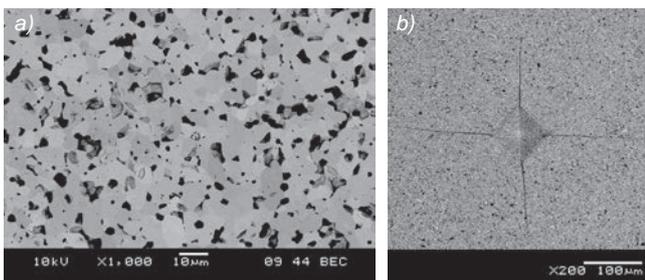


Fig. 5. Microstructure (a) and indentation cracks (b) in the  $ZrB_2 + 10 \text{ wt.}\% B_4C$  obtained by SPS at  $1900^\circ\text{C}$ , 35 MPa and 10 min system created during the indentation with load of 98 N

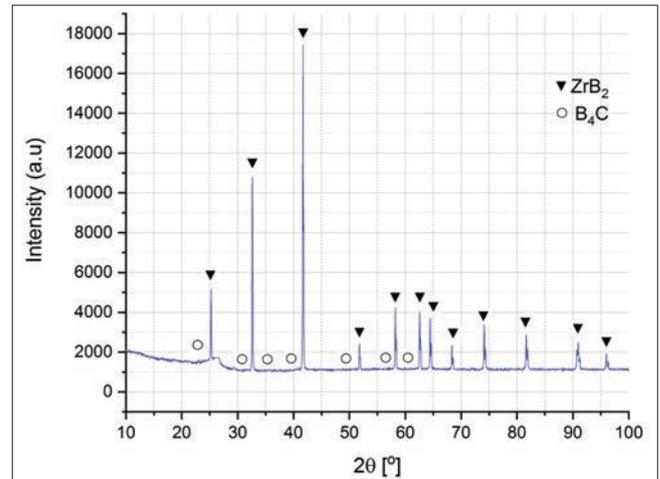


Fig. 6. XRD pattern of sintered  $ZrB_2 + 10 \text{ wt.}\% B_4C$  obtained by SPS at  $1900^\circ\text{C}$ , 35 MPa and 10 min

fig. 5a whereas the XRD pattern of sintered material are presented in fig 6.

A partial combination of particles is visible in the microstructural image. The material is characterized by high porosity and brittleness. Differences in the shades of gray of  $ZrB_2$  grains result from their different crystallographic orientation. Analysis of the phase composition showed the presence of  $ZrB_2$  and  $B_4C$  phases in the amount of 96 and 4% by mass.

The obtained test results can be analyzed and presented in the aspect of the influence of modifiers and sintering techniques on the change of microstructure and selected physical and mechanical properties of

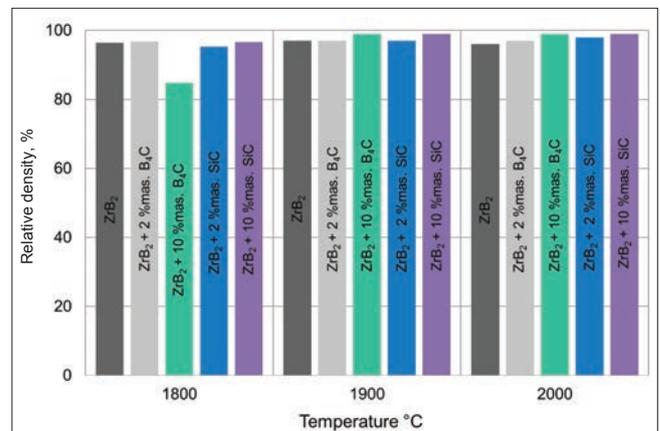


Fig. 8. Relative density of sintered materials obtained by SPS method in the temperature range of  $1800\text{--}2000^\circ\text{C}$

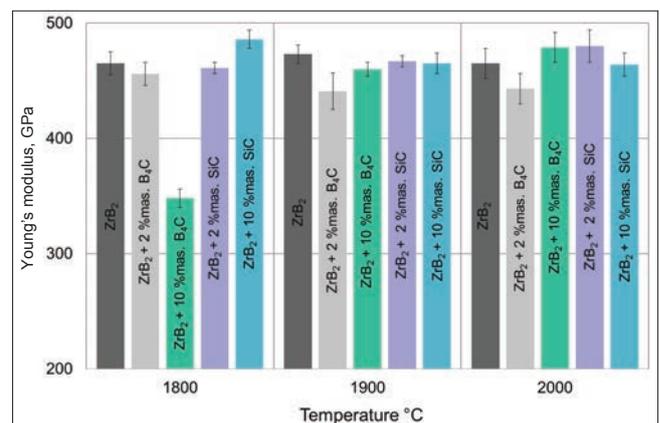


Fig. 9. Young's modulus of sintered materials obtained by SPS method in the temperature range of  $1800\text{--}2000^\circ\text{C}$

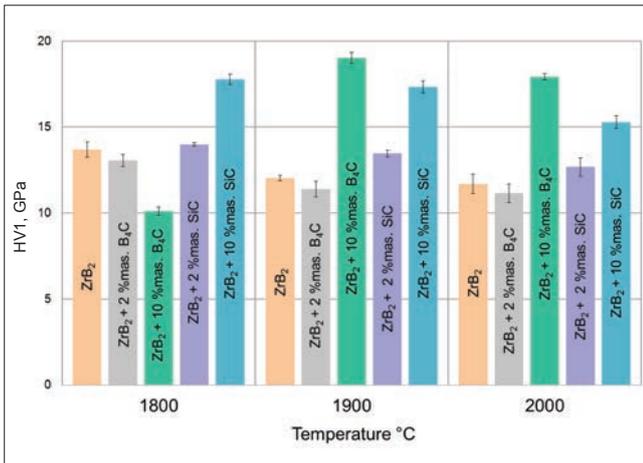


Fig. 10. Hardness of sintered obtained by SPS method in the temperature range of 1800÷2000°C

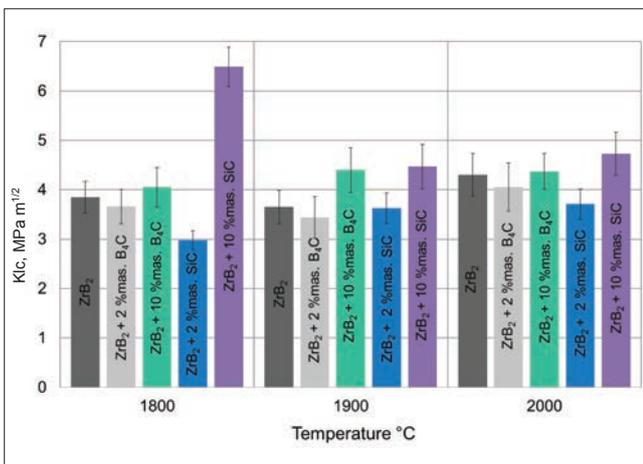


Fig. 11.  $K_{1c}$  coefficient of sintered obtained by SPS method in the temperature range of 1800÷2000°C

sintered materials based on ZrB<sub>2</sub>. In figs. 8–11 presented are the results of physical and mechanical properties sintered materials by SPS method in the temperature range of 1800÷2000°C for mixtures containing 2 and 10% by mass. SiC and B<sub>4</sub>C.

The relative density of sintered materials ranged from 97÷99%, Young's modulus in the range of 348÷486 GPa. The highest hardness (over 19 GPa HV1) was characterized by sintered materials at 1900°C. The crack resistance value  $K_{1c}$  (HV10) was in the range of 2.9 MPa · m<sup>1/2</sup>÷6.5 MPa · m<sup>1/2</sup> for sintered containing 10 wt.% SiC. Analysis of the obtained data showed that for the using sintering process parameters the best properties are characterized by materials obtained at 1900 and 2000°C.

## Conclusions

The performed research allowed us to determine the effect of additions on the properties of sintered materials based on ZrB<sub>2</sub>. The obtained materials are characterized by good physical and mechanical properties, the value of which does not differ from those presented in the literature, produced by other methods [1, 9–10]. The SiC and B<sub>4</sub>C addition sustains the densification of the composites which results in a high density, approximately 97, 99 and 99% for ZrB<sub>2</sub>, ZrB<sub>2</sub> + 10 wt.% B<sub>4</sub>C and ZrB<sub>2</sub> + 10 wt.% SiC, respectively. The best SPS sintered materials were characterized by Young's modulus above 450 GPa, hardness

over 19 GPa (for sintered with 10% B<sub>4</sub>C addition). The fracture toughness increased with addition of SiC and B<sub>4</sub>C.

The toughening mechanisms in both composites were similar, mainly in the form of crack deflection. The addition of the additives improved the sinterability and inhibited grain growth.

Due to the low sinterability of ZrB<sub>2</sub> powders, resulting from their strong covalent bonds. Additives were added to facilitate the sintering process and increase resistance to cracking and bending. The SPS method used in the work allowed us to obtain UHTC materials characterized by a unique combination of physical, thermal and mechanical properties, such as high refractoriness, high electrical and thermal conductivity, chemical inertness against molten metals and slags, good thermal shock resistance, low density and high resistance to ablation in oxidizing environments. Those properties are associated in the fields of energy (nuclear fission and fusion, energy harvesting, concentrated solar power), materials processing (high temperature electrodes, high speed machining tools, molten metal containment), microelectronics (conductors, barrier layers, lattice matched substrates), and others.

**The POWROTY/2016-1/3 project is carried out within the Powroty / Reintegration programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.**

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