ELECTRICALLY CONDUCTIVE CERAMIC COMPOSITES

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1. Abstract

Basic results on the development of an electrically conductive, wear and corrosion resistant ceramic composite material are presented. From a closer examination of the composition dependence of the electrical conductivity in the binary system $\text{ZrB}_2\text{-B}_4\text{C}$ we determined the percolation threshold at which an interconnected network of electrically conductive phase arises: for the system investigated, at a critical volume fraction of about 10 up to 25 Vol.-% ZrB_2 the electrical conductivity increased rapidly and above 40 Vol.-% ZrB_2 an electrical conductivity similar to metals was observed ($\sigma_e = 10^5\text{-}10^7 \text{ S}\cdot\text{m}^{-1}$).

Based on ZrB_2 as major component and mainly B_4C as minor component a ceramic composite material was obtained by net shape processing procedures. It exhibits a metal-like electrical conductivity, a high resistance against wear and oxidation as well as promising mechanical properties.

Keywords: percolation threshold, net shape, hot-isostatic pressing, mechanical properties.

2. Introduction

Ceramic materials exhibit striking properties for high performance applications where high temperature stability, wear resistance and chemical inertness are demanded [1, 2]. Up to now, several toughening techniques [3-6] were developed to overcome the problem of inherent brittleness of ceramics allowing ceramic parts to become more and more used in engineering, chemical processing and medical applications [3, 4, 7-9].

Wear and corrosion resistant, electrically conductive ceramics (ECCs) are interesting materials for applications where electrically conductive components or small precision parts with complex geometries are applied, e.g., electrodes, sensors, or precision parts in micromechanic and electronic devices. The development of ECCs with an electrical conductivity in the range of metals and with mechanical properties matching the requirements for technical applications is not straightforward: inherent ECCs [10] like transition metal carbides and borides are too brittle or poorly sinterable, and typical engineering ceramics are insulators. A promising approach to ECCs is to combine insulating engineering ceramics, e.g., SiC, B₄C, Al₂O₃, ZrO₂, Si₃N₄ with an electrically conductive phase, e.g., TiB₂, ZrB₂, TiC, Mo₂C, Mo, W, MoSi₂ yielding ceramic/ceramic matrix or metal/ceramic matrix composites [11 - 15].

The goal of this work was to evaluate processing procedures which allow a net-shape fabrication of small but complex shaped components. Narrow tolerances, a very smooth surface finish, high wear resistance, and desired electronic conductivity should be reached without final machining.

3. Experimental

As a very promising system investigations were made with ZrB₂ and B₄C as major components.

Raw materials: ZrB₂ ($d = 6.09 \text{ g cm}^{-3}$, grade B, H.C. Starck, Germany), B₄C ($d = 2.51 \text{ g cm}^{-3}$, grade HS, H.C. Starck, Germany), detailed information on the powder characteristics are listed in table 1.

TABLE 1: Characteristic data on the ZrB₂ and B₄C raw materials

	density (g cm ³)	particle size distribution			specific surface area, BET		oxygen content		
		d ₁₀	d ₅₀	d ₉₀ (μm)	m ² /g	m ² /cm ³	wt.-%	g/cm ³	g/m ²
ZrB ₂	6.09	0.86	2.7	5.2	2.04(2)	12.4(1)	0.99(5)	6.0(3)	0.48
B ₄ C	2.51	0.36	1.4	5.9	17.0(1)	42.6(2)	-	-	-

Powder blend preparation: The $\text{ZrB}_2\text{-B}_4\text{C}$ compositions were prepared by vigorous dry-mixing the as-purchased powders in a melamine mortar for 10 minutes. For the synthesis of the ZrB_2 composite materials an aqueous slurry of ZrB_2 , B_4C and sinter-promoting additives was prepared. Using a pearl mill (PML-H/V, Drais, Germany) with polyurethane lining and WC-Co milling bodies (6 wt.-% Co, $\varnothing$ 1 mm) the average particle size was reduced from about 3 μm to far below 1 μm ($d_{50} \approx 0.5 \mu\text{m}$). Then, organics were added to the slurry, i.e., surfactants to adjust the viscosity of the slurry for spray drying, pressing aids to improve the particle re-arrangement during powder compaction and polyvinylalcohol as binder to increase the strength of the resulting green bodies [16]. By spray drying (spray dryer Mobile Minor, type "Hi-Tec", Niro, Denmark) a granulated powder consisting of spherical granules up to 200 μm in diameter with excellent flowability and good compaction behaviour was obtained.

These granulated powder blends were compacted by uniaxial die pressing (30 MPa) to cylindrical pellets ($\varnothing$ 15 mm, thickness 8 mm) which were additionally cold-isostatic pressed (150 MPa) in a wet-matrix press (type 110-350-200, VITEK N.V., Belgium). Densities of the green bodies were determined from geometric dimensions and weight of the samples.

The *sintering* was performed in a graphite furnace equipped with a dilatometer device for rate-control sintering (KCE Rödental, Germany). Initial sintering was done in vacuum up to 1800 K and final sintering in Ar atmosphere (1 bar, $>1800^\circ\text{K}$).

For *hot-isostatic pressing* a laboratory HIP (EPSInt, Belgium) with graphite heater, shielding and crucibles, (Ar, HIP gas) was used.

Characterisation of sintered material was done by following equipment and procedures:

Optical microscopy: ZEISS Axiovert 100 A, magnification 100 $\times$.

Scanning electron microscope (SEM): JEOL JSM-6300F, 20 kV, BSE mode, magnification 1000 $\times$.

X-ray diffractometry: Siemens diffractometer, $\Theta/2\Theta$ scan, continuous mode: $0.1^\circ \Theta\cdot\text{s}^{-1}$.

Thermogravimetric analysis: Perkin Elmer TGA 7, alumina crucibles, sample weight: 20-30 mg, heating rate: $10 \text{ K}\cdot\text{min}^{-1}$, atmosphere: oxygen.

Particle size distribution: Laser diffraction (MasterSizer X, Malvern Instruments) isopropanol as dispersing liquid.

Specific surface area (BET): BET measurement according to DIN 66'131, nitrogen adsorption, sorption apparatus (PMI).

Oxygen content: combustion of carbon using ultrapure Ni as catalyst at about 3300 K in an induction furnace, quantitative determination of generated CO_2 by infrared detection (LECO TC-336), mean value from 5 measurements, sample weight: 10 – 20 mg.

Density (d): ARCHIMEDES principle, water/air.

Electrical conductivity (σ_e): 4-point van der Pauw method, $10 \times 5 \times 2$ mm sample plates, current: 0.500 ± 20 A ($\sigma_e > 10^4$ S·m⁻¹), 0.15 ± 20 A ($\sigma_e > 10^4$ S·m⁻¹).

Vickers hardness (HV10): according to standard proposal ENV 843-4, 10 kN load, microhardness tester *Durimet KLHP*.

Bending strength (σ_b): $2.0 \times 2.5 \times 25.0$ mm test bars and 4-point bending strength measurements according to standard EN 843-1, test time: 10 ± 1 s, 20 / 10 mm distance of power transmitter, screw driven compression test apparatus Zwick; calculation of mean bending strength values from five measurements according to standard proposal ENV 843-5.

Fracture toughness (K_{IC}): SEVNB method, $2.0 \times 2.5 \times 25.0$ mm test bars according to standard EN 843-1, V-notch: radius = 0.01 – 0.03 mm, depth = 0.5 – 0.8 mm, 20 / 10 mm distance of power transmitter, load speed: ≈ 0.25 MPa·√m·s⁻¹, screw driven compression test apparatus (Zwick), calculation of K_{IC} values according to DIN 51'109.

Young's modulus (E): impulse-echo technique, ultrasonic apparatus (USIP 12 Krautkrämer) using honey as coupling agent, longitudinal wave generator head (Harisonic HLI CM1002), transversal wave generator head (Krautkrämer MB4Y, 10 MHz NB / 5 MHz BB).

4. Results and Discussion

ZrB₂-B₄C composites: For densification of the powder compacts a simple pressureless sintering procedure with continuous heating rate up to the maximal sintering temperature (2450 K, hold time: 20 min.) was applied. Composites containing 40 to 80 Vol.-% ZrB₂ yield the highest densification with densities greater than 93 % relative to the theoretical density value (Figure 1).

Figure 1: Electrical conductivity, green density and sintered density vs. composition of $\text{ZrB}_2 - \text{B}_4\text{C}$ composite materials

The pure ceramic powder compacts of B_4C and ZrB_2 resp., instead showed only poor sinterability with 90 % resp. 85 % relative density. Therefore, expensive hot-pressing was usually applied to the manufacturing of dense ceramic parts of both, pure B_4C and ZrB_2 . [4, 5]. For B_4C the inherent poor sintering properties have been traced back to the covalent character of its framework resulting in low self-diffusion coefficients and high grain boundary energies [17, 18]. Most efforts to obtain dense boride materials concern TiB_2 which possesses excellent resistance against metallic melts [4, 5]. It was stated that the high oxygen loading of the TiB_2 surface is the main reason for its poor sintering properties. This argument was confirmed by producing and handling TiB_2 powders under inert atmosphere conditions which resulted in pressureless sintered ceramic parts with nearly theoretical density [19,20]. We suppose that for ZrB_2 similar considerations are valid. From this point of view, the excellent densification of ZrB_2 - B_4C powder compacts may be explained by reduction of the oxygen covered ZrB_2 surface by B_4C which forms volatile B_2O_3 and CO_2 . From the processing of SiC it is well known that small additions of carbon and B_4C cause a significant increase in the sinter reactivity of SiC [21]. Beside the reduction of the oxide layer on the SiC particles by carbon, the formation of an eutectic liquid SiB_6 phase by reaction of SiC with B_4C occurs which promotes the sintering kinetics by dissolution/recrystallization processes (liquid phase sintering) [4, 18, 22]. From optical microscopy and X-ray diffractometry within the actual investigation no indications of the formation of a comparable glassy phase or other crystalline phases than B_4C and ZrB_2 are observed (Figure 2).

Figure 2: X-ray diffractogram of ZrB_2 (*) - B_4C (+) composite material (50 Vol.% ZrB_2)

A comparison of the lattice constants of the composite phases with literature values of standard materials (table 2) shows excellent coincidence for the ZrB_2 phase and good agreement for B_4C which is the carbon-rich limiting composition in the broad composition field [17]. Hence, we suppose that solid solution mechanisms enhancing the sintering relevant diffusion processes are neglectable.

TABLE 2: Refined lattice constants of reference materials in comparison to the corresponding phases in the sintered composite material:

	ZrB_2			B_4C		
reference material ^a	$a = 3.169 \text{ \AA}$	$c = 3.530 \text{ \AA}$	$\gamma = 120^\circ$	$a = 5.60 \text{ \AA}$	$c = 12.10 \text{ \AA}$	$\gamma = 120^\circ$
$\text{ZrB}_2\text{-B}_4\text{C}$	$a = 3.169 \text{ \AA}$	$c = 3.531 \text{ \AA}$	$\gamma = 120^\circ$	$a = 5.595 \text{ \AA}$	$c = 12.071 \text{ \AA}$	$\gamma = 120^\circ$

^a ref. 4, p. 791 and 805.

The electrical conduction behaviour is strongly dependent on the volume fraction of ZrB_2 present in the composite system (Figure 1). It agrees with the statements of the percolation theory which means that in a binary system consisting of an insulating and an electrically conductive phase at a critical volume fraction V_C , the conductive phase forms a three-dimensional interconnected network of conduction paths allowing the electrons to percolate through the material (Figure 3) and so yielding a sharp increase in the specific conductivity [23].

Figure 3: Microstructure vs. composition of $\text{ZrB}_2 - \text{B}_4\text{C}$ composite materials (SEM micrographs of fracture surfaces: white - ZrB_2 , grey - B_4C , dark grey - pores or materials pull out).

Up to now, it was not possible to develop a theoretical model for binary ceramic composites for a predictive simulation of their electrical conductivity [23]. This fact results mainly from the complexity of such ceramic systems since factors influencing the critical volume fraction like particle size ratio, particle morphologies and particle interfaces are not only strongly dependent on the initial powders used, but also on the processing conditions especially on sintering which directly controls grain growth. For the investigated binary system the critical volume fraction V_c is about 10 Vol.-% ZrB_2 , between 10 and 25 Vol.-% the percolation threshold is reached and above 50 Vol.-% ZrB_2 a close network is present which results only in minor increase in electrical conductivity with rising ZrB_2 content (Figure 1).

In Figure 4 the thermally induced weight loss of a ZrB_2 - B_4C powder blend (50-50 Vol.-%) in oxygen atmosphere is depicted. Up to about 700°K organic additives are burned out and at about 800°K the oxidative degradation of the ceramic components occurs.

Figure 4: Thermogravimetric graph depicting the oxidative removal of organic additives and the oxidation resistance of ZrB_2 - B_4C composite material (50 Vol.-% ZrB_2).

ZrB_2 composite material: The addition of sinter promoting additives to the ZrB_2 - B_4C composite made it possible to obtain a composite material with almost theoretical density, at least higher than 95% of the relative density. Figure 5 shows micrographs of polished composite surfaces after different densification procedures which depict the importance of sintering conditions with respect to microstructural development and hence to mechanical properties (Table 3).

Table 3: Properties of ZrB_2 composite materials after different densification procedures.

sintering conditions	density d (g/cm^3)	Vickers hardness HV10	4-point bending strength σ_b (MPa)	fracture toughness K_{IC} ($\text{Mpa} \sqrt{\text{m}}$)	Young's modulus E (GPa)	electrical conductivity σ_e (S/m)
pressureless sintering with linear heating: $T_{\text{max}} = 2450 \text{ K}$	4.17	1340(50)	300(60)	3.5(6)		
pressureless rate- control sintering (r.c.s.): $T_{\text{max}} = 2420 \text{ K}$	4.17	1700(80)	460(60)	3.4(6)	381 (4)	$8(2) \cdot 10^5$
r.c.s. + hot-isostatic pressing (HIP): $T_{\text{HIP}} = 2220 \text{ K}$, $P_{\text{HIP}} = 195 \text{ MPa}$	4.37	2090(90)	480(60)	3.5(1)	498(5)

Figure 5: Microstructure of ZrB₂ composite materials after different densification procedures: a) pressureless sintering with continuous heating rate, b) pressureless rate-control sintering, c) process b) with subsequent hot-isostatic pressing (optical micrographs of polished surfaces: white - ZrB₂, grey - mainly B₄C, black - pores or materials pull out).

By adjusting the temperature program of pressureless sintering (2450°K , 20 min.) and using rate-control a tremendous decrease in grain growth was achieved and by additional hot-isostatic pressing (195 MPa, 2200 K, 20 min.) the grain contacts were improved which is evident from the significant decrease in porosity and of grain pull outs due to the polishing procedure and the large increase in hardness. Comparison of the achieved densities after pressureless sintering ($d = 4.17 \text{ g}\cdot\text{cm}^{-3} = 96.5 \% \text{TD}$) and sinter-HIPing ($d = 4.37 \text{ g}\cdot\text{cm}^{-3}$, 101.2 % TD) with the theoretical value ($4.32 \text{ g}\cdot\text{cm}^{-3}$) shows a significant positive discrepancy for the sinter-HIP material indicating that B_4C ($d = 2.51 \text{ g}\cdot\text{cm}^{-3}$) indeed was consumed during sintering as already stated above.

5. Conclusions

With the present work we have elaborated net shape processing procedures for the fabrication of composite components with the following properties:

- ◆ *Electrical Conductivity:* In $\text{ZrB}_2\text{-B}_4\text{C}$ composites the percolation threshold is observed at 10 to 25 vol.-% ZrB_2 giving rise to an increase in the electrical conductivity from about 10^2 to $10^6 \text{ S}\cdot\text{m}^{-1}$. Hence, more than about 25 vol.-% ZrB_2 are necessary to achieve an electrical conductivity similar to metals.
- ◆ *Densification and Microstructure:* Both pure B_4C and pure ZrB_2 powder compacts are harder to densify than their composites. Fine dispersed powder blends with average particle sizes in the micron to submicron range and optimized sintering conditions yield microstructures with grain sizes below $5 \mu\text{m}$ allowing the desired surface finish for net shape fabrication.
- ◆ *Phase Composition:* X-ray diffractograms of $\text{ZrB}_2\text{-B}_4\text{C}$ composites show only ZrB_2 and B_4C as crystalline phases. The refined lattice parameters agree with literature data. With SEM and optical micrographs no amorphous phases were observed. Therefore, no indication for liquid phase sintering is evident in this system.
- ◆ *Oxidation Resistance:* Thermogravimetric analysis on ZrB_2 composite powder blends in oxygen atmosphere demonstrate the high resistance of the material against oxidation which begins only above 800°K . Therefore, complete oxidative removal of organic additives (binder, pressing aid, surfactants) as crucial step in ceramic processing should be possible in air.
- ◆ *Mechanical Properties:* The mechanical properties are improved with higher densification, decreasing porosity and finer microstructure. Due to closer grain contacts the strength and hardness of the ZrB_2 composite are enhanced remarkably.

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