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Combined effects of WC and SiC on densification and thermo-mechanical stability of ZrB_2 ceramics

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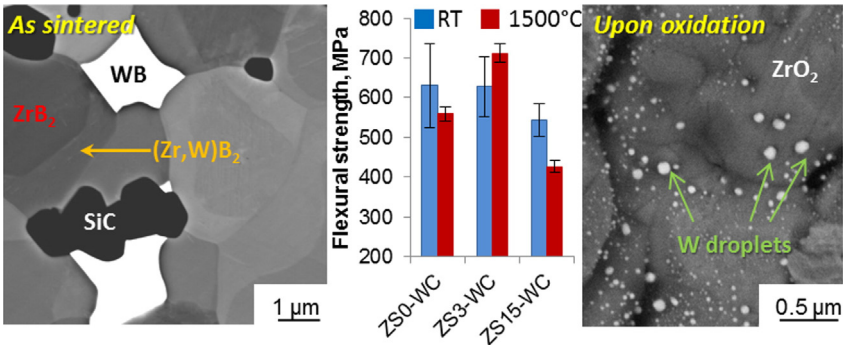
HIGHLIGHTS

- Fabrication of ZrB_2–WC–SiC composites with density above 94%.
- Development of "core-rim" substructures in the matrix and mixed W, Zr–boride and carbide.
- Room temperature strength passed from 540 to 630 MPa to over 700 MPa at 1500 °C in air.
- W, enclosed in the solid solution shells, retarded the oxygen diffusion compared to pure ZrB_2.

GRAPHICAL ABSTRACT



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ABSTRACT

ZrB_2-based mixtures containing WC and SiC in various amounts were hot-pressed at 1930 °C, achieving final relative densities above 94%. The diboride matrix of the sintered ceramics was constituted by $(Zr,W)B_2$ solid solution shells grown onto original ZrB_2 grains. WC phase reacted during sintering leaving W-monoboride and mixed Zr,W-carbide as secondary phases. Room temperature flexure strength ranged from 540 to 630 MPa, but performances of major significance were determined at 1500 °C in air, with values exceeding 700 MPa. SiC was vital to improve the oxidation resistance at 1500 °C compared to SiC-free ZrB_2-based ceramic. W, encased in the shell, retarded the inward diffusion of oxygen compared to the pure ZrB_2.

1. Introduction

Zirconium diboride (ZrB_2) belongs to the well-known class of compounds conventionally named as ultra-high-temperature ceramics (UHTCs) because of their melting point above 3000 °C. Research activity of recent years has been addressed to continuously improve its thermo-mechanical capabilities, failure tolerance, and ablation/oxidation resistance through the tailored addition of various secondary phases [1–5].

SiC has been repeatedly added in a range of 5–30 vol% to transition metal diborides (MeB_2), owing to its proven ability to help densification of MeB_2, as well as to limit the growth rate of the diboride matrix by pinning the grain boundary migration during the final stage of densification, typically above 1900 °C in the case of hot-pressing [1,6]. The presence of SiC has also proved to increase flexure strength owing to a refined and dense microstructure [7], as well as the resistance to

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oxidation up to 1650 °C, thanks to the in situ formation of a multilayered protective oxide scale [8,9].

Additional third phases able to bring benefit to the high temperature performance of MeB_2–SiC systems include carbides and silicides of W, Ta, or Mo [3,10–13]. In this respect, the incorporation of WC has recently gained great attention thanks to an attractive ability [10,14,15] to favor the flexure strength retention at temperatures up to 1600 °C.

Also the resistance to oxidation was reported to take advantages from the presence of W-carrying refractory phases inside the resulting microstructure of ZrB_2 ceramics [16–19]. No matter if WC is initially added as second phase [19] or as impurity [7], improved performances at high temperatures were recorded anyways. Average flexure strengths up to 640 MPa at 1600 °C in protective Ar atmosphere were achieved as long as a starting quantity of 5 vol% WC was introduced into a ZrB_2–20 vol% SiC powder mix [10]. The potential of the ZrB_2–SiC–WC system has been further disclosed thanks to measurements of residual flexure strength (tested at room temperature) after 24 h of exposure to static air at 1400 °C [20]. This material, object of the present work and thereafter designated as ZS15–5WC, despite the adverse influence of 6 vol% residual porosity, lost only 28% of its average room temperature flexure strength, decreasing from 543 to 390 MPa.

As far as the resistance to oxidation is concerned, the beneficial effects to the oxidation rates of ZrB_2 and ZrB_2–SiC ceramics which arise from the presence of tungsten has been already outlined in previous works [10,16–18,21]. The improvement was ascribed to a number of phenomena: i) the occurrence of an eutectic between WO_3 and ZrO_2 at 1275 °C activates a liquid phase sintering of the in situ growing zirconia scale decreasing its porosity [10,16]; ii) the oxidation product, WO_3, performs as barrier itself due to the volume increase associated to oxidation of W-species to WO_3 [16]; iii) the incorporation of W atoms in the borate glass increases the stability of the glass itself [17,18].

In this study, we report on advances in the understanding of the densification and oxidation behavior of W-doped ZrB_2-based ceramics and their thermo-mechanical improvements attained through the addition of refractory carbides such as SiC and WC. The main novelty of this work is related to the achievement of flexure strength values overpassing 700 MPa when tested at 1500 °C in air.

2. Experimental procedure

Commercial powders of ZrB_2, SiC, and WC (see Table 1) were used to produce three different compositions in the ZrB_2–WC–SiC system. The initial nominal compositions were all based on ZrB_2, with SiC and/or WC as secondary phases in varying amounts, as follows (vol%):

ZS0-15WC:	ZrB_2 + 15WC
ZS3-5WC:	ZrB_2 + 3SiC + 5WC
ZS15-5WC:	ZrB_2 + 15SiC + 5WC

With these three compositions, multiple purposes were addressed. ZS0-15WC was designed to keep the system as simple as possible to study the reaction products during sintering. In ZS15-5WC, the amount of SiC was set as that typically introduced in the majority of the studies on ZrB_2–SiC [1–3], while ZS3-5WC was conceived as optimization of the previous two compositions, in an effort to reduce the amount of SiC phase under the percolation limit, as main responsible of strength decrease at high temperature.

Base component (ZrB_2) and secondary phases (SiC, WC) were weighed according to the rule-of-mixture, batched into a PET bottle and then ball-milled for 24 h in absolute ethanol using SiC milling media. Subsequently, the slurries, dried using a rotary evaporator, were sieved through a 150 μm metallic screen. 30 mm diameter pellets were cold compacted using a uniaxial press with 20 MPa applied pressure. The *green* pellets were directly positioned into the graphite die located inside the vacuum chamber of the hot-press furnace. The inner walls of the graphite die were precautionary protected by a BN-sprayed graphitized 0.5 mm thick foil. The pellets were thus hot-pressed in the vacuum range of 0.1–1 mbar using an induction-heated graphite die and applying a constant uniaxial pressure of 30 MPa during ramping up to 1930 °C, 15–20 °C/min of heating rate. Once the target temperature was reached, the linear pressure was increased up to 40 MPa and maintained up to 35 min to promote full densification. The change in thickness (dL) of the *green* pellets under hot-pressing was recorded during heating up and final dwell. The experimental dL values were then converted into relative density data, under the hypothesis of a full mass conservation. The temperature was monitored by means of an optical pyrometer focused into a blind hole dug on the external surface of the graphite die. At the end of the dwell, free cooling followed.

Crystalline phases of the sintered ceramics were identified by X-ray diffraction (XRD, mod. D8 Advance – Bruker, Germany). The cell parameters of the secondary phases indexed in the hot-pressed ZrB_2 ceramics were determined using the Rietveld refinement approach. Specific XRD patterns were acquired on a polished surface of a bulk sample, imposing the strongest tabulated ZrB_2 reflections along the 2-theta scanned range of 20°–80° as the internal calibrating known phase. The microstructure of the as-hot-pressed ZrB_2 ceramics were also analyzed on fractured and polished surfaces by field-emission scanning electron microscopy (FESEM, mod. ΣIGMA, ZEISS NTS Gmbh, Germany) coupled to an energy dispersive X-ray micro-analyzer (EDS, mod. INCA Energy 300, Oxford instruments, UK). Key microstructural features like residual porosity, mean grain size, and volumetric content of the secondary phases were evaluated thanks to FESEM micrographs elaborated with the support of the commercial software package Image Pro Plus (v.7, Media Cybernetics, USA).

The bulk densities (ρ_B) of the as-hot-pressed ceramics were measured by Archimedes' method in distillate water at 25 °C, while the theoretical densities ($\rho_{TH,0}$) were computed according to the rule-of-phase mixture. Residual porosity was first calculated dividing ρ_B by $\rho_{TH,0}$ and then adjusted/confirmed by scanning electron microscopy inspection on polished sections. The expected final densities ($\rho_{TH,1}$) were updated according to the estimated quantities of the secondary phases. The final relative densities (RD^*) were established according to the image analysis approach.

The 4-pt. flexure strength (σ) was measured at room temperature (RT) and at 1500 °C in air using the guidelines of the European standards for advanced ceramics ENV843-1:2006 and EN820-1:2002, respectively. Chamfered bars with dimensions 25.0 × 2.5 × 2.0 mm^3 (length by width by thickness, respectively) were tested at RT using a semi-articulated steel-made 4-pt fixture (lower span 20 mm, upper span 10 mm) in a screw-driven load frame (Zwick-Roell mod. Z050, Germany), 1 mm/min of cross-head speed. Flexure strength at high temperature was instead measured using an Instron apparatus (mod. 6025) equipped with a 4-pt fixture made of SiC. Before applying the load during testing at 1500 °C, a dwell of 18 min was set to reach

Table 1
Main characteristics of the starting powders used. ρ_{TH}: theoretical density, d_{50}: median of the granulometric distribution.

Powder	Grade and supplier	ρ_{TH} (g/cm^3)	d_{50} (μm)	Purity (wt%)	Main impurities (wt%)
ZrB_2	Gr. B, H.C. Starck, Germany	6.1	2.1	>98	O:1.5, Hf:0.2
SiC	Gr. BF-12, H.C. Starck, Germany	3.21	0.6	>99	O:0.9
WC	Gr. SD0.5, Treibacher Industries AG, Germany	15.74	0.5	99.5	–