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Development and characterization of metal-diboride-based composites toughened with ultra-fine SiC particulates

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Abstract

Two metal-diboride-based ceramics containing up to 15 vol%. ultra-fine α-SiC particulates were developed from commercially available powders. The primary matrix of the composites was ZrB_2 or a mixture of ZrB_2 and HfB_2. With the assistance of 4.5 vol%. ZrN as a sintering aid, both the compositions achieved nearly full density after hot-pressing at 1,900 °C. The microstructure was characterized by fine diboride grains (≈ 3 μm average size) and SiC particles dispersed uniformly. Limited amounts of secondary phases like MO_2 and M(C,N), $M =$ Zr or Zr/Hf, were found. The thermo-mechanical data of both the materials offered a promising combination of properties: about 16 GPa of micro-hardness, 5 MPa$\sqrt{m}$ of fracture toughness and Young's moduli exceeding 470 GPa. The ZrB_2–SiC composite showed values of strength in air of 635 ± 60 and 175 ± 15 MPa at 25 and 1,500 °C, respectively. Likewise, the ($ZrB_2 + HfB_2$)–SiC composite exhibited values of strength in air of 590 ± 25 and 190 ± 20 MPa at 25 and 1,500 °C, respectively. The composites also displayed good tolerance of conditions of repeated short exposures, 10 minutes each, at 1,700 °C in stagnant air. In such oxidizing conditions, the resistance to oxidation was provided by the formation of a protective silica-based glass coating, the primary oxidation product of SiC. Such a coating encapsulated the specimen coherently, and provided protection to the faces exposed to the hot atmosphere.

Keywords: ZrB_2; HfB_2; Hot-pressing; Microstructure; Mechanical properties; Oxidation resistance

1. Introduction

Ultra-high-temperature ceramics (UHTCs) include some refractory metal diborides that were historically studied and developed since the 1970s [1]. In recent years, interest has been renewed in ZrB_2 and HfB_2. Their striking thermo-chemical stability in terms of extremely high melting point, resistance to ablation/oxidation at high temperatures and thermal-shock resistance represent key requirements applicable to thermal protection systems for re-entry space vehicles with sharp leading-edge profiles [2–4].

The relatively early stage of development of massive UHTCs means they have often exhibited deficiencies in strength and thermal shock resistance, which have been attributed to an inappropriate control over the manufacturing steps like the powder processing or the pressure-assisted sintering cycles.

Composites made of ZrB_2–SiC and HfB_2–SiC are currently considered the baseline UHTCs. Indeed, varying the starting composition by changing the SiC content has given added flexibility in optimizing specific microstructural designs: adjusting the SiC content in ZrB_2 and HfB_2 matrices, for instance, has proven beneficial for oxidation and ablation resistance, without being detrimental to high-temperature stability [4–6].

The intentional introduction of some nitrides as additives, Si_3N_4 [7,8] or HfN [9] for instance, has consistently enhanced the intrinsically poor sinterability of strongly covalent metal-diboride-SiC powder mixtures. This design variant has permitted a reduction of densification temperatures to around 1,900 °C. In this way, a more control over the development of the desired microstructures was realized.

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The objective of the present study is to report on the fabrication of ZrB_2- and $ZrB_2 + HfB_2$-based ceramics containing 4.5 vol%. ZrN as sintering aid and up to 15 vol%. ultra-fine SiC particles. Densification behaviour during hot-pressing, microstructural evolution and some thermo-mechanical properties are investigated and discussed.

2. Experimental procedure

2.1. Processing

Two mixtures from commercially available powders (vol%.)

$$ZrB_2 + 15\alpha\text{-SiC} + 4.5ZrN, \quad \text{(ZSZ)}$$

$$ZrB_2 + 35HfB_2 + 10\alpha\text{-SiC} + 4.5ZrN, \quad \text{(ZHSZ)}$$

were ball-milled for 1 day in a polyethylene bottle using absolute ethanol and zirconia balls, dried with a rotating evaporator under a continuous stream of nitrogen, and sieved (250 μm mesh size). For ease of describing the two compositions mentioned above, they will be referred to as (ZSZ) and (ZHSZ), respectively. Table 1 shows some characteristics of the raw powders. The ultra-fine α-SiC fraction was dispersed ultrasonically in absolute ethanol before pouring it into the mixtures described above.

The as-homogenized (ZSZ) and (ZHSZ) powder mixtures were hot-pressed at low vacuum (0.5 mbar) using a BN-lined induction-heated graphite mould. The external pressure along the non-isothermal and the isothermal stage during hot-pressing was 40 and 50 MPa, respectively. The linear shrinkage of the green pellets was recorded by measuring the displacement of the rams. The highest sintering temperature during the hot-press runs, measured with a pyrometer focused on the graphite mould, was 1,900 °C for both the mixtures. The holding times for (ZSZ) and (ZHSZ) were 5 and 20 minutes, respectively.

Table 1
Characteristics of the starting raw powders (producers datasheets): granulometric size distribution (D_{90}), specific surface area (s.s.a.)

Phase (symmetry)	Producer	Grade	Size		Impurity (wt%)
			D_{90} (μm)	s.s.a. (m^2/g)	
ZrB_2 (hexagonal)	H.C. Starck, Germany	B	4–6		O 2, Hf 0.2
HfB_2 (hexagonal)	Cerac Inc., USA	325 mesh	–	1.72[a]	Zr 0.4
α-SiC (hexagonal 6H)	H.C. Starck, Germany	UF25	0.8	23–26	O 2.5
ZrN (cubic)	H.C. Starck, Germany	A	13–21	–	Hf 0.2

[a] μm: Fisher size (APS).

2.2. Characterization

The bulk density was measured using Archimedes method. The phase composition was analyzed with an X-ray diffractometer (XRD, Ni-filtered CuKα radiation, mod. D500, Siemens, Germany) and a scanning electron microscope (SEM, mod. S360, Leica Cambridge, UK) equipped with an energy dispersive microanalyzer (EDX, mod. INCA Energy 300, Oxford Instruments, UK). The specimen surfaces were imaged by SEM using secondary electrons (SEs), and did not require a conductive coating. Polished sections of the hot-pressed materials were prepared using diamond abrasives. Thermo-chemical calculations were executed using the HSC software package [10].

The Young's modulus (E) and Poisson's ratio (ν) were measured on a 28.0 × 8.0 × 0.8 mm^3 plate using the resonance frequency method in bending. Micro-hardness (Hv1.0) was evaluated by a Vickers indenter, using a 9.81 N applied load for 15 s. Flexural strength (σ) in a 4-pt. configuration was tested in ambient air at room temperature (5 specimens tested) and 1,500 °C (3 specimens tested) on 25.0 × 2.5 × 2.0 mm^3 chamfered bars using 20 mm and 10 mm as outer and inner span, respectively, and a cross-head speed of 0.5 mm/min. Fracture toughness (K_{Ic}) was measured through the chevron-notched beam method (5 specimens tested) using a 25.0 × 2.5 × 2.0 mm^3 bar on the same jig used for the flexural strength (cross-head speed 0.05 mm/min). The thermal expansion behaviour was tested up to 1,300 °C in a stream of Argon (5 °C/min heating rate).

The composites were oxidized at 1,700 °C in stagnant air, iterating three exposures of 10 minutes each using a bottom-loading box furnace. Test coupons of dimensions 12.0 × 2.5 × 2.0 mm^3 were cleaned in boiling acetone, dried at 80 °C overnight, and then placed upon SiC supports with minimal contact area. Once the specimen had been slotted into the hot chamber, the furnace temperature of 1,700 °C was reached within 2 minutes. Mass and dimensional changes of the specimens before and after repeated exposures were evaluated. The microstructural damage inside the oxidized specimens, evaluated observing their relative polished cross-sections by SEM-EDX, was utilized as an empirical indicator of the resistance to oxidation.

3. Results

3.1. Densification behaviour and microstructural evolution

Table 2 shows some microstructural attributes of the hot-pressed composites. The bulk densities of (ZSZ) and (ZHSZ) were 5.66 and 7.55 g/cm^3, respectively. The SEM observation of polished sections provided evidence of residual porosity of about 1% and less than 0.5% in (ZSZ) and (ZHSZ), respectively.

Fig. 1 plots the densification curves during hot-pressing. The temperature T_{ON} was associated to the onset of the ex-