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High-Strength Zirconium Diboride-Based Ceramics

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Zirconium diboride (ZrB_2) and ZrB_2 ceramics containing 10, 20, and 30 vol% SiC particulates were prepared from commercially available powders by hot pressing. Four-point bend strength, fracture toughness, elastic modulus, and hardness were measured. Modulus and hardness did not vary significantly with SiC content. In contrast, strength and toughness increased as SiC content increased. Strength increased from 565 MPa for ZrB_2 to >1000 MPa for samples containing 20 or 30 vol% SiC. The increase in strength was attributed to a decrease in grain size and the presence of WC.

I. Introduction

ULTRA-HIGH-TEMPERATURE CERAMICS (UHTCs) can be defined as ceramic materials with melting points >3000°C.[1,2] Compounds considered UHTCs include ZrB_2, ZrC, HfB_2, HfC, and TaC. Because of their high melting points, oxidation resistance, and chemical attack resistance, UHTCs have been investigated for applications that include thermal protection materials for advanced reentry vehicles, molten-metal crucibles, and high-temperature electrodes.[3–6] The strong covalent bonding in non-oxide UHTCs gives them high melting temperatures, but makes them difficult to densify.[7] As a result, UHTCs are usually consolidated by hot pressing.[8,9] Metals or other additives are often intentionally incorporated to control microstructure and decrease the temperature required to achieve full density.[10,11] The impurities concentrate in the grain boundaries and decrease the high-temperature strength. Alternative processing routes, such as reactive hot pressing, self-propagating high-temperature synthesis, and polymer precursors have been investigated to improve the purity and densification behavior of UHTCs.[12–14]

From the larger family of UHTCs, refractory metal diborides have been identified as candidates for ultra-high-temperature aerospace applications.[4] In particular, ZrB_2-based ceramics have been investigated because of a unique combination of thermal shock resistance, strength at high temperature, and low density.[15,16] Previous investigations have demonstrated that SiC particulate additions increase the oxidation resistance of ZrB_2 by promoting the formation of silicate-based glasses that inhibit oxidation at temperatures between 800° and 1700°C.[17–20] Some reported properties of ZrB_2 and ZrB_2–SiC materials are summarized in Table I.

The purpose of this communication is to report on the processing method and an initial investigation of the microstructure and room-temperature mechanical properties of ZrB_2-based UHTCs.

II. Experimental Procedure

(1) Processing

Commercially available precursor powders were used in this study. The ZrB_2 powder (Grade B, H.C. Starck, Newton, MA) had a purity of >99% (metals basis) and a particle size of 2 μm. The SiC powder (Grade UF-10, H.C. Starck) was predominantly α-SiC, and it had a reported purity of 98.5% and a particle size of 0.7 μm. After they were batched, the powders were attrition milled (Model 01-HD, Union Process, Akron, OH) in hexane at 600 rpm for 2 h in a Teflon-coated tank, using cobalt-bonded WC media and a cobalt-bonded WC spindle. To minimize segregation by sedimentation during drying, solvent removal was performed using rotary evaporation (Model Rotavapor R-124, Buchi, Flawil, Germany) at a temperature of 70°C, a vacuum of 200 mm Hg (~27 kPa), and a rotation speed of 150 rpm.

Milled powders were hot-pressed (Model HP-3060, Thermal Technology, Santa Rosa, CA) in graphite dies lined with graphite foil and coated with BN. Above ~800°C, the temperature of the graphite die was monitored using an infrared thermometer (Model OS 3708, Omega Engineering, Stamford, CT). Powder compacts were heated under vacuum (~130 mtorr (~17 Pa)) to 1650°C with an average heating rate of ~5°C/min. After the hot press was held at 1650°C for 1 h, it was backfilled with argon and heated at ~17°C/min to 1900°C. When the die temperature reached 1900°C, a uniaxial load of 32 MPa was applied. After 45 min, the hot press was cooled at ~20°C/min to room temperature. The load was removed when the die temperature dropped below 1750°C. A minimum of two and a maximum of four billets were prepared for each nominal powder composition.

(2) Characterization

To account for an unknown amount of WC contamination from milling and loss of volatile species during hot pressing, the true density of each hot-pressed sample was determined using helium pycnometry (Model 1305 Multivolume, Micromeretics Instrument

Table I. Reported Properties of ZrB_2 and ZrB_2–SiC Ceramics

Material	Flexure strength at room temperature (MPa)	Reference
ZrB_2	275–480	1, 7
ZrB_2–20 vol% SiC	350	15
ZrB_2–25 vol% SiC	506	12
ZrB_2–20 vol% SiC	408	19
ZrB_2–20 vol% SiC–4 vol% Si_3N_4	730	11

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Corp., Norcross, GA). Hot-pressed samples were ground to −325 mesh (<44 μm) using a high-purity Al_2O_3 mortar and pestle to expose as much closed porosity as possible. The density measured using pycnometry was compared with the density predicted from the nominal ZrB_2 and SiC content as well as the bulk density of the hot-pressed billets determined using the Archimedes technique with water as the immersing medium. The microstructure of the samples was examined using scanning electron microscopy (SEM; Model S570, Hitachi, Tokyo, Japan). Chemical analysis was performed simultaneously with SEM using energy dispersive spectroscopy (EDS; Model AAT, X-ray Optics, Gainsville, FL). Samples were prepared for microscopy by cutting cross sections parallel to the hot-pressing direction and then polishing to 0.25 μm using diamond abrasives. Grain sizes were estimated using the lineal intercept method[21] by counting a minimum of 120 grains. Sample compositions were estimated by analyzing SEM images (NIH Image) and assuming that area and volume fractions were equivalent.

(3) Mechanical Testing

Hardness of the samples was determined using Vickers indentation (Model V-1000-A2, Leco, St. Joseph, MI) using a load of 1 kg and a dwell time of 15 s. Reported values were obtained from an average of 15 indentations. Elastic constants were measured according to ASTM Standard C1259−01 ("Standard Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio for Advanced Ceramics by Impulse Excitation of Vibration," *ASTM Book of Standards*, ASTM International, West Conshohocken, PA) for impulse excitation (Model MK4-I Grindosonic, J. W. Lemmens, St. Louis, MO). At least 10 measurements were averaged to obtain the reported value. Flexure strengths were measured in four-point bending using a fully articulated test fixture according to ASTM Standard C1161−02a ("Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature") for type-A bars (25 mm × 2 mm × 1.5 mm). A total of six ZrB_2, nine ZrB_2–10% SiC, eleven ZrB_2–20% SiC, and sixteen ZrB_2–30% SiC bars were fractured to determine the reported averages and standard deviations. Finally, fracture toughness was determined by fracturing five samples for each composition in four-point bending after Vickers indentation.[22] A load of 20 kg was used to produce radial–median cracks before bend testing.

III. Results

The measured densities of the hot-pressed ZrB_2–SiC billets ranged from 6.27 g/cm^3 for ZrB_2 to 5.43 g/cm^3 for ZrB_2 containing 30 vol% SiC (Table II). With the exception of the sample containing 10 vol% SiC, the densities determined using the Archimedes method were greater than the densities predicted from nominal (ZrB_2 plus SiC) compositions. True densities determined using helium pycnometry were ~3%–4% greater than densities calculated from nominal compositions. Analysis using SEM/EDS (Fig. 1) and X-ray diffractometry (XRD) (not shown) revealed the presence of WC, which was presumably incorporated during milling. Because of its high density (~15.0 g/cm^3 for WC with 6% cobalt), contamination from the WC milling media increased the true density of the hot-pressed billets. The amount of WC introduced into the samples varied from batch to batch; therefore, the WC content was estimated by comparing the predicted density with the density measured using helium pycnometry for each composition. By comparing predicted density with pycnometry density, WC volume fractions of 1.9, 1.4, 2.3, and 2.2 vol% were calculated for ZrB_2 containing 0, 10, 20, and 30 vol% SiC, respectively. Analysis of SEM images confirmed WC contents of ~2 vol% for each composition. When a combination of density measurements and SEM analysis was used, no indication of open or closed porosity was found in ZrB_2 or billets containing 20 or 30 vol% SiC (i.e., relative density >99%, saturated weight approximately equal to dry weight, and no porosity observed). However, billets containing 10 vol% SiC consistently had a relative density of ~93%.

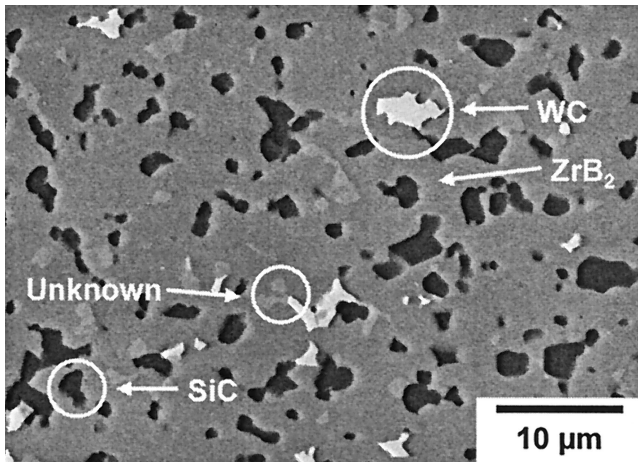

Fig. 1. Polished cross section of ZrB_2 containing 20 vol% SiC particulates.

Analysis using SEM/EDS also revealed the presence of an unknown phase in addition to ZrB_2, SiC, and WC (Fig. 1). Chemical analysis using EDS indicated that the phase contained tungsten and zirconium (no silicon or cobalt), but the phase could not be positively identified using EDS or XRD analysis. Beyond the expected ZrB_2, SiC, and WC peaks, two extra peaks were observed in XRD patterns collected from hot-pressed billets (not shown). The extra peaks could not be indexed to SiC polytypes, ZrC, W–B phases, or Co–B phases. A previous investigation of phase equilibria in the Zr-B-W system noted the possible existence of a ternary phase, but neither the composition nor the structure was identified.[23] The phase also could have been a solid solution of tungsten in ZrB_2, as has been observed in the Ti-B-W system.[24] Work is underway to isolate and identify this compound. Analysis of SEM images showed that hot-pressed billets contained ~9 vol% of the unknown phase.

Measured Young's modulus values varied <10% over the range of SiC contents (Table III). Measured moduli were consistent with the reported values for ZrB_2 (500 GPa)[1] and SiC (475 GPa).[2] The decrease in modulus for the material containing 10 vol% SiC was attributed to the presence of ~7 vol% porosity. Similar to modulus, hardness did not vary significantly with SiC content and was ~24 GPa for all compositions. In contrast to modulus and hardness, strength and toughness increased as SiC content increased. The measured fracture toughness increased with SiC content from 3.5 MPa·m$^{1/2}$ for ZrB_2 to 5.3 MPa·m$^{1/2}$ for ZrB_2–

Table II. Predicted, True, Measured, and Relative Density of Hot-Pressed ZrB_2–SiC Ceramics

SiC content (vol%)	Predicted density (g/cm^3)	True density (g/cm^3)	Measured density (g/cm^3)	Relative density (%)
0	6.09	6.27	6.26	99.8
10	5.80	5.94	5.54	93.2
20	5.51	5.74	5.72	99.7
30	5.23	5.46	5.43	99.4

Table III. Room-Temperature Mechanical Properties of ZrB_2–SiC Ceramics

SiC content (vol%)	Modulus (GPa)	Hardness (GPa)	Strength (MPa)	Toughness (MPa·m$^{1/2}$)
0	489	23 ± 0.9	565 ± 53	3.5 ± 0.3
10	450	24 ± 0.9	713 ± 48	4.1 ± 0.3
20	466	24 ± 2.8	1003 ± 94	4.4 ± 0.2
30	484	24 ± 0.7	1089 ± 152	5.3 ± 0.5

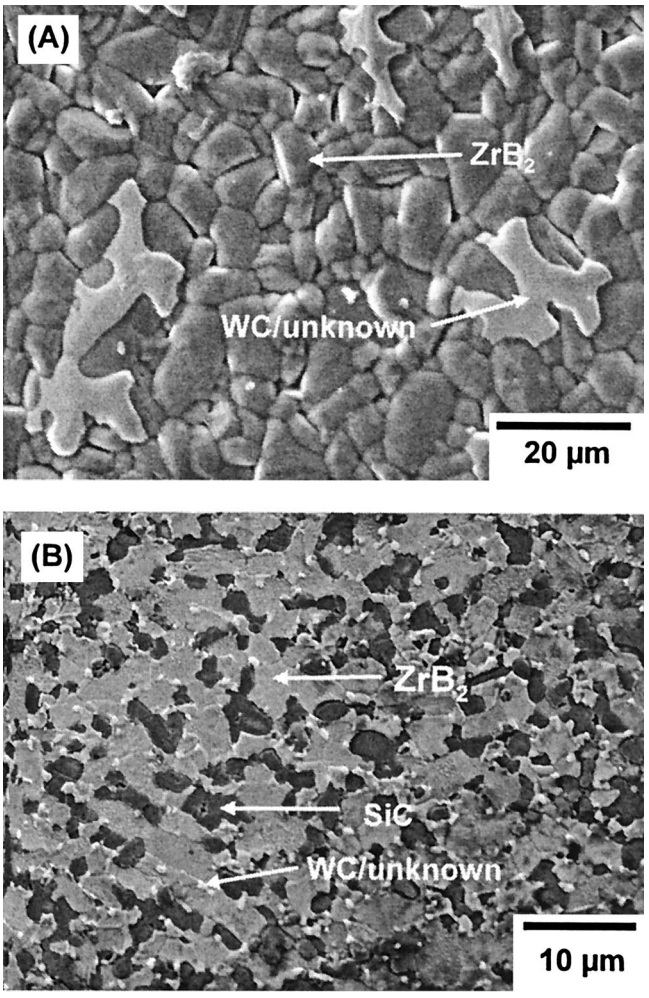

Fig. 2. Thermally etched cross sections of (A) ZrB_2 and (B) ZrB_2–30% SiC that show an average grain size of ~6 μm for ZrB_2 and ~3 μm for ZrB_2 containing SiC particulate additions.

30% SiC. Of particular note was the strength of the ZrB_2-based ceramics. An average strength of 565 MPa was measured for ZrB_2, which was significantly higher than strengths reported for phase-pure ZrB_2.[1,7] Strength increased to >1000 MPa for ZrB_2 containing 20 or 30 vol% SiC. The improvement in strength was attributed to a combination of a decrease in average grain size and the presence of WC. Analysis of polished, thermally etched cross sections (Fig. 2) showed that the grain size decreased from ~6 μm for ZrB_2 to ~3 μm for ZrB_2–SiC materials. Other investigators also have reported that SiC acts as a grain-growth inhibitor in TiB_2 and ZrB_2.[7] Furthermore, strengths approaching 1000 MPa were observed in TiB_2 samples to which W_2B_5 was added.[24] The increased TiB_2 strength was attributed to the formation of a $(Ti,W)B_2$ solid-solution phase, which was thought to enhance strength because of the development of favorable residual stresses.[24] The unidentified phase observed in the present materials may have a similar effect.

IV. Summary

Billets of ZrB_2 and ZrB_2 containing SiC particulate additions of 10, 20, and 30 vol% were produced using hot pressing of commercial powders. Powders were attrition milled with WC media, which led to the incorporation of ~2 vol% WC. Analysis by SEM revealed that SiC inclusions were dispersed uniformly in the ZrB_2 matrix and that the average grain size decreased from ~6 μm for ZrB_2 to ~3 μm for compositions containing SiC. The addition of SiC also resulted in a significant increase in the strength (to ~1000 MPa) compared with pure ZrB_2 (565 MPa). The increased strength was attributed to the decreased grain size and the presence of WC, which may have reacted with ZrB_2 to form a ternary Zr-B-W phase.

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