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Processing, microstructure, and mechanical properties of large-grained zirconium diboride ceramics

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ABSTRACT

Zirconium diboride ceramics produced using commercial ZrB_2 powders, and milled with zirconium diboride grinding media, were fabricated by hot-pressing at temperatures of 2100–2200 °C with hold times of 30–120 min. This ZrB_2 exhibits no additional impurities typically introduced by milling with grinding media of differing composition. Microstructure analysis revealed grain sizes ranging from ~25 to ~50 μm along with ~3 vol% porosity. Flexure strength ranged from 335 to 400 MPa, elastic modulus from 490 to 510 GPa, fracture toughness from 2.7 to 3.2 MPa $m^{½}$, and hardness from 13.0 to 14.4 GPa. Strength limiting flaws were identified as surface grain pullout induced by machining. Elastic modulus and hardness were found to increase with decreasing porosity. Compared to the fine grained ceramics typically reported, large grain zirconium diboride ceramics exhibit higher than expected room temperature strengths.

1. Introduction

Zirconium diboride (ZrB_2) is an ultra-high temperature ceramic (UHTC), a family of compounds characterized by melting points of 3000 °C or higher.[1,2] Properties such as high strength (565 MPa), hardness (23 GPa), thermal conductivity (60–125 W m^{-1} K^{-1}) and corrosion resistance have generated interest in the ZrB_2 system [2–4]. As a result, borides are candidates for applications including molten metal crucibles, electrodes, microelectronics, cutting tools, nuclear cladding and hypersonic aerospace vehicles [2,5–7]. These proposed applications for ZrB_2 require fully dense and relatively pure materials, which have been difficult to fabricate given factors inherent to this material system.

The processing and mechanical properties of ZrB_2 ceramics have been widely reported [2,8–10]. However, studies investigating the processing and properties of ZrB_2 have relied upon comminution of starting powders using grinding media typically comprised of tungsten carbide (WC), silicon nitride (Si_3N_4), silicon carbide (SiC), zirconium oxide (ZrO_2), or aluminum oxide (Al_2O_3) [8,11]. This poses a significant hurdle to the production of high purity ZrB_2 as the grinding media introduces impurities through wear and erosion during milling of this hard material. Numerous studies have investigated the effects of incorporated impurities on ZrB_2, typically showing benefits to densification and room temperature properties. Unfortunately, many of these impurities produce deleterious effects at proposed use temperatures (i.e., above 2000 °C) due to formation of liquid phases at these high temperatures [8,9]. Comminution with media of the same, or nearly the same, composition as the starting powder would eliminate the source of contamination and allow for the production of higher purity ZrB_2.

Studies of the mechanical properties of ZrB_2 have typically focused on the production of fine grain materials, with the goal being to maximize room temperature strength. Many papers are focused on ZrB_2 ceramics of 10 μm or less, with relatively few reporting grain sizes between 10 μm and 20 μm or of 20 μm or more. Monolithic ZrB_2 ceramics produced by various sintering methods with different sintering additives have demonstrated strengths ranging from as high as about 600 MPa for grain sizes of ~4 μm to ~350 MPa for grain sizes 10 μm [9]. ZrB_2 ceramics with grain sizes of approximately 20 μm have reported strengths in the range of 300–400 MPa, but strengths decrease to ~250 MPa for a grain size of ~40 μm. Further, ZrB_2 without sintering aids typically exhibits strengths between 300 MPa and 500 MPa, while ZrB_2 ceramics with sintering aids have higher strengths, which are usually between 400 MPa and 630 MPa. In addition to intentional sintering additives, impurities from grinding media contamination can have a significant influence on strength. For example, Chamberlain et al. produced ZrB_2 by attrition milling with WC media (~4 vol% contamination), which resulted in a strength of 565 MPa for ceramics with a grain size of 6 μm [12]. Those ceramics reached full density after hot pressing at ~1900 °C and had a hardness of 23 GPa and fracture toughness of 3.5 MPa $m^{½}$. Guo et al. produced

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ZrB_2 ceramics with a grain size of ~6 μm by ball milling with SiC media and hot-pressing at 2000 °C [13]. Those ceramics had a strength of 460 MPa, hardness of 16 MPa, and fracture toughness of 4.8 MPa $m^{½}$. Neuman et al. fabricated ZrB_2 ceramics with a grain size of ~20 μm by adding 0.5 wt% carbon and ball milling with WC media (0.21 wt% contamination) [14]. Those ceramics reached nearly full density by hot-pressing at 2150 °C for 1 h and had a strength of 380 MPa, hardness of 14 MPa, and fracture toughness of 2.9 MPa $m^{½}$. Thompson et al. reported ZrB_2 ceramics that were densified by pressureless sintering [15]. The powder was comminuted by attrition milling with WC media and had a carbon addition of 1.75 wt%, which produced ceramics a strength of 300 MPa for a ZrB_2 grain size of 32 μm.

For applications at elevated temperatures, fine grained materials may not be desirable due to their increased propensity for creep compared to ceramics with larger grain sizes [16]. Creep rates were studied as a function of grain size by Rhodes et al. for ZrB_2 ceramics that had been hot pressed to 98% relative density and then held at the final densification temperature to produce ZrB_2 grains sizes in excess of 8 μm on average [17]. Creep rates were measured at 2000 °C under a load of 120 MPa and reported to be approximately $4.1 \times 10^{-5}\ s^{-1}$ for a grain size of ~8 μm, $1.2 \times 10^{-5}\ s^{-1}$ for grain sizes between 18 μm and 23 μm, and $4.5 \times 10^{-6}\ s^{-1}$ for grain sizes of ~40–60 μm. The corresponding room temperature flexure strengths were approximately 330 MPa, 300–340 MPa, and 240–260 MPa, respectively. The ZrB_2 powder used in these studies had relatively high impurity levels (up to 0.5 wt% C and 1.5 wt% O after hot-pressing) compared to more recent reports of ZrB_2 ceramics [12–15,18]. Additionally, Rhodes materials would be expected to contain WC contamination from comminution of the coarse raw powders, though specific amounts of contamination from milling were not reported.

The objective of the present study was to investigate the microstructure and room-temperature mechanical properties of hot-pressed ZrB_2 ceramics produced without sintering aids or contamination from common oxide or carbide based grinding media. The effect of processing condition on microstructure and properties were characterized.

2. Experimental procedure

2.1. Processing

This study used commercially available ZrB_2 powder (Grade B, H.C. Starck, Newton, MA) with a reported purity of 98.2% and an average particle size of 2 μm, and a reported Hf impurity of 1.9 wt%. The ZrB_2 powder was ball milled with ZrB_2 grinding media[2] in hexanes. After ball milling for 48 h, the slurry was dried by rotary evaporation (Rotavapor R-124, Buchi, Flawil, Germany) at a temperature of 60 °C, under low vacuum (~27 kPa), and at a rotation speed of 60 rpm. Grinding media were weighed before and after milling to estimate contamination. The dried powder was lightly ground and passed through a 50 mesh screen prior to hot pressing.

Milled powders were hot-pressed (Model HP20-3060-20, Thermal Technology, Santa Rosa, CA) in 44.5 mm circular graphite dies lined with BN coated graphite foil. Powders were cold compacted at ~2 MPa and then heated under at 20 °C/min under vacuum (~15 Pa) to 1450 °C. The powders were held for two hours at 1450 °C and then heated at 20 °C/min to 1650 °C. The furnace was held for one hour at 1650 °C and then backfilled with UHP-He and a uniaxial load of 32 MPa was applied. As reported previously, the isothermal holds were used to remove surface oxides from the powder particles [19,20]. The furnace was then heated at ~50 °C/min to 2100, 2150, or 2200 °C. After holding at the peak temperature for 30, 60, or 120 min, the furnace was cooled at ~40 °C/min. The load was removed when the die temperature dropped below 1600 °C. Specimen designation is "hot-pressing temperature-hot-pressing time", e.g. 210-6 represents hot pressing at 2100 °C with a hold time of 60 min.

During hot-pressing, the change in thickness of the specimens was measured in-situ using a linearly variable differential transducer (LVDT) attached to the hot-press rams. The effect of linear thermal expansion of the rams and load train during heating to process temperatures on the calculated densities was corrected using the coefficient of thermal expansion calculated from ram displacement during cool down from the process temperature. Time-dependent density values were calculated using Eq. (1):

$$\rho_i = \rho_f\left(1 + \frac{L_i - \alpha_{HP}\left(T_f - T_i\right)}{L_f}\right) \tag{1}$$

where L_f is the final length, L_i is the change in length at time i, α_{HP} is the measured CTE of the hot-press load train, T_f is the maximum furnace temperature, T_i is the furnace temperature at time i, and ρ_f is the final density. The instantaneous densification rate was calculated using a step-wise numerical process from the measured ram displacement [Eq. (2)]:

$$\dot{\rho}_i = \frac{1}{\rho_i}\frac{\left(\rho_i - \rho_{i-1}\right)}{\left(t_i - t_{i-1}\right)} \tag{2}$$

where ρ_i is the relative density at time i, and t_i is time i. The calculated instantaneous densification rate was smoothed using 10 point weighted adjacent averaging with repeated boundary condition (OriginPro 9.1, OriginLab Corp., Northampton, MA).

2.2. Characterization

Bulk density of hot pressed specimens was measured by Archimedes' method using distilled water as the immersing medium according to ASTM C373. Relative density was calculated by dividing the Archimedes' density by the density predicted from the nominal ZrB_2, and milling media contents. Microstructures were examined using scanning electron microscopy (SEM; Helios NanoLab 600, FEI, Hillsboro, OR) with simultaneous chemical analysis by energy dispersive spectroscopy (EDS; Oxford Instruments, Abingdon, UK). Specimens were prepared for microscopy by cutting cross sections perpendicular to the hot-pressing direction and polishing to a 0.25 μm finish using successively finer diamond abrasives. The ZrB_2 was etched using molten 2:1 KOH:H_2O in a nickel crucible at ~200 °C for ~1 s. Grain sizes were determined from SEM images using image analysis software (Photoshop CS5, Adobe Systems, San Jose, CA and ImageJ, National Institutes of Health, Bethesda, MD) by measuring the equivalent area diameter (EAD), fitted ellipse, and Ferets diameter of at least 500 grains. X-ray diffraction (XRD; X'Pert Pro, PANalytical, Almelo, Netherlands) analysis was used for phase identification using coarsely crushed material.

Grain growth kinetics were described using a general form of the grain growth model [Eq. (3)] [21]:

$$G^n = G_0^n + kt \tag{3}$$

where G_0 is the initial grain size at time zero, G is the grain size at time t, K is the grain growth constant, and n is the growth exponent. For this study, the initial grain size was neglected by

[2] Fabricated using ZrB_2 with additions of 1 wt% B_4C and 1 wt% C (phenolic source), ball milled with WC-6Co (~1 wt% added to powder through erosion). Uniaxially pressed into cylinders (0.5 in D × 0.5 in H), cold isostatically pressed, then pressurelessly sintered at 2050 °C for 90 min in flowing Ar/H_2.