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High-energy Ball-milling of ZrB_2 and HfB_2 Powders: Effect on Particle Size and Crystalline Grain Distribution*

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Introduction: Ultra-High-Temperature Ceramics (UHTCs) such as ZrB_2 and HfB_2 with incorporation of SiC are being considered as structural materials for applications in propulsion and thermal protection systems such as turbine-engine hot section components, leading edge of hypersonic vehicles, where extremely high heat fluxes generate very high temperatures and steep temperature gradients [1]. We used high energy ball milling of the precursor powders to increase lattice distortion enhanced inter-diffusion, uniform distribution of SiC, and reduce grain growth during Spark plasma sintering (SPS). Here, we study the effect of high energy ball milling of ZrB_2 or HfB_2 with 20 vol% SiC on the particle size and crystalline-grain distribution.

Experimental: Coarse (250-650 nm) precursor powders (99.9% purity) ZrB_2 (240 nm), HfB_2 (600 nm) and SiC (640 nm – wide size distribution) were obtained from Electronic Space Products International (ESPI), Ashland, Oregon. The powders of ZrB_2 or HfB_2 and 20 vol% SiC were mixed with about 1/3 weight SiC balls of 10 mm dia. in a stainless steel container with a 2 mm inner layer coating of silicone based polymer. The mixing is performed in a glow box with Argon inert gas and sealed the container for high-energy planetary ball milling. The particle size distribution and crystalline grain distribution are examined after 24 hrs and 48 hrs of ball milling using Dynamic Light Scattering Technique and x-ray diffraction (XRD), respectively.

Results and discussion:

a) High-energy ball milling of MB_2 (M = Zr or Hf) and SiC powders – effect on particle size distribution: Dynamic Light Scattering Technique is used to obtain the particle size distribution after 24 hrs and 48 hrs of high energy ball milling. Unlike ZrB_2 and HfB_2 particles, SiC particles did not disperse in the solution to measure particle size. So, even though MB_2 and SiC powder mixers were ball milled, in all cases the particle distribution is for HfB_2 and ZrB_2 particles only.

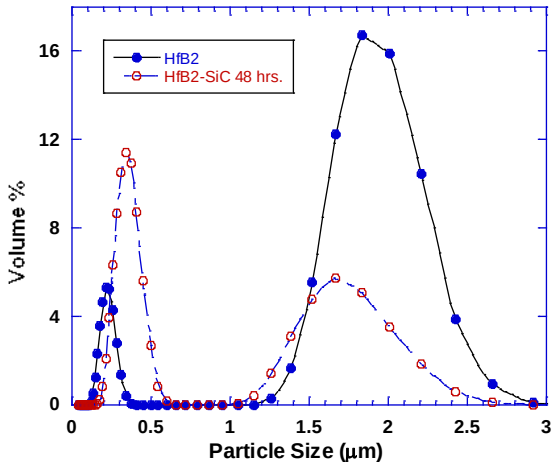

Figure 1: Particle size distribution of HfB_2 powders as supplied and after 48 hrs high energy ball milling.

Figure 1 shows the particle distribution of as supplied and 48 hrs high energy ball milled HfB_2 powders. The particle distribution shows bi-model distribution. Upon ball milling the larger size particles decreased and smaller size particles increased indicating some break down of larger particles due to high energy ball milling. Table 1 summarizes the size distribution of as supplied, 24 hrs, and 48 hrs high energy ball milled HfB_2 powders. The average size of particles decreased from 1.39 µm to 0.75 µm due to high energy ball milling. The large particle volume% decreased from 66% to 27% due to ball milling with corresponding increase in small particle volume%.

Table 1: Particle size distribution of HfB_2

BM time (hrs)	Avg. size (μm)	Small (Vol%)	Large (Vol%)
0	1.39	33.71	66.29
24	0.89	62.80	37.20
48	0.75	72.60	27.10

Table 2: Particle size distribution of ZrB_2

BM time (hrs)	Avg. size (μm)	Small (Vol%)	Large (Vol%)
0	0.73	73.59	26.41
24	0.61	83.15	16.85
48	0.63	72.90	27.10

Similar trend is seen for ZrB_2 particle distribution as summarized in Table 2. But the effect is much smaller compared to HfB_2 powders indicating less breakdown of ZrB_2 particle due to ball milling, indicating HfB_2 powders are more brittle compared to ZrB_2 powders.

b) Figure 2 shows the XRD peaks for ZrB_2 and HfB_2 for the powders as-supplied, 24 hrs, and 48 hrs high energy ball milled.

Table 3: XRD Av. crystalline grain size

Sample	Θ_B (degree)	Crystal grain size (nm)
ZrB_2	20.943	85
ZrB_2 24 hrs BM	20.938	39.1
ZrB_2 48 hrs BM	20.928	32.8
HfB_2	12.93	102
HfB_2 24 hrs BM	12.893	56.6
HfB_2 48 hrs BM	12.891	42

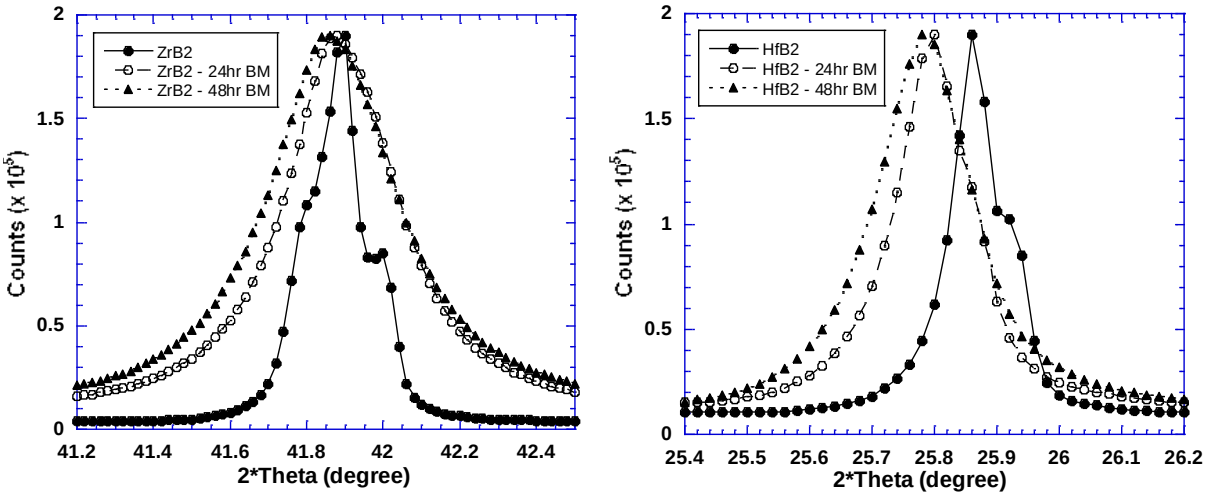

Figure 2: XRD peaks for ZrB_2 and HfB_2 as-supplied, 24 hrs and 48 hrs high energy ball milled powders

Figure 2 shows that the XRD peaks shift lower 2Θ angle and broadens as the ball milling time increases. Peak shift to lower angle indicates crystal lattice distortion to increase the lattice parameter and the broadening of the peak indicates the crystalline grain size decreases as a result of either breaking-up of larger particles to smaller ones as shown by the light scattering results (Table-1) or decrease in crystalline region as the high level lattice distortion changes some crystalline part to amorphous. The as supplied powder peaks show an overlap of three (for ZrB_2) or two (for HfB_2) peaks. We resolved these peaks and used the highest intensity peak to estimate the crystalline grain size using Sherrer's equation. Table 3 summarizes the crystal grain size variations with different levels of high energy ball milling. For both ZrB_2 and HfB_2 powders decreasing crystallinity with increasing ball milling time is evident.

Ref. [1] W. G. Fahrenholtz, et al, J. Am. Ceram. Soc. 90 (2007) 1347-1364.

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