

Fabrication of UHTCs by Conversion of Dynamically Consolidated Zr+B and Hf+B Powder Mixtures

Mathieu Brochu,^{†,‡} Bryan Gauntt,[§] Tony Zimmerly,[¶] Alicia Ayala,[§] and Ronald Loehman[§]

[‡]Mining, Metals and Materials Engineering Department, McGill University, 3610 University Street, Montreal, Quebec, Canada H3A 2B2

[§]Advanced Materials Laboratory, Sandia National Laboratories, 1001 University SE, Albuquerque, New Mexico, 87106

[¶]Energetic Materials Research and Testing Center, New Mexico Tech, 1001 South Road, Socorro, New Mexico, 87801

Mixtures of Zr+B and Hf+B were shock compacted into bulk samples possessing relative densities above 95.5% and were subsequently converted to ZrB₂ and HfB₂ ceramic components by a heat treatment. The conversion temperature was varied between 1600° and 2000°C. The conversion temperature was found to have no effect on the final density of the ceramics. Theoretical densities of 72% and 62% were obtained for the converted ZrB₂ and HfB₂ ceramics, respectively. Increasing the heat-treatment temperature promoted grain growth rather than densification for the ZrB₂ samples. The grain size increased from 1.8 ± 0.6 to 5.6 ± 1.3 to 8.5 ± 3.3 µm, for heat treatments at 1600°, 1800°, and 2000°C, respectively. No grain growth was observed for the HfB₂ system, which exhibited a grain structure of 5.0 \pm 1.6, 3.3 \pm 1.5, and 4.4 \pm 2.2 μ m for the same temperature range studied. Microhardness values for the ZrB₂ decreased from 19.4 ± 0.4 to 17.2 ± 0.6 down to 13.7 ± 0.6 GPa, while similar hardness results of 19.1 ± 0.8 , 17.1 ± 1.0 , and 17.8 ± 0.5 GPa were observed for the HfB₂ samples.

I. Introduction

The melting temperatures of zirconium diboride (ZrB₂) and hafnium diboride (HfB₂) above 3200° and 3500°C, respectively, and the improvements in ceramic processing have revived the interest in ultra high temperature ceramics (UHTCs) for numerous severe applications. The highly covalent nature of these ceramics results in superior mechanical properties (hardness and four-point bending strength), and thermal shock and oxidation resistance.¹⁻⁴ These properties render these ceramic systems potential candidates as thermal protection systems for hypersonic flight and atmospheric reentry, and rocket propulsion.^{5,6}

Several successful attempts at pressure-assisted densification of UHTCs are reported in the literature. In particular, processes such as hot pressing without^{4,7} and with metallic^{8,9} or ceramic/ glass additives^{10,11} allowed the fabrication of fully dense monolithic or composite ceramics. In these cases, the hot-pressing parameters were typically temperatures of 1900°C and above and applied pressures of 20–30 MPa or more. On the other hand, advances in pressureless sintering are required to fabricate near-net-shape components, which will drastically reduce subsequent needs for diamond machining. By nature, the diborides have low intrinsic sinterability, which is attributed to their highly covalent bonds and low volume and grain boundary diffusion rates.¹² Despite this difficulty, significant advances were made in the last few years in this field. Chamberlain *et al.*¹³ studied pressureless sintering of attrition-milled ZrB₂ and showed that a high sintering temperature, i.e. $T > 2150^{\circ}$ C, with a prolonged soaking time (>540 min) were necessary to obtain a 98% dense ZrB₂ ceramic from a green compact of 65% density. They also associated densification with the presence of WC impurities from milling. The properties obtained are slightly lower than for the hot-pressed sample and were attributed to their larger grain size. Mishra *et al.*^{14,15} studied pressureless sintering of ZrB₂ made from self-propagating high-temperature synthesis of ZrB₂ powders (final purity of 95%) and obtained theoretical densities of up to 94%. The high sinterability of the powder was attributed to the presence of residual ZrO₂ on the particles, which sinters at a lower temperature, as well as metallic contaminants such as Mg, Cr, and Fe, which cause liquid state sintering. Unfortunately, the presence of this eutectic phase lowers the maximum operating temperature and may render this material useless in harsh environments.

Reactive sintering is another attractive alternative to pressureless sintering of ZrB_2 powders that is readily applicable to the ZrB_2 and HfB_2 ceramic systems. The formation of ZrB_2 and HfB_2 ceramics from elemental powders is possible because the conversion reactions are thermodynamically favorable, as illustrated by Eqs. (1) and (2).³

$$\operatorname{Zr} + 2\operatorname{B} \to \operatorname{ZrB}_2 \quad \Delta G_{\mathrm{f},2000\mathrm{K}} = -279.6\mathrm{kJ/mol}$$
(1)

$$\mathrm{Hf} + 2\mathrm{B} \rightarrow \mathrm{HfB}_2 \quad \Delta G_{\mathrm{f},1000\mathrm{K}} = -324.5\mathrm{kJ/mol}$$
 (2)

The potential advantages of reactive sintering, when compared with pressureless sintering, are lower processing temperatures, increased control over microstructural development and properties, and the use of cheaper and more abundant precursors.¹⁶ Among the controllable parameters, the initial density of the compact plays an important role. Independent of the sintering schedule, use of a green body with a porosity as low as possible maximizes the chance of obtaining the highest final density. Lee and Thadhani¹⁷ studied fabrication of a TiC ceramic from a shock-compacted mixture of Ti and C powder, followed by a solid-state reaction synthesis. The shock wave parameters were adjusted to obtain densification of the Ti+C mixture without initiation of the conversion reaction. The shock-compacted samples had theoretical densities above 90% and the converted TiC ceramic had an average grain size $< 6 \,\mu m$ and hardness of approximately 2000 kg/mm². The hardness values of shock-consolidated/converted TiC are lower than the reported hardness values for hot isostatic-pressed TiC (2850 kg/mm^2) ,¹⁸ and the difference is attributed to the pore fraction (<10%) remaining in the bulk ceramic.

Because diborides are well known to coarsen during sintering,¹⁹ the effect of the green density on pressureless solid-state reaction sintering was minimized through the use of nearly fully dense compacts. For the first time, ZrB₂ and HfB₂ ceramics were fabricated from mixtures of fully dense elemental powders

T. Besmann-contributing editor

Manuscript No. 24213. Received January 13, 2008; approved May 18, 2008. [†]Author to whom correspondence should be addressed. e-mail: mathieu.brochu@ mcgill.ca

obtained by dynamic consolidation. The particle size distribution of the raw materials and the consolidation parameters were selected to avoid self-propagating high-temperature synthesis (SHS) during consolidation. Advantageously, the shock consolidation process generates defects and other features that can enhance the solidsolid diffusivity, such as dislocations, shorter diffusion distances, subgrain size structures, and clean/fresh interfaces,¹⁷ which could improve the densification behavior. This analysis will show the possibility of fabricating UHTCs using this new method. The competitive densification and coarsening mechanisms will be discussed in terms of the evolution of the diboride microstructures and the properties of the ceramics will be compared with values of ceramics produced using more conventional processing methods.

II. Experimental Procedures

Elemental powders of zirconium (98.5%+2% Hf nominal, -325 mesh, Alfa Aesar, Ward Hill, MA), hafnium (99.6%+2 -3.5% Zr nominal, -325 mesh, Alfa Aesar), and crystalline boron (98%, -325 mesh, Alfa Aesar) were mixed in a molar ratio of 1 Zr:2 B and 1 Hf:2 B using a mortar and pestle in an isopropyl alcohol medium to obtain a homogeneous mixture. The powder mixture was cold pressed in seamless-steel tubing (12 mm diameter), under a pressure of 325 MPa, reaching $\approx 65\%$ of the theoretical density. The end plugs were welded using the gas tungsten arc welding process. The shockwave consolidation experiments were conducted at the Energetic Materials Research Testing Center according to their standard procedures.²⁰ A thorough description of the shock consolidation process can be found elsewhere.²¹ In this work, a single-tube cylindrical-implosion system was used to consolidate the samples. The test tubes were centered in a 15 cm diameter cardboard tube and subsequently filled with an ammonium nitrate/fuel oil (ANFO) explosive (detonation velocity of 2.6 km/s). A sheet of C3 was used as a booster to initiate the detonation. After the compaction, the enclosed sample containers were recovered and the consolidated samples were extracted by machining.

The cylindrical samples were sectioned to a thickness of 10 mm using a diamond blade cutoff saw. The samples were then heat treated in a controlled atmosphere furnace (Centorr, Nashua, NH) equipped with tungsten heating elements. The heating rate was 20° C/min up to sintering temperatures of 1600°, 1800° , or 2000° C, held for 1 h, and cooled to room temperature at 20° C/min. The heat treatment temperatures were selected according to previous work carried out by the authors showing that a minimum heat-treatment temperature of 1600° C with a soaking time of 1 h were necessary to obtain full conversion. Flowing argon (99.9% purity) was maintained during the cycle.

Densities were measured using the Archimedes method in water. The phase analysis was carried out on solid samples in a Philips PW1710 diffractometer (CuK α radiation) between 20° and 80° at $0.05^\circ/\text{step}$ for a 1-s dwell time. X-ray photoelectron spectroscopy (XPS) analysis was performed using Kratos Ultra XPS (Chestnut Ridge, NY), equipped with a monochromatic Al K-α X-ray source (1486.6 eV). Oxygen 1s, boron 1s, and zirconium 3d binding energies were analyzed for phase identification. Cross sections of selected samples were mounted and polished down to 0.25 µm using an automatic polishing machine (Buehler Ecomet 3[®], Lake Bluff, IL). The final polishing (0.02 µm colloidal silica) was performed on a Vibromet 2^{ss} (Buehler, Lake Bluff, IL) for 2 h. The microstructures were examined with a JEOL-840 (Tokyo, Japan) scanning electron microscope coupled with an EDAX (Mahwah, NJ) energy-dispersive spectrometer (EDS). The microstructures were revealed by thermal etching and the samples were coated with gold-palladium before SEM examination. Grain size measurement was performed using a Clemex Vision system (Longueuil, Canada) on a minimum of 200 grains/sample taken randomly at the surface of the samples.

Vickers microhardness was determined using a Clark CEM microhardness indenter (Crystal Lake, IL) with a load of 25 g. Reported values are an average of 10 indents.

III. Results and Discussion

(1) Powder Characterization

Figure 1 depicts the morphologies of the starting powders, respectively, (a) zirconium, (b) hafnium, and (c) boron. As depicted by the micrographs, the Zr and Hf powders exhibit irregular shapes, while the B particles have an angular morphology. Figure 1(d) depicts the particle size distribution for the elemental powders. The average particle size for Zr, B, and Hf is 19, 18, and 22 μ m, respectively. The similarity in particle size distribution will favor a packing closer to the ideal and random packing and consequently having a homogeneous void volume within the green compact, resulting in better control over the compaction process.²²

(2) Shock Consolidated Samples

The relative densities of the compacts after shockwave consolidation, measured using the Archimedes method, were assessed and a summary of the theoretical, measured, and relative densities are presented in Table I. As depicted, all samples for both systems had relative densities of 95.5% and above. Figure 2(a) shows a picture of a bulk Hf-B rod after compaction and removal from the tube enclosures. The final dimensions of the bulk samples were approximately 11 mm diameter and 30 mm length. Figure 2(b) presents a representative SEM micrograph of the postconsolidated Hf-B sample. As can be seen, no significant pores were observed in the compact, which is attributed to plastic deformation of the metallic phase filling the initial pores of the green compact. Cracks through some B particles are present and arise from the consolidation step. Both Hf (light gray phase) and B (dark phase) are clearly distinct from one another. EDS analysis shows that there was no interdiffusion of Hf and B, which demonstrates that the shockwave pressure was sufficient to consolidate the sample but insufficient to initiate the self-propagating synthesis. The XRD diffraction spectrum of the postconsolidated Hf–B mixture shown in Fig. 3(b) supports this statement as no change in phase is present and the same positions were observed before and after the consolidation. The larger peak broadening observed represents the residual lattice strain left in the compact after dynamic consolidation. Similar results were obtained for the Zr–B samples.

(3) Characterization of Ceramic Samples After Reaction Conversion

Figure 3(a) shows the XRD patterns for the Zr+B mixture after consolidation and ZrB₂ after heat treatment at 1600°C for 1 h. The diffraction pattern for the mixture corresponds solely to Zr (JCPDS # 05-0665), due to weak X-ray scattering from B and high absorption by Zr, while the spectrum for the ZrB₂ ceramic corresponds to the reference pattern JCPDS # 06-0610. Figure 3(b) presents the diffraction patterns for the Hf system heat treated at 1600°C. Similarly, the pattern for the mixture corresponds solely to Hf (JCPDS # 05-0670), and for the same reason as for ZrB₂ the reference pattern for the HfB₂ ceramic corresponds to the pattern JCPDS # 06-0638. As depicted for both systems, complete transformation was achieved after the heat treatment. Similar results were obtained for the higher heat treatment temperature, which could be observed for the Zr–B system in Fig. 3(c).

Table II and III present summaries of the measured density, relative density, grain size, and hardness as a function of the heat-treatment temperature for both the ZrB_2 and the HfB_2 samples. As shown, increasing the heat-treatment temperature does not have any effect on the final density of either ceramic. The ZrB_2 samples reached a relative density of 72%, while the HfB_2 samples possessed relative densities of 62%. For the



Fig. 1. Scanning electron micrographs of as-received (a) zirconium, (b) hafnium, (c) boron, and (d) particle size distribution of the three elemental powders.

same sintering temperatures, ranging between 0.5- and 0.6- $T_{\rm m}$, the relative densities obtained in this work are 7% higher than for the samples produced by pressureless sintering of attrition-milled ZrB₂ powders, soaked for 360 min at 2000°C.¹³ This lack of densification for the temperature studied is attributed to the covalent character of the bonding as well as the low-volume and grain boundary diffusion rates in the diborides.¹² No work on pressureless sintering of HfB₂ was found in the literature and, therefore, no comparison can be made.

Figure 4 presents the evolution of the microstructure for the ceramic samples as a function of the heat-treatment temperature. Figure 4(a–c) correspond to the ZrB₂ system heat treated at 1600°, 1800°, and 2000°C, respectively, while Fig. 4(d–f) correspond to the HfB₂ system heat treated at 1600°, 1800°, and 2000°C. The morphology of the larger pores ($\sim 20 \,\mu$ m) seems to correspond to the original location of B particles viewed along their larger cross section. The smaller pores are believed to also correspond to original B particle locations, but are cross sections that do not intersect a major diameter. The pore disappearance is in agreement with the reaction mechanism proposed by Fahrenholtz¹⁶ for the formation of ZrB₂ by reactive hot pressing of Zr and B mixtures. Their studies concluded that the B diffuses into the Zr phase to form the ZrB₂ phase. Increasing the conversion temperature from 1600° to 2000°C resulted in

 Table I.
 Measurement of Relative Density After Shock

 Compaction Without Reaction

	Theoretical density of M+2B (g/cm ³)	Measured density of shock compacted M+2B (g/cm ³)	Relative density (%)
Zr	4.88	4.69	96.1
Hf	8.81	8.41	95.5

progressively rounder pores in the ZrB_2 ceramics. However, the temperature range studied here seems to be too low to effect any change in the pore morphology in the HfB₂ system because angular pores are still observed after the heat treatment at 2000°C. Note that the grain structure can be observed inside the larger pores due to the thermal etching occurring during the heating cycle.

Figure 5 shows a representative micrograph of the etched grain structure of a ZrB₂ ceramic sample heat treated at 2000°C and used for the measurement of grain size distribution. The average grain size as a function of heat-treatment temperature is presented in Table II. For the temperature range studied, the average grain size of the ZrB_2 increased from 1.8 ± 0.6 to 5.6 ± 1.3 to 8.5 ± 3.3 µm, for heat-treatment temperatures of 1600°, 1800°, and 2000°C. Figure 6(a) shows the grain size distribution as a function of the heat-treatment temperature for the ZrB₂ system. The grain size distribution is narrow for the low heat treatment temperature but becomes wider as the temperature is increased. The results obtained on the densification behavior and the grain growth show that the structure of the ZrB₂ coarsens at the expense of densification. This suggests that a nondensifying vapor phase transport mechanism may be dominant for the temperature range studied here.¹³ A higher temperature may be necessary to obtain significant densification. Examination of the etched microstructures for the samples converted at 1600° and 1800°C revealed that the pores are located solely at the grain boundaries. As depicted in Fig. 5 for the samples converted at 2000°C, most of the pores are still located at the grain boundaries but some are present within the grains. The presence of pores at grain boundaries is believed to minimize grain coarsening.¹³ However, results in other systems have shown that if pores are observed within the grains, grain coarsening is well underway and will not be affected by the residual pores at grain boundaries.¹² For comparison, hot-pressed ZrB_2 had an average grain size of $4.0 \pm 1.2 \mu m$.



Fig. 2. (a) Picture of a bulk Hf–B sample after dynamic compaction and (b) scanning electron micrograph of the microstructure of the compact shown in (a).

Table III shows the average grain size and Fig. 6(b) depicts the grain size distribution as a function of heat-treatment temperature for the HfB₂ system. For the temperature range studied, the average grain size of the HfB₂ remains statistically constant even when the conversion temperature is increased. The average grain size measured was $5.0 \pm 1.6 \mu m$ for treatment at 1600°C, $3.3 \pm 1.5 \mu m$ for treatment at 1800°C, and $4.4 \pm$ $2.2 \mu m$ for treatment at 2000°C. As shown in Fig. 6(b), the grain size distribution is similar, whether the heat treatment occurred at 1600°, 1800°, or 2000°C. This result shows that grain growth mechanisms are not active, even at 2000°C. Independent of the heat-treatment temperature used, the pores are located at the grain boundaries.

Combining the densification and microstructure results, a conversion sequence for reactive processing is proposed. Tables I-III present the results for the theoretical and measured densities of shock-compacted ZrB₂ and HfB₂, both before and after heat treatment. If reaction is complete and all porosity is eliminated during formation of ZrB2 and HfB2 ceramics from their respective elemental powders, an increase in density of $\sim 24\%$ should be observed for the ZrB_2 system, whereas the density should increase by $\sim 26\%$ for HfB₂. With conservation of mass, a significant volume decrease should be observed for the reacting mixtures due to the large reduction in atomic volumes during conversion for both systems, as presented in Table IV. However, instead of increasing, the densities of both ZrB₂ and HfB₂ are lower than their compacted, unreacted mixtures. This means that not only was there no pore removal during reactive sintering, but that additional porosity was created. The resulting microstructures suggest that the heat-treatment temperatures used in this work are too low to promote densification because no increase in relative density was observed (no significant volume change). Vapor transport is one possible nondensifying mechanism¹³ but there is nothing in the observed microstructures to suggest such an effect. Therefore, the pores observed after conversion arise from either holes left from the diffusion of



Fig. 3. XRD patterns of powder mixture/ceramic systems after transformation for (a) ZrB_2 and (b) HfB_2 , and (c) comparison of phases present after transformation of ZrB_2 at 1600° and 2000° C.

B into the metallic phase, as proposed by Fahrenholtz,¹⁶ by the formation of new pores due to the shrinkage during conversion, or by the persistence of original pores after the shock consolidation. The large changes in density during the conversion should cause an estimated linear shrinkage of $\sim 8.7\%$ for ZrB₂ and $\sim 9.5\%$ for HfB₂ to form fully dense ceramics.

Comparing the increase in average grain size and observed lack of densification, it is apparent that under our conditions,

 Table II.
 Summary of Measured Density, Relative Density,

 Grain Size and Hardness of Shock-Compacted ZrB2

 Samples After Conversion Heat Treatment

 (Theoretical Density 6.09 g/cm³)

Heat treatment	Measured density (g/cm ³)	Relative	Grain	Vickers
temperature (°C)		density (%)	size (µm)	hardness (GPa)
1600	4.34	71.3	1.8 ± 0.6	19.4 ± 0.4
1800	4.37	71.9	5.6 ± 1.3	17.2 ± 0.6
2000	4.33	71.1	8.5 ± 3.3	13.7 ± 0.6

Table III. Summary of Measured Density, Relative Density, Grain Size and Hardness of Shock-Compacted HfB₂ Samples After Conversion Heat Treatment (Theoretical Density 11.1 g/cm³)

Heat treatment	Measured density (g/cm ³)	Relative	Grain size	Vickers
temperature (°C)		density (%)	(µm)	hardness (GPa)
1600	6.89	62	5.0 ± 1.6	$19.1 \pm 0.8 \\ 17.1 \pm 1.0 \\ 17.8 \pm 0.5$
1800	6.84	61.6	3.3 ± 1.5	
2000	6.81	61.3	4.4 ± 2.2	

 ZrB_2 coarsens without significant densification. Previous works on pressureless sintering of TiB₂ and B₄C have shown the detrimental influence of oxygen contamination on the densification behavior, where reduced densification rate and large grain growth were correlated with increased oxygen contamination.^{23,24} The presence of oxygen contributed to the formation of a B₂O₃ surface film, which was associated with the premature coarsening of the grain structure.^{13,23,24} Thus, to better understand the effect of oxygen on the densification of ZrB₂ and to detect any oxygen present as a contaminant, the surfaces of the as-received powders and samples heat treated at 2000°C were analyzed by XPS and the results are presented in Fig. 7. Figure 7(a) shows the binding energies for the as-received Zr powders. The measured binding energies of the Zr $3d_{3/2}$ and Zr $3d_{5/2}$ peaks were, respectively, 184.5 and 182.1 eV, which are higher than the reference values for pure Zr (Zr $3d_{3/2}$: 181 eV and Zr $3d_{5/2}$: 179 eV).²⁵ This shift in binding energy corresponds to the reference values for ZrO₂²⁵ and thus indicates the presence of a native ZrO₂ film at the surface of the as-received Zr powder. Figure 7(b) shows the XPS spectrum for a sample



Fig. 4. Evolution of microstructure and porosity of ZrB_2 ceramics heated at (a) 1600°C, (b) 1800°C, and (c) 2000°C and of HfB₂ ceramics heated at (d) 1600°C, (e) 1800°C, and (f) 2000°C.



Fig.5. Grain structure of ZrB_2 ceramic after heat treatment at 2000°C for 1 h.

heat treated at 2000°C. The spectrum depicts binding energies corresponding to ZrB₂ (Zr 3d_{3/2}: 180.45 eV, Zr 3d_{5/2}: 179.08 eV, and B 1s: 187.15 eV), to a ZrO₂ surface film (Zr 3d_{3/2}: 185.26 eV, Zr 3d_{5/2}: 182.84 eV), and to B₂O₃ (B 1s: 191.92 eV). This analysis suggests that B₂O₃ remains on the particle surfaces. Scarce literature is found regarding the boiling temperature of B2O3, which is reported to range between 1860° and 2065°C.²⁴ Because the boiling point is the temperature where the vapor pressure of the liquid equals the total pressure of the surrounding atmosphere, the gas pressure in the furnace during sintering has a strong influence on the boiling temperature. Chamberlain et al.¹³ reported the equilibrium vapor pressure of B_2O_3 as a function of temperature. From this relation, at atmospheric pressure, which was the pressure used in this work (flowing argon), the calculated boiling temperature is 2136°C. Secondly, assuming the current heat-treatment conditions and using the ZrB_2 volatility diagram reported by Fahrenholtz,²⁶ the coexistence of $ZrO_2(s)$ and $B_2O_3(l)$ is predicted. Lee and Speyer² suspected the presence of remaining B₂O₃ liquid up to 2010°C during sintering of B_4C under flowing He gas. Thus, all these facts support the XPS observations of residual B₂O₃ after sintering because the process was performed under flowing inert gas rather than in a vacuum environment. B₂O₃ is suspected to reduce the ceramic densification and favor grain coarsening, which would explain the poor densification and strong grain coarsening observed in ZrB₂ ceramics. Chamberlain et al.¹³ reported that the presence of WC impurities from milling played a vital role in the removal of the surface oxide film. Despite all precautions taken to avoid contamination, oxygen present as surface contamination of the starting Zr and, most probably, B powders affected densification. Despite the fact that neither densification nor grain growth was observed for the HfB₂ ceramics, it is expected that similar grain coarsening may occur because Hf has similar affinity for oxygen. Thus, the formation of B₂O₃ would also be favored for HfB₂ but the grain coarsening would occur at a higher temperature than for ZrB₂. As demonstrated by the XPS results, the major source of oxygen contamination is the presence of surface oxide films at the surface of the starting powders.

These results suggest that heat-treatment temperatures higher than those used here will be required to produce denser ceramics using conventional ceramic processing techniques and commercially available starting powders that have a surface oxide coating. These higher temperatures, of course, would result in even more grain coarsening than was observed in this study. The application of an external pressure during the conversion cycle, for example by hot isostatic pressing, will help close the pores formed from the phase changes. Such an approach has been



Fig. 6. (a) Grain size distribution as a function of heat-treatment temperature of (a) ZrB_2 and (b) HfB_2 ceramics, respectively.

found to be useful in reactive synthesis of other ceramics and ceramic matrix composites.^{19,27–29}

(4) Mechanical Properties

As presented in Table II, the microhardness values for the shock-compacted ZrB_2 samples decrease from 19.4 ± 0.4 to 17.2 ± 0.6 down to 13.7 ± 0.6 GPa with increasing heat-treatment temperature. The hardness results presented here are similar to the values obtained when pressureless sintering of ZrB_2 for material with a similar grain size (14.5 GPa for 9.1 μ m grain size),¹³ but are higher for the samples with a smaller grain size. However, the microhardness is lower than the values obtained for hot-pressed samples $(23 \pm 0.9 \text{ GPa})$.⁴ The inverse relation between hardness and grain size is due to the effect of grain boundaries in reducing plastic deformation, cohesion between grains, and the association of smaller pores with smaller grains. In addition, in the ZrB₂ system, it is expected that the level of internal stress from the conversion transformation increases with grain size due to the increase in thermal mismatch along the two crystallographic directions ($\alpha_a = 5.61 \times 10^{-6}$; $\alpha_c = 6.74 \times 10^{-6}$)³⁰ because the dimensions of the indent are of a similar magnitude to the grains. The hardness values obtained

 Table IV.
 Lattice Parameters for the Elemental Powders and Converted Ceramics and Respective Unit Cell Volumes

	a (Å)	c (Å)	Unit cell volume ($Å^3$)	JCPDS
Zr	3.232	5.147	139.685	05–0665
ZrB_2	3.169	3.530	92.102	06-0610
ΗΓ	3.196	5.057	134.202	05-0670
${\rm Hf}{\rm B}_2$	3.141	3.470	88.944	06–0638



Fig. 7. XPS spectra of (a) starting Zr powders and (b) ZrB mixture shock consolidated, followed by conversion at 2000°C.

for the HfB₂ samples with different heat treatments, presented in Table III, are the same, within statistical error: 19.1 ± 0.8 , 17.1 ± 1.0 , and 17.8 ± 0.5 GPa.

The results of this work suggest a few avenues for increasing the densities of the UHTCs produced by dynamic compaction of elemental powders, followed by ceramic conversion. First, because it is known that the B diffuses into the Zr, smaller B particles will result in smaller pores after conversion, which will have a higher driving force for disappearance caused by their increased radius of curvature. However, the faster densification of smaller particles will be opposed by their higher concentrations of deleterious surface impurities. Also, finer particles will modify the packing of the green compacts and their densities and packing, which could make control of the shockwave compaction process without initiating the self-propagating high-temperature reaction more difficult. Another research route might be to combine processing in vacuum to facilitate vaporizing of any B_2O_3 liquid film with a faster heating rate, which would minimize the coarsening effect. This improvement in densification behavior was observed previously in pressureless sintering of B₄C ceramics.²⁴

IV. Summary and Conclusions

ZrB2 and HfB2 ceramics were processed in a two-step route: first, the respective elemental powder mixtures were compacted using a dynamic process to density >95% TD and then conversion to ceramic was performed by heat treatment at temperatures between 1600° and 2000°C. The shock energy was optimized to obtain compaction while avoiding an SHS reaction.

A relative density of 72% was obtained for the ZrB₂ and this was found to be independent of the heat-treatment temperature. The grain size analysis shows grain growth as the heat-treatment

temperature is increased from 1600° to 2000°C, increasing from 1.8 ± 0.6 to 5.6 ± 1.3 to 8.5 ± 3.3 µm. The XPS analyses have revealed the presence of oxygen impurities, in the form of ZrO_2 and B₂O₃, which are believed to cause the coarsening of the microstructure rather than its densification. The major source of oxygen impurity arises from the native oxides on the starting powders. The SEM observations of the rounding of the pores are in agreement with the proposed coarsening mechanism. The microhardness values for the ceramics heat treated at 1600° and 1800°C are similar to those for pressureless-sintered specimens.

Similar results were obtained for the HfB₂ system, where a theoretical density of 62% was obtained, independent of the heat-treatment temperature. Neither grain growth nor change in microhardness was observed for the tested temperature. It is believed that the grains will coarsen in this system similar to the ZrB₂, but the effect is expected at higher heat-treatment temperatures. Similarly, the coarsening would be caused by the oxygen impurity present at the surface of the precursor elemental powders. For both systems, the use of heat-treatment conditions, such as a vacuum environment and a faster heating rate, could yield an improvement in densification.

Acknowledgments

The authors would like to thank Luke Boyer and Matthieu Dubus for their help in characterizing the microstructure and performing the hardness measurements.

References

¹C. R. Wang, J.-M. Yang, and W. Hoffman, "Thermal Stability of Refractory Carbide/Boride Composites," Mater. Chem Phys., 74, 272-8 (2002)

²M. M. Opeka, I. G. Talmy, E. J. Wuchina, J. A. Zaykoski, and S. J. Causey. "Mechanical, Thermal and Oxidation Properties of Refractory Hafnium and Zirconium Compounds," J. Eur. Ceram. Soc., 19, 2405-14 (1999).

³R. A. Cutlerin, pp. 787–803, Engineering Properties of Borides, Ceramic and Glasses, Engineered Materials, Handbook Vol. 4, Edited by S. J. Schneider. ASM International, Metals Park, OH, 1992.

⁴A. L. Chamberlain, W. G. Fahrenholtz, G. E. Hilmas, and D. T. Ellerby, "High-Strength Zirconium Diboride-Based Ceramics," J. Am. Ceram. Soc., 87 [6] 1170-2 (2004).

⁵S. R. Levine, E. J. Opila, M. C. Halbig, J. D. Kiser, M. Singh, and J. A. Salem, "Evaluation of Ultra-High Temperature Ceramics for Aeropropulsion Use," J. Eur. Ceram. Soc., 22, 2757-67 (2002).

⁶J. Bull and D. Rasky "Stability Characterization of Diborides Composites Under High Velocity Atmospheric Flight Conditions," 24th International SAMPE Conference, October 20-22, 1992.

W. G. Fahrenholtz, G. E. Hilmas, A. L. Chamberlain, and J. W. Zimmermann, "Processing and Characterization of ZrB2-Based Ultra-High Temperature Monolithic and Fibrous Monolithic Ceramics," J. Mater. Sci., 39, 5951-7 (2004).

⁸S.-K. Woo, I.-S. Han, H.-S. Kim, E.-S. Kang, J.-H. Yang, and C.-H. Kim, "Sintering of Zirconium Diboride Through Fe-Based Liquid Phase," Kor. Ceram. Soc., 33 [3] 259-68 (1996).

⁹J. J. Melendez-Martinez, A. Dominguez-Rodriguez, F. Monteverde, C. Melandri, and G. de Portu, "Characterization and High Temperature Mechanical Properties of Zirconium Diboride-Based Materials," J. Eur. Ceram. Soc., 22, 2543-9 (2002).

¹⁰F. Monteverde, S. Guicciardi, and A. Bellosi, "Advanced in Microstructure and Mechanical Properties of Zirconium Diboride Based Ceramics," Mater. Sci.

Eng. A, **346**, 310–9 (2003). ¹¹F. Monteverde, A. Bellosi, and S. Guicciardi, "Processing and Properties of Zirconium Diboride-Based Composites," J. Eur. Ceram. Soc., 22, 279–88 (2002). ¹²R. Telle, L. S. Sigl, and K. Takagi, "Boride-Based Hard Materials"; pp.

802-945 in Handbook of Ceramic Hard Materials, Vol. 2, Edited by R. Riedel. Wiley-VCH, Weinheim, 2000.

¹³A. L. Chamberlain, W. G. Fahrenholtz, and G. E. Hilmas, "Pressureless Sintering of Zirconium Diboride," J. Am. Ceram. Soc., 88 [2] 450-6 (2006).

¹⁴S. K. Mishra, S. Das, S. K. Das, and P. Ramachandrarao, "Sintering Studies on Ultrafine ZrB2 Powder Produced by a Self-Propagating High-Temperature Synthesis Process," J. Mater. Res., 15 [11] 2499-504 (2000).

¹⁵S. K. Mishra, S. Das, and P. Ramchandrarao, "Microstructure Evolution During Sintering of Self-Propagating High-Temperature Synthesis Produced ZrB2

 Powder," J. Mater. Res, 17 [11] 2809–14 (2002).
 ¹⁶W. G. Fahrenholtz, "Reactive Processing in Ceramic-Based Systems," Int. J. Appl. Ceram. Technol., 3 [1] 1–12 (2006).

J. H. Lee and N. N. Thadhani, "Enhanced Solid-State Reaction Kinetics of Shock-Compressed Titanium and Carbon Powder Mixtures," J. Mater. Res., 13 [11] 3160–73 (1998).
 ¹⁸J. F. Shackelford and W. Alexander, *CRC Materials Science and Engineering*

Handbook, Vol. 471, 3rd edition, CRC Press, Boca Raton, 2000.

⁹W. G. Fahrenholtz, G. E. Hilmas, I. G. Talmy, and J. A. Zaykoski, "Refractory Diborides of Zirconium and Hafnium," J. Am. Ceram. Soc., 90 [5] 1347-64 (2007)

²⁰M. Brochu, T. Zimmerly, L. Ajdelsztajn, E. Lavernia, and G. Kim, "Dynamic Consolidation of Nanostructured Al-7.5%Mg Powder," Mater. Sci. Eng. A, 466

 [1-2] 84-9 (2007).
 ²¹M. A. Meyers and S. L. Wang, "An Improved Method for Shock Consolidation of Powders," *Acta Metall.*, **36** [4] 925–36 (1988).
 ²²K. P. Staudhammer and L. E. Murr, "Principles and Applications of Shock Wace Compaction and Consolidation of Powdered Materials"; p. 237 in *Shock* Waves for Industrial Applications, Edited by L. E. Murr. Noyes Publications, New

 ²³S. Baik and P. F. Becher, "Effect of Oxygen Contamination on Densification
 ²³G. 1915 (1987) of TiB2," J. Am. Ceram. Soc., 70 [8] 527-30 (1987).

²⁴H. Lee and R. F. Speyer, "Pressureless Sintering of Boron Carbide," J. Am. *Ceram. Soc.*, **86** [9] 1468–73 (2003). ²⁵J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, "*Handbook of*

X-ray Photoelectron Spectroscopy. pp. 108-9, Perkin-Elmer Corporation, Eden Prairie, MN, 1992.

²⁶W. G. Fahrenholtz, "The ZrB₂ Volatility Diagram," J. Am. Ceram. Soc., 88 $[12]_{27}^{3509-12}$ (2005).

I. Gotman, N. A. Travitzky, and E. Y. Gutmanas, "Dense in Situ TiB2/TiN and TiB2/TiC Ceramic Matrix Composites: Reactive Synthesis and Properties," Mater. Sci. Eng. A, 244, 127-37 (1998).

²⁸I. Zlotnikov, I. Gotman, and E. Y. Gutmanas, "Processing of Dense Bulk MgB2 Superconductor Via Pressure-Assisted Thermal Explosion Mode of SHS,"

J. Eur. Ceram. Soc., **25** [15] 3517–22 (2005). ²⁹F. Monteverde, "Progress in the Fabrication of Ultra-High-Temperature Ceramics: In Situ Synthesis, Microstructure and Properties of a Reactive Hot-Pressed HfB2-SiC Composite," Comp. Sci. Technol., 65 [11-12] 1869-79

(2005). ³⁰N. L. Okamoto, M. Kusakaari, K. Tanaka, H. Inui, and S. Otani, "Temper-³⁰N. L. Okamoto, M. Kusakaari, K. Tanaka, H. Inui, and S. Otani, "Temper-temperature of the second se ature Dependence of Thermal Expansion and Elastic Constants of Single Crystals of ZrB2 and the Suitability of ZrB2 as a Substrate for GaN Film," J. Appl. Phys., 93 [1] 88-93 (2003).