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Pressureless Sintering of ZrB_2 Prepared by Colloidal Processing: Particle Packing, Sintering Conditions and Additives

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Abstract

Non-aqueous colloidal processing in cyclohexane and slip casting allowed the preparation of green ZrB_2 compacts with 67.3 %TD (theoretical density), which upon pressureless sintering at 2100°C densified to a final density of 92.4 %TD. The effect of controllable sintering parameters (temperature, time and heating rate) on the sintered properties of ZrB_2 compacts prepared using the non-aqueous colloidal processing method was also studied, in order to maximize the sintered density and tailor the desired microstructure (i.e. dense final object with small grain size). The competition between pore elimination and grain growth mainly controls the final density achievable. ZrB_2 compacts with maximum sintered densities of 93 %TD could be achieved by controlling the sintering conditions. Finally, the use of carbon and B_4C additives to improve the sintered density and microstructure of ZrB_2 compacts was also investigated. The additives, compatible with colloidal processing, allowed compacts with greater sintered densities (96-98 %TD) and finer grain sizes to be achieved by pressureless sintering, even at a lower temperature of 1900°C .

I. Introduction

Zirconium diboride (ZrB_2) is a highly covalent refractory ceramic with a hexagonal crystal structure.^{1,2} This material exhibits an extremely high melting point above 3000°C ,³ superb strength and hardness, high thermal conductivity and excellent corrosion resistance.⁴⁻⁵ Such advanced properties make ZrB_2 and ZrB_2 -based ceramics suitable for many high performance applications, including high temperature aerospace and propulsion components.^{1,6,7}

Despite its promising applications, densification of ZrB_2 to full or near-full density is often difficult due to its strong covalent bonding, low volume and grain boundary diffusivities, and the presence of surface oxide impurities in the powder.⁸⁻¹⁰ In this case, high sintering temperatures and pressure are often required.^{6,11} Hot-pressing of ZrB_2 is typically carried out at 2100°C or above with moderate applied pressures (20-30 MPa),¹² or at lower temperatures ($\sim 1800^\circ\text{C}$) with extremely high pressures (> 800 MPa).¹³ Because of the pressures required for densification of ZrB_2 , pressureless sintering was not considered as a possible approach to produce dense ZrB_2 objects until the late 1980s.⁶ To achieve highly-dense products ($> 95\%$ TD (theoretical density)) with sintering temperatures comparable to those of hot-pressing (1800 - 2100°C), various strategies have been proposed to enhance densification during pressureless sintering of ZrB_2 , including the use of fine starting particle size,^{8,10} homogenous and closely-packed particles in the green bodies¹⁴ and sintering additives.^{9,15-17} Each strategy may work in combination with others to achieve a better overall result.

In our previous work, colloidal processing was employed to control the interaction forces between particles in the suspensions, in order to stabilize the powder particles after breaking down the agglomerates.^{14,18} The homogenous dispersion of particles in suspensions aid the formation of green bodies with high density and less defects.^{14,18,19} In addition, colloidal processing also enables near-net shaping of ceramic components by slip casting, gelcasting, freeze casting and other colloidal forming techniques. Aside from our previous work^{14,18} which began to investigate the dispersion of ZrB_2 in cyclohexane, the majority of other colloidal processing of ZrB_2 -based ceramics was conducted in aqueous suspensions.^{16,20-22} Only two papers reported the processing of ZrB_2 in non-aqueous solvents.^{23,24} In the present study, the green and sintered properties

of ZrB_2 components prepared by colloidal processing (using aqueous and non-aqueous solvents) are investigated in comparison to a robust technique like dry pressing.

Various sintering conditions and schedules to densify ZrB_2 and ZrB_2 -based components have been reported by other researchers,^{6,8-10,15-17,25,26} but a thorough investigation on controllable sintering parameters (sintering temperature, time and heating rate) have not been reported on colloidally processed samples. Therefore, it is also the aim of this work to investigate the influence of these sintering parameters in order to obtain the desired sintered properties. Fahrenholtz *et al.*^{9,15,17} demonstrated that the use of carbon and B_4C additives was effective to remove the surface oxides (ZrO_2 and B_2O_3) of ZrB_2 powder that will otherwise promote coarsening of microstructure during sintering and hence, enhancing the densification process. The reactions between the additives (carbon and B_4C) and surface oxides were detailed in their work.^{9,17} A further aim of the present work is to determine if the addition of C and B_4C is compatible with the colloidal approach.

II. Experimental Procedures

(1) Materials

Commercially available zirconium diboride (ZrB_2 ; grade B, $D_{50} = 2.3 \mu\text{m}$, specific surface area = $1.0 \text{ m}^2/\text{g}$, H. C. Starck, Karlsruhe, Germany) was used in this study. Carbon (in the form of carbon black powder (Printex 60, $D_{50} = 20 \text{ nm}$, specific surface area = $120 \text{ m}^2/\text{g}$, Degussa, Frankfurt, Germany), novolac-type phenolic resin (Rezicure 3056, Schenectady, NY, USA)) and boron carbide (B_4C ; grade HD15, $D_{50} = 0.8 \mu\text{m}$, specific surface area = $19 \text{ m}^2/\text{g}$, H. C. Starck) were selected as sintering additives. Previous characterization of the powders was in a good agreement with manufacturer's data.^{14,18} Upon thermal degradation, phenolic resin yields ~40 wt% carbon.¹⁰

Cyclohexane (Sigma-Aldrich, Sydney, Australia) and Hypermer A70 (Croda, Goole, East Yorkshire, UK) were selected as the solvent and dispersant, respectively, for preparing non-aqueous suspensions. Hypermer A70 is a block copolymer comprising hydroxyl and amino functional groups, with molecular weight of $4.8 \times 10^5 \text{ g/mol}$.

Dolapix CE 64 (Zschimmer and Schwarz, Lahnstein, Germany) dispersant was used to disperse ZrB_2 powder in aqueous suspensions. This dispersant has been reported as an ethanolaminic salt of citric acid with molecular weight of 320 g/mol.^{27,28}

(2) *Suspension preparation and slip casting*

Firstly, the Hypermer A70 dispersant (previously optimized to be 0.5 wt% with respect to the weight of powder¹⁸) was dissolved in cyclohexane. Non-aqueous suspensions (100 mL) containing 50 vol% solid were then prepared by transferring the as-received ZrB_2 powders and cyclohexane-dispersant mixture into a polyurethane-lined milling jar (Paul O. Abbe, Bensenville, IL; ID = 10.5 cm, height = 11 cm) containing 100 mL of tungsten carbide (WC) milling media (diameters of 6.35, 9.525, 12.70, 15.875 mm (25 mL of each size) from Glen Mills, Inc., Clifton, NJ). The powder mixture was ball-milled (Paul O. Abbe) at 250 rpm for 7 hours to break down aggregates and ensure homogenization but the particle size distribution did not change. Some of the cyclohexane vapor was lost due to evaporation during this process and the actual solid content in the slurry became higher than the initial composition by approximately 4 vol%. In this case, the actual solid content of 54 vol% was obtained when preparing 50 vol% solid suspensions. The actual solid concentration of the suspensions was measured based on the weight loss (cyclohexane) during drying the suspensions.

B_4C (2-4 wt%) or carbon black (1.2-2 wt%), added in wt% with respect to the weight of ZrB_2 powder, was mixed with ZrB_2 powder and cyclohexane-dispersant solution to yield suspensions with initial solid concentration of 50 vol%. When phenolic resin (1-2 wt% or equivalent to 0.4-0.8 wt% carbon upon thermal degradation) was used as a sintering aid, the ZrB_2 powder was pre-coated with the resin prior to mixing with cyclohexane-dispersant solution. Phenolic resin was first dissolved in acetone (Merck, Darmstadt, Germany) and mixed with ZrB_2 powder, and the mixture was sonicated (Misonix S-4000 Sonicator, Qsonica, LLC, Newton, CT) for 10 minutes. The solvent (acetone) was evaporated at room temperature and the dried powder was ground using a mortar and pestle before it was used to prepare suspensions. The powder mixtures containing sintering additives were ball-milled in a similar manner to suspensions with no additives. All suspensions were equilibrated on a horizontal roller overnight prior to slip casting.

The suspensions were poured into cylindrical stainless steel rings (ID = 22 mm, OD = 25.5 mm, height = 20 mm) placed on a flat plaster of Paris base to form cylindrical green bodies with approximate diameter and height of 22 and 10 mm, respectively. The inner surface of the rings was previously greased with Krytox GPL 205 (DuPont, Wilmington, DE) to ensure an easy release of the green bodies. After casting, the top of the rings was immediately covered with plastic film (Parafilm M, Chicago, IL) to prevent evaporation of cyclohexane. The green bodies were demolded after 24 hours and placed in an oven at 80°C overnight to fully remove the solvent.

For comparison with the non-aqueous system, aqueous suspensions (45 vol% ZrB₂ in water prepared with 0.05 wt% Dolapix CE 64 dispersant (Zschimmer and Schwarz, Lahnstein, Germany) at pH 10 optimized in the previous work¹⁸) were also ball-milled and slip cast under the same procedure. The terms aqueous and non-aqueous colloidal methods will be used to refer to the preparation of green bodies by slip casting of aqueous and non-aqueous suspensions, respectively. In addition, dry pressed pellets of approximate diameter and height of 16 and 10 mm, respectively, were also prepared by loading as-received ZrB₂ powder into a hardened steel tool die greased with oleic acid (Ajax Finechem, Sydney, Australia) and uniaxially pressing (Labtechnics, Adelaide, SA, Australia) the powder at ~416 MPa for 30 seconds.

(3) *Sintering*

All samples were pressureless sintered in a graphite vacuum furnace (Red Devil, R. D. WEBB, Natick, MA, USA). Specimens were placed in a graphite crucible and heated at 5°C/min from room temperature to 400°C in a mild vacuum (~1 x 10⁻¹ mbar), followed by 2 hours isothermal hold at this temperature to ensure the complete removal of organics. The samples were then heated at 5 or 20°C/min to the maximum temperature of 1900-2100°C and soaked for 30-120 minutes. Most experiments were conducted using a heating rate of 5°C/min and isothermal hold period of 60 minutes (1 hour) at a maximum temperature of 2100°C. Above 1800°C, the furnace was backfilled with argon to protect the furnace elements. The samples were cooled down at 5°C/min from the maximum temperature to 1500°C and at 10°C/min from 1500°C back to room temperature.

(4) Characterization

The bulk density of green and sintered specimens was determined using Archimedes' principle. To prevent liquid ingress into the green bodies, a wax of a known density was melted and used to cover the exterior of the green samples prior to green density measurement. Using the measured weight of wax and its known density, the wax volume can be determined so that the volume of the wax is subtracted from the volume of the immersed wax coated green body to determine the density of the green body. The sintered samples were not coated with wax. The average of between 2 to 4 samples is presented. The sintered specimens were cut in cross-section (accutom-50, Struers, Copenhagen, Denmark), mounted in epoxy resin (Struers), and polished with SiC papers and diamond suspensions down to 6 μm using the TegraPol-21/TegraForce-5/TegraDoser-5 polishing system (Struers). Microstructures were characterized using a Quanta scanning electron microscope (SEM; FEI, Hillsboro, OR), equipped with an energy dispersive X-ray spectrometer (EDS; INCA x-act analytical silicon drift detector, Oxford Instruments, UK). The average grain and pore sizes of sintered specimens were determined using the line counting method. At least 100 grains or pores from images taken at three different areas within the same specimen were used to determine the average grain or pore size.

III. Results

(1) Effect of processing method

The non-aqueous colloidal method (slip casting) was found to produce green compacts with the highest green density (**Table 1**) and more homogenous microstructure compared to those processed by the aqueous colloidal and dry pressing techniques (the green microstructures corresponding to the processing methods investigated in this study are shown in **Figure S1** in the supplementary material available on-line).

Ball-milling the suspensions only contributed to the deagglomeration of the as-received powder, producing a narrow size distribution with a D_{v50} of 2.3 μm in agreement with the data of the supplier and our previous work.^{14,18} This gentle ball milling using WC

media only introduced 0.20 wt% W (tungsten) into the ZrB_2 powder (measured by Shaun Kenny (ALS, Brisbane, QLD, Australia) using X-ray fluorescence (XRF) spectroscopy (Axios sequential wavelength dispersive XRF, PANalytical, Netherlands)), considered too insignificant to influence the green and sintered densities of ZrB_2 . The oxygen contents of the green compacts prepared by different methods were measured by Cheryl McHugh (CSIRO, Clayton, VIC, Australia) using a Leco analyzer (TCH600, Leco, St. Joseph, MI). The unprocessed ZrB_2 powder contains 1.0 wt% oxygen, while the oxygen contents of the green ZrB_2 compacts processed by the aqueous colloidal, non-aqueous colloidal and dry pressing methods were 1.4 %, 1.1 % and 1.0 %, respectively.

Comparison of the sintered densities of ZrB_2 specimens processed by different methods is also presented in **Table 1**, which shows that the sintered density increased with increasing green density. The poorly compacted aqueous slip cast compacts (green density of 57.0 %TD (theoretical density)) resulted in a very little densification (an increase of density by ~2%) upon sintering. Compared to the aqueous processing, the dry pressed ZrB_2 compacts with a slightly better particle packing (59.0 %TD) resulted in a more significant increase of density by ~8% after sintering, even though the final density was still 67.6 %TD. More importantly, the closely and homogeneously packed ZrB_2 particles in non-aqueous slip cast compacts (with green density of 67.3 %TD) can be sintered to yield a much denser final component of 92.4 %TD. SEM observation of the sintered specimens is in a good agreement with the density values provided in **Table 1** (see **Figure S2** in the supplementary material). Dry pressing and aqueous colloidal processing yielded final products with densities which are considered too low for any further optimizing work. Given the promising green and sintered densities, the non-aqueous slip cast compacts were employed to study the influence of sintering temperature, soaking time and heating rate on the sintered properties of this material.

(2) Effect of sintering temperature

The final density, average grain and pore sizes of non-aqueous slip cast ZrB_2 compacts sintered at 1900, 2000 and 2100⁰C (the soaking time and heating rate were fixed to 1 hour and 5⁰C/min, respectively) are presented in **Figure 1**. A sintered density of 88.9 %TD was achieved when sintering at 1900⁰C. The SEM micrograph of the specimen

sintered at 1900⁰C (**Figure 2(a)**) shows a microstructure consisting of fine grains and pores with average sizes of 4.3 and 1.9 μm , respectively. The transition from an open to closed porosity occurred close to this temperature, as indicated by the elongated pores observed in **Figure 2(a)**. At this point, the pores remain attached to the grain boundaries.

An increase of density by ~3% (from 88.9 to 92.1 %TD) was obtained by increasing the sintering temperature to 2000⁰C. As presented in **Figure 1**, the average grain and pore sizes also increased with increasing sintering temperature and sintered density. The pore shape gradually became more circular and the presence of some trapped pores can be observed in **Figure 2(b)**. A further increase of sintering temperature to 2100⁰C resulted in no significant change of density (92.4%TD). However, the grain size continuously grew larger to an average size of 12.5 μm . The microstructure of the specimen sintered at 2100⁰C also contains fewer, larger pores (average size of 3.4 μm) and more trapped pores than that observed in the specimens sintered at lower temperatures. See **Figures 2(c) and (d)**.

(3) Effect of soaking time

Increasing the soaking time from 30 to 120 minutes (with the sintering temperature and heating rate fixed to 2100⁰C and 5⁰C/min, respectively) did not produce a significant increase of density. Sintered compacts of 92.0 and 92.9 %TD were obtained when soaked for 30 and 120 minutes, respectively. However, the grain and pore size progressively grew with longer soaking time. The grain size increased from 11.8 to 15.0 μm as the soaking time increased from 30 to 120 minutes (the complete results corresponding to specimens sintered with different soaking times are provided in **Figure S3** in the supplementary material).

(4) Effect of sintering additives

Rheological measurements indicated that the suspensions containing phenolic resin (1-2 wt%), carbon black (1.2-2 wt%) and B₄C (2-4 wt%) maintained a low viscosity and shear thinning behavior (refer to **Figure S4** in the supplementary material) suitable for slip casting. Addition of more than 2 wt% phenolic resin or carbon black resulted in destabilization of the suspensions and undesirable flow properties. Therefore, the

amount of carbon black or phenolic resin incorporated in this work was limited to the maximum of 2 wt%. On the other hand, no significant effect on the suspension viscosity was observed upon addition of B₄C additive up to 4 wt%.

The green and sintered densities of ZrB₂ compacts with and without additives are compared in **Table 2**. It can be seen that incorporation of phenolic resin and carbon black decreased the green density, while addition of B₄C resulted in improved green density. Upon sintering at 5°C/min to 2100°C with 1 hour soaking, all additives increased the final density of ZrB₂ specimens, with compacts containing 2 wt% carbon black and 4 wt% B₄C resulted in the highest sintered densities (97.3 and 97.0 %TD respectively). SEM images of ZrB₂ specimens containing 2 wt% carbon black and 4 wt% B₄C additives are shown in **Figure 3** (SEM images of other specimens listed in **Table 2** are provided in **Figure S5** in the supplementary material). Along with increased sintered density, specimens containing phenolic resin additive also showed increased average grain and pore sizes (**Table 2**). Meanwhile, compacts containing carbon black and B₄C (with the exception of samples with 2 wt% B₄C) possessed smaller average grain and pore sizes compared to those with no additives.

The incorporation of carbon black and B₄C additives also allowed high sintered densities and fine grain microstructures to be achieved by sintering at 20°C/min to 1900°C with 1 hour soaking (**Table 2**). Under such sintering conditions, compacts of near full density (97-98 %TD) with fine grain and pore sizes were obtained using B₄C additive (see **Table 2** and **Figure 4** and **Figure S6**).

The presence of second phase particles in ZrB₂ samples containing carbon and B₄C additives can be seen in **Figures 3** and **4**. SEM/EDS analysis of the samples confirmed that these second phase particles contain mainly B with Zr and C as shown in **Table 3**. The matrix material contained no C and a much greater wt% of Zr.

IV. Discussion

(1) Influence of processing and green microstructure

As seen in **Table 1**, different processing methods (aqueous colloidal, non-aqueous colloidal and dry pressing) produced compacts with different green properties, which in

turn affect the sintered density and microstructure. As demonstrated earlier,¹⁸ the aqueous suspensions contain particles that are weakly attractive and the dry-pressed compacts have particles interacting via Van der Waals attraction. The attraction leads to the presence of aggregates and agglomerates in the green bodies, resulting in lower green densities. Apart from their low green densities, powder compacts containing aggregates are also expected to contain a greater number of larger pores surrounded by many grains.²⁹ Such green bodies are known to be difficult to densify.^{19,30,31} Therefore, the dry pressed and aqueous slip cast specimens due to the higher amount of porosity and larger pore sizes in the green bodies only experienced very limited densification compared to the non-aqueous slip cast compacts.

On the other hand, the well-dispersed particles in the non-aqueous suspensions can be processed into highly dense and uniform green bodies (**Table 1**). However, extra care must be taken to prevent evaporation of cyclohexane during the production of large non-aqueous slip cast components. The higher sintered density achieved by the non-aqueous colloidal specimens (92.4 %TD for non-aqueous colloidal processing compared to 58.9 and 67.6 %TD for aqueous colloidal processing and dry pressing, respectively) can be attributed to their higher green density and better packing uniformity (i.e. better dispersed particles in the powder compact and a more homogenous distribution of smaller pores). The sintered microstructures of non-aqueous slip cast ZrB₂ compacts (shown in **Figure 2(c)-(d)**) are typical for ceramics after the final stage of sintering, consisting of relatively dense solid grains (>90 %TD) and closed pores.³²

(2) Microstructure development: density, grain and pore size

Sintering of ZrB₂ to high final densities (>90 %TD) usually takes place at sintering temperatures ranging from 1850-2250⁰C.^{6,8-10,15-17,25} Although densification depends greatly on the sintering temperature, simply increasing the temperature does not guarantee full elimination of pores from the powder compacts. As shown in **Figures 1** and **2**, the sintered density of ZrB₂ compacts increased slightly from ~89 to 92 %TD with an increase of sintering temperature from 1900 to 2100⁰C, but significant coarsening of microstructure can be observed at higher temperatures. Nevertheless, such high densities above 90 %TD are usually difficult to achieve by pressureless sintering of ZrB₂ monoliths, even when ultrafine ZrB₂ powder (less than 0.5 μm) is employed.⁹

Significant densification of powder compacts usually takes place in the intermediate and final stages of sintering via the volume/lattice and grain boundary diffusion,³³ with grain boundary diffusion being the major transport mechanism due to its higher absolute magnitude compared to the lattice diffusion.³⁴⁻³⁶ Thus, grain boundary diffusion is expected to play a key role in densification of such a strong covalently bonded solid, like ZrB₂. Fahrenholtz *et al.*¹ reported that lattice and grain boundary diffusion occur in ZrB₂ compacts at sintering temperatures above 1800°C. This agrees with our work in which a significant densification (from 67.3 to 88.9 %TD) was obtained when sintering at 1900°C, and further improvement of density (to ~92 %TD) was achieved at 2000-2100°C.

Grain growth also takes place in the intermediate and final stages of sintering. Often, the grain size grows slowly with increasing sintered density independent of sintering conditions during the intermediate stage of sintering, suggesting that both densification and grain growth occur simultaneously at this stage.³⁷⁻³⁹ With increasing sintered density, there are more particle-particle contacts and grain boundaries to enable grain growth. An example of increasing grain size with sintered density in our work can be seen in **Figure 1**. On the other hand, when densification is inhibited by a large diffusion distance (as in the case of dry pressed and aqueous colloidal samples shown in **Figures S2(a) and (b)** in the supplementary material), grain growth cannot proceed due to the limited number of grain boundaries. The absence of grain growth is indicated by compacts of such low sintered densities having final grain sizes of more or less equal to the initial particle size.

Grain growth also allows densification to be re-initiated by effectively reducing the pore coordination number (N , i.e. number of grains attached to the pore) such that it decreases below the critical value (N_c). The angle formed by the surface tangents and the new grain boundaries (φ) will be less than the equilibrium dihedral angle (φ_e) and densification can re-initiate.^{19,29} Grain growth can aid densification as long as the grain growth process does not progress too rapidly. The transition from a slow to rapid grain growth usually takes place when the sintered density reaches above 90 %TD in the final stage of sintering.^{37,39} As seen in **Figure 1**, a significant increase of grain sizes can be observed in samples with final densities of >90 %TD, compared to those with densities

below 90 %TD. Densification or pore removal is associated with the elimination of solid-vapor surface area, while grain growth is driven by the elimination of solid-solid boundary area.⁴⁰ Thus, it is not surprising for the densification to slow down and the rate of grain growth to become increasingly rapid once the sintered density is above 90 %TD, where the pore area has been significantly reduced and more solid-solid grain boundaries have been formed.

Pore growth also takes place concurrently with grain growth (see **Figure 1**), as a result of several pores coalescing into one larger pore accompanying grain growth.^{32,40} Rapid grain growth (usually when the sintered density > 90%TD) may cause the separation or breakaway of pores from grain boundaries, resulting in pores trapped within the grains,^{34,41,42} as shown in **Figure 2(c)-(d)**. The presence of large, stable pores as well as pores trapped within the grains in the compacts often hinders further densification. When densification is impeded, mass transport can only lead to further grain coarsening.^{35,38}

The reason for ZrB₂ compacts not densifying further than ~92 %TD even when the temperature was raised to 2100⁰C can be attributed to the dominating grain growth process. In the final stage of sintering where densification was slow and grain growth was rapid, inducing more mass transport by increasing the sintering temperature only led to more coarsening of microstructure of ZrB₂ compacts with limited densification (see **Figure 2**). In addition to the rapid grain growth, the pores attached to the grain boundaries also gradually grew larger and the amount of trapped pores significantly increased, inhibiting the already slow densification of ZrB₂ compacts.

Apart from the temperature-dependency of sintering, densification and grain growth are usually affected by the soaking time. However, this study found that varying the soaking time did not result in a significant improvement of final density in ZrB₂ compacts. It appears that the ZrB₂ compacts might have reached the density of ~92 %TD very quickly (less than 30 minutes) upon reaching the maximum temperature (2100⁰C) of the sintering cycle. With increasing soaking time (from 30 to 120 minutes), the ZrB₂ compacts experienced a minor densification (from 92.0 to 92.9 %TD) and a significant grain growth (from 11.8 to 15.0 μm). The average pore sizes (determined from pores in the grain boundaries and those trapped within the grains) increased

slightly (from 2.8 to 3.5 μm) with increasing soaking time (see **Figure S3**). SEM observation indicated that the dimensions of the trapped pores remain more or less the same, which indicates that pores do not exhibit significant growth or shrinkage once they are isolated within the grains. Meanwhile, the majority of the pores in the grain boundaries gradually became larger through the pore coalescence mechanism that accompanied the grain growth.

(3) Effect of sintering additives

The aim of this work is to show that C and B_4C (sintering aids already known to improve the sintering of ZrB_2)^{9,15,17} are compatible with the colloidal approach. The green density after slip casting was found to vary with different additives (**Table 2**). The slight reduction in green density upon addition of phenolic resin may be due to the change in the particle surface characteristics caused by the resin coating. The incorporation of finer-sized powder additives can potentially increase the green density, because the finer additive particles can fit into the interstices of the larger ZrB_2 particles.⁴³ This beneficial effect of finer-sized additive can be observed when B_4C was incorporated into the powder mixture. As seen in **Table 2**, the green density of ZrB_2 compacts increased with increasing amount of B_4C additive. However, an opposite effect was observed with carbon black additive. The decrease of green density suggests that the suspensions gradually destabilised with increasing concentration of carbon black, due to its smaller particle size. Thus, the beneficial effect of finer-sized additive was cancelled by the presence of aggregates, causing a decrease in the green density.

The Hypermer A70 dispersant (0.5 wt% with respect to the solid content) may result in a small amount of residual carbon after pyrolysis (up to as much as 0.5 wt% assuming the polymer contains nothing but carbon). Even as little as 0.5wt% of carbon will aid densification⁹ so the additional carbon from the dispersant will help densification in all the non-aqueous colloiddally processed samples. Upon sintering under the same condition (5⁰C/min to 2100⁰C, 1 hour soak), all additives studied increased the final density of ZrB_2 compacts (**Table 2**). This suggests that the additives reacted with the surface oxides of ZrB_2 and hence, minimising the coarsening caused by the vapour phase transport at the early stage of sintering. Higher final densities could then be achieved given the smaller diffusion distance. In addition to the oxide removal, the

densification of ZrB_2 compacts containing B_4C additives was also enhanced by the high green densities. The SEM/EDS analysis indicates the presence of non-stoichiometric ZrB_2 and ZrC in the ZrB_2 specimens containing additives (see **Figure 3**), which might be derived from reactions between the carbon/ B_4C additive and the $\text{ZrO}_2/\text{B}_2\text{O}_3$ surface oxides (as per reactions proposed by Zhu *et al.*⁹ and Zhang *et al.*¹⁷). These newly-formed species and the unreacted additives with either very limited solubility (~ 2 mol%) or no intersolubility with the ZrB_2 component then present as stable secondary phase inclusions within the matrix of ZrB_2 .^{44,45}

As seen in **Table 2**, incorporating a small amount of additives was found to result in larger average grain sizes along with increased sintered densities, with an exception for specimens containing carbon black additive that showed decreased grain sizes. For all the additives studied (including carbon black), increasing the concentration of additive resulted in an increase of sintered density and a decrease of average grain size. The most distinctive change of average grain size can be observed with B_4C additive where incorporation of 2 wt% B_4C resulted in compacts of 96.4 %TD with an average grain size of $18.4\text{ }\mu\text{m}$, while compacts of 97.0 %TD with an average grain size of $8.6\text{ }\mu\text{m}$ were obtained using 4 wt% B_4C . It appears that the incorporation of 2 wt% B_4C was sufficient to react with the surface oxides and the excess B_4C remained in the grain boundaries. Further addition of B_4C up to 4 wt% had a little effect on the final density and resulted in more excess B_4C that restricted the grain growth. As pointed out by Hsueh and Evans,³⁴ the presence of second phases can minimise grain growth by presenting drag on the grain boundaries and hence, limiting the boundary mobility. Similar result with B_4C additive was obtained by Zhang *et al.*,¹⁷ in which compacts containing attrition-milled ZrB_2 powder (average particle size of $\sim 0.1\text{ }\mu\text{m}$) and 2 wt% B_4C additive yielded a final density of $\sim 98\text{ %TD}$ with an average grain size of $\sim 12\text{ }\mu\text{m}$, while compacts containing 4 wt% B_4C prepared and sintered under the same conditions reached the same final density but with a smaller average grain size of $\sim 8\text{ }\mu\text{m}$.

The present work also shows that an addition of 1-2 wt% of phenolic resin (equivalent to 0.4-0.8 wt% amorphous carbon after pyrolysis)⁴⁶ resulted in sintered compacts with slight improved densities (by $\sim 2\text{ wt\%}$) and larger average grain sizes, possibly because there was not enough carbon to completely react with the surface oxides and pin the

grain growth. The small amount of phenolic resin (1-2 wt% based on the weight of powder) should not cause a significant gas evolution during pyrolysis.⁴⁶ Thus it is expected that the structural change in phenolic resin does not affect the pressureless sintering of ZrB_2 , apart from the resulting carbon (after pyrolysis) enhancing the densification of ZrB_2 by reacting with the surface oxides. On the other hand, carbon black was found to be effective in improving the sintered density and controlling the grain growth. As shown in **Table 2**, high sintered densities (96-97 %TD) and finer grain sizes compared to other specimens were achieved with carbon black additive. Given the large size difference between the carbon black (average particle size of 50 nm) and ZrB_2 (average size of 2 μm) particles, each ZrB_2 grain might be surrounded by many carbon black particles. The presence of many fine-sized carbon black particles on the grain boundaries of ZrB_2 efficiently restricted the boundary movement and slowed the grain growth.

Phenolic resin and carbon black have been found to have different effect on sintering ceramics such as SiC and B_4C ,⁴⁷⁻⁴⁹ based on their dispersion behavior. The carbon black produced lower densities because it was not well dispersed in the SiC and B_4C suspensions compared to the phenolic resin. Shi, et al, 2015⁴⁹ showed that similar density could be achieved with 5.5 wt% carbon black as with 1.5 wt% carbon equivalent form phenolic resin. In this case, the carbon black was not likely used efficiently since it was not well dispersed (solvent was water in this work). In the present work we found that the carbon black (1.2 to 2 wt%) was more effective a sintering aid than 1 to 2 wt% phenolic resin (0.4 to 0.8 w% carbon equivalent). We believe this is because the carbon black was well dispersed in the cyclohexane using the Hypermer a70 dispersant so it was used more effectively than when poorly dispersed as described in the previous work.^{47,48} So the effect of carbon black well dispersed at 1.2 to 2 wt% is a more effective sintering aid than the lower concentration of carbon from phenolic resin (0.4 to 0.8 wt%).

When sintered at 1900⁰C for 1 hr after heating at 20⁰C /min (**Table 2**) monolithic ZrB_2 reaches 90.7 %TD. The incorporation of additives (carbon black and B_4C) has been shown to improve the sintered properties of ZrB_2 specimens, even at a lower temperature of 1900⁰C. The faster heating rate (20⁰C /min) likely aided the densification

and reduced grain size.⁵⁰⁻⁵⁴ Although the specimens containing carbon black additive did not reach densities higher than 94 %TD (**Table 2**), an improvement in density and finer microstructures were obtained compared to monolith ZrB₂ sintered under the same condition (90.7 %TD) and at 2100⁰C (~92 %TD). Meanwhile, specimens containing B₄C additives were sintered to near full density (97-98 %TD) at 1900⁰C, while maintaining very fine grain and pore sizes.

(4) Comparison to previous ZrB₂ processing approaches

Comparison of the sintered densities of ZrB₂ with and without additives obtained in our work with the values reported in the literature is provided in **Table 4**. The sintered densities achieved in this work, without additives, are relatively high compared to those reported in the literature under pressureless sintering. Compared to other results obtained using hot pressing and spark plasma sintering, our results show that colloidal processing in combination with pressureless sintering is a suitable approach to prepare highly dense ZrB₂ ceramics with complex shape. Our results with carbon and B₄C additives produce similar densities as shown previously for similar level of additives in dry pressed pellets. The results presented here are a slight improvement on the aqueous colloidal processing of Huang et al.²⁰ The likely reason why the non-aqueous slip cast ceramics produced in the current study are easier to sinter to high density at lower temperature and without pressure is the higher green density (63 – 69 %TD) compared to other colloiddally processed ZrB₂ (approx. 48 % TD).^{21,23} The higher green density is due to the better state of dispersion between particles in the cyclohexane than in aqueous solvent¹⁸ and the tape casting organic solvent formulations.²³ The state of dispersion of particles influences the suspension viscosity which can be used as a measure of dispersion quality. **Table S1** in the supplementary material gives a comparison of the viscosity of ZrB₂ suspensions in aqueous^{18,20-22,57} and non-aqueous²³ solvents with several different types of dispersants (the best result from each investigation cited is presented). The lowest viscosities are found using Hypermer A70 dispersant in cyclohexane at the highest solids concentrations. Specifically, aqueous suspensions and other non-aqueous suspensions with lower solids concentrations have higher viscosities than the results presented in ref 18 and in **Figure S4** in the supplementary material.

We note that in this section of the discussion, we have not addressed the issue of particle size. The finer particle size of the milled materials will produce stronger driving force for sintering, but will increase the viscosity of suspensions and decrease the packing density.⁵⁸

V. Conclusion

Non-aqueous colloidal processing in cyclohexane was found to be the most suitable approach to process dense ZrB_2 components. The closely and homogeneously packed particles within the green bodies prepared by the non-aqueous colloidal approach allow the powder compacts to be sintered to much higher final densities compared to other processing methods (aqueous colloidal and dry pressing) investigated. When analyzing the effect of sintering temperature, significant densification of ZrB_2 up to 88.9 %TD was achieved at 1900°C , while compacts of ~92 %TD were obtained by sintering at $2000\text{--}2100^\circ\text{C}$ for 1 hr. Varying the soaking time and heating rate when sintering at 2100°C did not result in significant change of sintered density (varied by ~1%) and amount of porosity of ZrB_2 . However, increasing the soaking time caused the average grain and pore sizes of ZrB_2 specimens to increase. Our results indicate that high sintered densities of 92-93 %TD can be obtained when colloidal processing (in cyclohexane) and pressureless sintering using the right conditions ($2000\text{ to }2100^\circ\text{C}$, 1hr, $5^\circ\text{C}/\text{min}$) were employed to maximize the green and sintered density, respectively. Finally, the incorporation of additives (carbon black and B_4C) into non-aqueous ZrB_2 suspensions was compatible with the colloidal approach and improved the sintered density from ~92 %TD for monolith ZrB_2 to 97-98 %TD with carbon black (1.2-2 wt%) or B_4C (2-4 wt%) additive when sintered at 2100°C . The additives also acted as a grain growth inhibitor, allowing final microstructures with finer grain sizes to be achieved. With the additive enhancing the densification process, sintering of ZrB_2 to almost full density (97-98 %TD) can also be conducted at a lower temperature of 1900°C using B_4C additive.

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Figure captions

Figure 1. Sintered densities (% theoretical density, TD), average grain sizes (μm) and average pore sizes (μm) of non-aqueous colloidal ZrB_2 specimens sintered at 1900-2100 $^{\circ}\text{C}$ with a soaking time of 1 hour and heating rate of 5 $^{\circ}\text{C}/\text{min}$. The error bars show the range of the values for between 2 to 4 samples. Where not visible, the error bars are smaller than the symbols used.

Figure 2. SEM images showing the morphologies of non-aqueous slip cast ZrB_2 compacts sintered at (a) 1900, (b) 2000 and (c) 2100 $^{\circ}\text{C}$ for 1 hour with a heating rate of 5 $^{\circ}\text{C}/\text{min}$. Figure (d) is the low magnification image of the same specimen shown in (c).

Figure 3. Backscattered (a1, b1) and secondary (a2, b2) electron SEM images of ZrB_2 doped with (a) 2 wt% carbon black and (b) 4 wt% B_4C . The specimens were sintered using a heating rate of 5 $^{\circ}\text{C}/\text{min}$ and soaked for 1 hour at 2100 $^{\circ}\text{C}$. The light regions in the secondary electron SEM images correspond to the ZrB_2 matrix, and the dark regions contain pores and second phase particles. The pores in the secondary electron images appear to have bright rims or halos around them, while the second phase particles (indicated by the white arrows) can be identified as dark regions with no rim or halo around them.

Figure 4. Backscattered (a1, b1) and secondary (a2, b2) electron SEM images of ZrB_2 doped with (a) 2 and (b) 4 wt% B_4C . The specimens were sintered for 1 hour at 1900 $^{\circ}\text{C}$ with a heating rate of 20 $^{\circ}\text{C}/\text{min}$. The light regions in the secondary electron SEM images correspond to the ZrB_2 matrix, and the dark regions contain pores and second phase particles. The pores in the secondary electron images appear to have bright rims or halos around them, while the second phase particles (indicated by the white arrows) can be identified as dark regions with no rim or halo around them.

Table 1. Green and sintered densities of ZrB₂ compacts prepared by different processing routes. The heating rate was 5⁰C/min, and the soaking time and the maximum sintering temperature were 1 hour and 2100⁰C, respectively.

ZrB₂		
Processing route	Green density (%TD)*	Sintered density (%TD)*
Dry pressing	59.0	67.6
Colloidal + slip cast (aqueous)	57.0	58.9
Colloidal + slip cast (non-aqueous)	67.3	92.4

*the variation in green and sintered density between samples prepared under the same conditions is less than 1%.

Table 2. Green and sintered densities, average grain sizes and average pore sizes of ZrB₂ compacts with and without additives. The green compacts were slip cast using suspensions containing 54 vol% solid (with cyclohexane solvent and 0.5 wt% Hypermer A70 dispersant).

Sintering conditions: 5⁰C/min to 2100⁰C and 1 hour soaking				
Additive	Green density	Sintered density	Average grain	Average pore

	(%TD)*	(%TD)*	size (μm)	size (μm)
None	67.3	92.4	12.4 ± 3.4	3.4 ± 1.6
1 wt% phenolic resin	64.3	94.8	19.7 ± 7.5	3.6 ± 1.9
2 wt% phenolic resin	65.6	94.8	16.6 ± 5.3	4.0 ± 2.4
1.2 wt% carbon black	66.5	96.1	9.9 ± 3.1	2.4 ± 1.5
2 wt% carbon black	63.4	97.3	8.4 ± 4.1	2.4 ± 1.3
2 wt% B ₄ C	67.9	96.4	18.4 ± 5.7	1.8 ± 1.3
4 wt% B ₄ C	69.0	97.0	8.6 ± 2.4	1.6 ± 1.1
Sintering conditions: 20⁰C/min to 1900⁰C and 1 hour soaking				
Additive	Green density (%TD)*	Sintered density (%TD)*	Average grain size (μm)	Average pore size (μm)
None	67.3	90.7	8.1 ± 2.8	2.8 ± 1.3
1.2 wt% carbon black	66.5	94.3	3.6 ± 1.3	1.3 ± 0.7
2 wt% carbon black	63.4	93.8	3.2 ± 1.3	1.4 ± 0.7
2 wt% B ₄ C	67.9	97.0	7.6 ± 2.4	1.0 ± 0.5
4 wt% B ₄ C	69.0	98.1	4.0 ± 1.5	1.1 ± 0.5

*the variation in green and sintered density between samples prepared under the same conditions is less than 1%.

Table 3. Elemental composition (wt%) of ZrB₂ matrix and second phases as determined by EDS analysis.

	ZrB ₂ matrix	Phenolic resin second phase	C black second phase	B ₄ C second phase
Zr	69-75 wt%	17-22 wt%	22-27 wt%	22-33 wt%
B	24-30 wt%	55-62 wt%	52-60 wt%	52-58 wt%
C	not detected	18-25 wt%	18-26 wt%	10-19 wt%
Hf	1.3- 2.0 wt%	not detected	not detected	not detected

Table 4. Comparison of sintered density of ZrB₂ compacts obtained in this work with the literature.

Additive	Starting particle size (μm)	Green body	Sintering conditions	Final density (%TD)	Ref
None	2.3	Non-aqueous slip cast	2100°C, 60 mins dwell, 5°C/min (PS)	92	Our work
1-2 wt% phenolic				95	
1.2-2 wt% C black				96-97	
2-4 wt% B ₄ C				96-97	
None	2.3	Non-aqueous slip cast	1900°C, 60 mins dwell, 20°C/min (PS)	91	Our work
1.2-2 wt% C black				93-94	
2-4 wt% B ₄ C				97-98	
None	2.1	HP die	2000°C, 60 mins dwell, 50°C/min, 30 MPa (HP)	90.4	12
None	2.0	HP die	5°C/min to 1650°C, 17°C/min to 1900°C, 45 mins dwell at 1900°C, 32 MPa (HP)	99.8	55
None	0.6-2.3	SPS die	1900°C, 3 mins dwell, 300°C/min, 50 MPa (SPS)	97-98	56
8 wt% WC	0.1	DP 19 MPa +	2050°C, 240 mins dwell,	95	17
2-4 wt% B ₄ C	2.0	CIP 310 MPa	10°C/min (PS)	97	
8 wt% WC + 2-4 wt% B ₄ C	0.1	DP 19 MPa + CIP 310 MPa	1850°C, 60 mins dwell, 10°C/min (PS)	98	17
None	2.0	DP 30 MPa + CIP 300 MPa	10°C/min to 1650°C, 30°C/min to 1900°C, 120 mins dwell at 1900°C (PS)	61.0	9
2 wt% phenolic-C	2.0			95.5	
2 wt% phenolic-C	0.5			99-100	
2 wt% B ₄ C + 1 wt% phenolic-C	2.0	DP 30 MPa + CIP 300 MPa	10°C/min to 1600°C, 30°C/min to 1900°C, 240 mins dwell at	99-100	15

			1900 ⁰ C (PS)		
3.5 wt% B ₄ C + 2.5 wt% C	0.3	Aqueous freeze form extrusion	120 min dwell at 2000 ⁰ C (PS)	96%	20

DP = dry pressed, CIP = cold isostatic pressed, PS = pressureless sintering, HP = hot pressing, SPS = spark plasma sintering.

*the heating rate or soaking time was not reported.

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