# ROOM-TEMPERATURE INJECTION MOLDED, PRESSURELESSLY SINTERED BORON CARBIDE

by

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## **A Dissertation**

Submitted to the Faculty of Purdue University In Partial Fulfillment of the Requirements for the degree of

**Doctor of Philosophy** 



School of Materials Engineering West Lafayette, Indiana August 2021

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Dedicated to my parents, who told a skeptical twelve-year-old he would enjoy college so much that he would go for eight years instead of just four like normal people.

# ACKNOWLEDGMENTS

I would like to thank Rodney Peterson and the Office of Naval Research (Award Number N000141712155), through whom portions of this research was funded. I would also like to thank Adam Maisano, Bruce Tretheway, the Johns Hopkins Applied Physics Laboratory and the Department of State (Contract No. SAQMMA14D0135) through whom other portions of this research were funded. I would also like to thank the National Defense Science and Engineering Graduate Fellowships program who provided funding to me during my time at Purdue. I would like to thank the School of Materials Engineering staff, notably Timothy Vanmeter, Shannon Heidrick, Jameson Root, and Talukder Alam, for their equipment expertise and troubleshooting assistance. I would also like to thank the undergraduate students who have assisted me through the past four years: Benjamin Stegman, Yew Wei See, and Lillian Koczwara. And a special thanks to Andrew Schlup and Tess Marconie, without whom this research would not have been possible.

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## ABSTRACT

Boron carbide (B<sub>4</sub>C) is a promising material for ballistic armor applications due to its extreme hardness and low density. However, utilizing these unique properties requires sintering B<sub>4</sub>C components to full density. This dissertation explores methods for sintering B<sub>4</sub>C to full near fully density without the application of external pressure. These pressureless sintering methods allow for B<sub>4</sub>C to be produced in a variety of geometries that would be impossible to achieve using current industrial methods. Highly loaded (51 vol. %) aqueous B<sub>4</sub>C suspensions were developed and injection molded at room temperature followed by pressureless sintering up to 2075 °C. Three different sintering aids (Y<sub>2</sub>O<sub>3</sub>, Al, and Al<sub>2</sub>O<sub>3</sub>) were used to aid the densification process. B<sub>4</sub>C parts were sintered to high density (up to 97.7 % relative density) and high hardness values (up to 3200 Vickers). The flexural strength of the samples was limited by grain pullout during polishing of the tensile surface; the strength was correlated to the maximum grain pullout flaw measured at the intersection of the tensile surface and the fracture surface ( $R^2 > 0.98$ ). Five compositions (undoped B4C, 5 wt. % WC, 5 wt. % WC + 10 wt. % Y2O3, 10 wt. % Y2O3, and 10 wt. % ZrB2) were studied for their relative density (up to 96.0 %), hardness (up to 3458 Vickers), and differential efficiency factor (up to  $3.7 \pm 0.7$ ) during depth of penetration ballistic impact testing. The differential efficiencies of the samples were comparable with a commercially hot-pressed sample but were limited by their relative densities as opposed to their hardnesses, indicating that increasing densities through different sintering parameters could further improve performance relative to commercial armor alternatives. Potentially bonding B<sub>4</sub>C either in-situ or post-sintering is also explored as a method of overcoming the critical cracking thickness of B<sub>4</sub>C suspensions. Powder mixtures of  $B_4C + Y_2O_3$  were used during the sintering process, with low concentrations of  $Y_2O_3$ yielding the most complete bond formation. Powder mixtures of SiC + C + Si with additional Si infiltration were used create bonds between B<sub>4</sub>C with a strong cohesive interface, but samples cracked due to a mismatch in thermal expansion coefficients between B<sub>4</sub>C and the bonding layer. This dissertation demonstrates the potential of room-temperature injection molding and pressureless sintering as an alternative means to produce highly dense B<sub>4</sub>C components with complex geometries not possible in traditional processing methods.

# **1. INTRODUCTION**

## 1.1 Boron Carbide Properties and Motivation

Boron carbide (B<sub>4</sub>C) is known for its extreme hardness (>30 GPa Vickers), high melting point (2450 °C), and low density (2.52 g/cm<sup>3</sup>), among other favorable properties. It is widely used in abrasive applications such as sand-blasting nozzles, grinding and polishing media, water jet cutter nozzles, and wear-resistant coatings. The high hardness of B<sub>4</sub>C also makes it ideal material for lightweight armor applications. Due to the neutron absorption cross-section of boron, B<sub>4</sub>C is also used as a neutron absorber in nuclear reactors<sup>1</sup>.

The beneficial properties of  $B_4C$  can only be realized using pore-free, fully dense bodies. Like other ceramics, perhaps even more so due to its extreme hardness, bulk machining of  $B_4C$  is impractical and expensive. Instead, "green-bodies" of  $B_4C$  are prepared using a wide variety of powder processing techniques like tape casting, slip casting, gel casting, and injection molding<sup>2–6</sup>. The green-bodies are then sintered to full density. However, sintering  $B_4C$  is notoriously difficult. Due to its strong covalent bonds, densification mechanisms like grain boundary and bulk diffusion only become effective at temperatures above 2000 °C. However, before these can begin, several other mechanisms occur at lower temperatures (<1800 °C) that can inhibit the densification of  $B_4C$ .

To understand these mechanisms, it is important to note that during the production of B<sub>4</sub>C, a thin layer of boria (B<sub>2</sub>O<sub>3</sub>) forms on the surface of B<sub>4</sub>C particles<sup>7</sup>. In addition, B<sub>2</sub>O<sub>3</sub> has a significantly lower melting point compared to B<sub>4</sub>C (450 °C), and even vaporizes below routine sintering temperatures (1860 °C). While the exact role of B<sub>2</sub>O<sub>3</sub> in the sintering process is unknown, the literature suggests that its role is twofold. First, the presence of a layer of B<sub>2</sub>O<sub>3</sub> prohibits B<sub>4</sub>C particles from contracting one another at low temperatures<sup>8</sup>. Without contact between particles, there is no way for densification processes to occur. Second, B<sub>2</sub>O<sub>3</sub> promotes surface-to-surface diffusion between B<sub>4</sub>C particles. The exact method through which this occurs is unknown, but there have been several proposed mechanisms. Due to the low melting point of B<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C could dissolve into a B<sub>2</sub>O<sub>3</sub> liquid and then precipitate on neighboring particles<sup>8,9</sup>. Alternatively, Dole et al. suggested the high vapor pressure of B<sub>2</sub>O<sub>3</sub> above 1500 °C could result in oxide gases such as CO and BO participating in vapor-phase surface-to-surface transport<sup>9</sup>. No matter which method,

the result is clear: undoped  $B_4C$  undergoes significant particle coarsening at temperatures under 2000 °C, which limits the ability to sinter  $B_4C$  to nearly full densities.

Historically, the challenges associated with sintering B<sub>4</sub>C have been overcome through the addition of pressure to the sintering process, by either hot-pressing or hot isostatic pressing (HIP). In hot-pressing, powders are packed into a die and then sintered while a uniaxial pressure is applied. The applied pressure enhances grain boundary diffusion kinetics, results in improved densification. Typically B<sub>4</sub>C is hot pressed at temperatures at or above 2100 °C and at pressures above 30 MPa to achieve full densities<sup>10,11</sup>. The drawback to hot-pressing is that only simple, geometric shapes can be produced; any complex features or internal structures will simply be eliminated by the high uniaxial pressures involved. HIP, unlike hot-pressing, is capable of producing complex shapes. In HIP, parts are pre-sintered to eliminate all open porosity (for  $B_4C$ , 93-97% of theoretical density)<sup>12</sup>. They are then placed in an autoclave and heated in argon gas to extremely high temperatures and pressures. The pre-sintering is required to create a large pressure differential between the surface of the part and internal, closed porosity. The result is a fully dense (>99% of theoretical density) part. However, HIP is extremely energy intensive. For B<sub>4</sub>C, temperatures of up to 2000 °C and pressures of 70-200 MPa are required<sup>12,13</sup>. In order to produce commercially viable B<sub>4</sub>C components with complex geometries, methods other than pressure-assisted sintering must be used. Pressureless sintering of B<sub>4</sub>C allows the use of a wide variety of techniques for green-body formation, such as tape casting, slip casting, gel casting, and injection molding. However, the challenge of densifying these parts while maintaining their complex features remains.

Another necessary component to consider for densifying  $B_4C$  to full density is the use of sintering aids. Sintering aids have been widely shown to improve the densification, microstructure, and mechanical properties of  $B_4C^{6,8,14,15}$ . Carbon has been the most widely used sintering aid for  $B_4C$  industrially. Alexander et al. found that adding small amount of carbon nanotubes (< 5 vol. %) during hot pressing allowed them to achieve greater than 99% of theoretical densities at only 1950 °C while also improving flexural strength and hardness<sup>16</sup>. Lee and Speyer added carbon to pressurelessly sintered  $B_4C$  to produce parts of greater than 98 % theoretical density<sup>8</sup>. Bougoin and Thevenot added polycarbosilane to pressurelessly sintered  $B_4C$  to produce dense composites of  $B_4C$  and silicon carbide (SiC)<sup>17</sup>. It has been proposed that carbon benefits densification by reacting with the layer of  $B_2O_3$  on particle surfaces, allowing earlier contact between particles<sup>8,9</sup>. A wide variety of other possible sintering aids have also been proposed. Titanium boride (TiB<sub>2</sub>)

has been used in pressureless and spark plasma sintering to produce dense components of up to 98 % theoretical density<sup>18,19</sup>. Mashhadi et al. used small additions of aluminum (4 wt. %) to produce parts up to 94% dense<sup>20</sup>. Of particular interest are sintering aids that undergo a reaction during the sintering process to form new phases. These phases are often liquid at sintering temperatures, and have a strong, beneficial effect on sintering.

#### **1.2 Liquid Phase Sintering of Boron Carbide**

Commonly during liquid-phase sintering, particles of a distinct second phase are added to the original green-body of packed particles. This second phase has a lower melting temperature than the bulk phase and forms a liquid during the heating process. Alternatively, as is commonly the case for B<sub>4</sub>C and its sintering aids, a reaction can occur between the first and second phase that results in a lower melting point phase forming in-situ during the sintering process. Several systems with potential for liquid-phase-forming reactions with  $B_4C$  have been studied, typically either metal oxides or borides. These compounds undergo reactions with B<sub>4</sub>C and/or the thin layer of B<sub>2</sub>O<sub>3</sub> on particle surfaces to form liquid phases containing a metal, boron, and carbon. Examples include aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), yttrium oxide (Y<sub>2</sub>O<sub>3</sub>), titanium oxide (TiO<sub>2</sub>), titanium boride  $(TiB_2)$  chromium carbide  $(Cr_3C_2)$ , chromium oxide  $(Cr_2O_3)$  and zirconium oxide  $(ZrO_2)^{14,15,18,19,21-10}$ <sup>24</sup>. The addition of a liquid phase allows for several additional densification mechanisms when compared to solid-state sintering. One notable benefit of this added liquid phase over solid-state mechanisms is faster sintering. Liquid phase sintering is typically considered in three stages: liquid flow particle rearrangement, particle dissolution and reprecipitation, and solid-state controlled sintering. The initial densification through particle rearrangement and particle dissolution and reprecipitation happen extremely fast compared to solid state sintering reactions. A homogenous microstructure in the green-body before sintering has been found to give the best densification results<sup>25</sup>. Figure 1-1 provides an overview of the microstructure changes that occur during liquidphase sintering $^{26}$ .



Figure 1-1 Illustration of microstructure evolution during liquid phase sintering of B<sub>4</sub>C. Adapted from German<sup>26</sup>.

## Liquid Flow Particle Rearrangement

The first stage of liquid-phase sintering takes place at the melting point of the liquid (or at the temperature where the reaction forming the liquid phase occurs, which depends on the sintering aid used). The liquid phase is pulled into the regions surrounding particle necks and the pores between particles due to capillary pressures, but also forms a continuous network of liquid between these areas by coating the surface of the solid particles<sup>27,28</sup>. Good wetting (i.e. a low contact angle) between the liquid phase and the solid particles is for the formation of the continuous liquid network<sup>25</sup>. Both titanium and aluminum have been found to have good wetting behavior with B<sub>4</sub>C due to their ability to form new boride or carbide phases at the interface<sup>29,30</sup>. Lee and Kim sintered a reaction couple of B<sub>4</sub>C and Al<sub>2</sub>O<sub>3</sub> at 2150 °C and found there to be good wetting between B<sub>4</sub>C particles and the resulting Al-B-C phase<sup>24</sup>. The contact angle is determined by the equation<sup>25</sup>:

$$\theta = \arccos\left(\frac{\gamma_{SV}}{\gamma_{LV}} - \frac{\gamma_{SL}}{\gamma_{LV}}\right)$$

Where  $\theta$  is the contact angle,  $\gamma_{SV}$  is the solid-vapor interfacial energy,  $\gamma_{SL}$  is the solid-liquid interfacial energy, and  $\gamma_{LV}$  is the liquid-vapor interfacial energy. With a low contact angle, the liquid spreads out over the solid particles and forms a liquid matrix where capillary pressure is working to close the internal pores. This capillary pressure has two effects – further driving densification and allowing rearrangement of particles<sup>28,31</sup>. The capillary pressure is determined by the equation:

$$P = \frac{-\gamma_{LV}}{r}$$

Where P is the capillary pressure and r is the radius of the liquid pore. If the capillary pressure exerted is great enough, the bridges between particles can be broken, and the particles can rearrange in a way that reduces the overall porosity in the system<sup>31</sup>. How much densification can be induced depends on several factors: the amount of liquid content, the size and shape of the solid particles, and the solubility of the solid particles in the liquid<sup>26</sup>. As higher liquid content is typically beneficial to densification (up to 35 vol. %)<sup>28</sup>, efforts to liquid-phase sinter B<sub>4</sub>C have used up to 30 wt. % sintering aid depending on the material chosen<sup>14,21,32</sup>. However, above a certain level of liquid, compact slumping becomes an issue<sup>26</sup>.

#### Particle Dissolution and Reprecipitation

The second phase of liquid-phase sintering, particle dissolution and reprecipitation, occurs during and after particle rearrangement. Particle dissolution requires that there be at least *some* solubility of the solid particles in the liquid phase. In the previously mentioned  $B_4C-Al_2O_3$  reaction couples, there was carbon and boron detected in the liquid phase after sintering<sup>24</sup>. Li et al. studied the addition of  $Cr_3C_2$  to  $B_4C$  and found evidence of small amounts of carbon within a post-sintering  $CrB_2$  phase, indicating that  $B_4C$  is soluble in the liquid phase formed<sup>21</sup>. Goldstein et al. found both  $YB_2C$  and  $YB_2C_2$  in sintered microstructures after using  $Y_2O_3$  as a sintering aid, showing that  $B_4C$  is soluble in that system as well<sup>14</sup>. There is an argument to be made that the presence of carbon and boron in these reaction-formed phases could be due to a solid state reaction, as suggested by

Goldstein et al.<sup>14</sup>; however, the highly irregular shape of the grains indicate that there was in fact a liquid phase present (Figure 4)<sup>14,21</sup>.

After particles begin to rearrange, they are usually separated by thin layers of the liquid phase<sup>28</sup>. The capillary pressure created by the liquid phase is supported by the regions where particles are contacting each other. The increase in pressure at these contact points increases the local solubility of the solid particles<sup>28</sup>. This causes solid atoms to dissolve into the liquid and diffuse away from the contact points due to the concentration gradient within the liquid. The solid atoms then reprecipitate away from the contact points where the local pressure is lower. Compared to solid-state mass transport mechanisms like grain boundary diffusion and bulk diffusion this process is kinetically fast<sup>26</sup>. "Contact flattening" not only increases density by decreasing the average particle-to-particle distance, but also flattens out irregular particle features making particle rearrangement easier<sup>25,26</sup>. After the initial surge in particle rearrangement due to the formation of the liquid phase, contact flattening is the major driving force for particle rearrangement.<sup>31</sup>. Particle dissolution and reprecipitation continues after the end of particle rearrangement, as the shape of particles is altered to allow for the elimination of pores and tighter particle packing<sup>25</sup>. Not accounting for particle rearrangement, densification during this phase occurs at a rate according to the equation<sup>29</sup>:

$$\frac{\Delta V}{V_0} \alpha \frac{t^{1/3}}{r^{4/3}}$$

Where  $\frac{\Delta V}{V_0}$  is the change in volume, t is the sintering time, and r is the average particle radius.

## Solid-State Controlled Sintering

The final stage of liquid-phase sintering is solid-state controlled sintering. This stage is functionally similar to traditional sintering. The solid particle network is now rigid enough to overcome the capillary force from the liquid phase<sup>31</sup>, so particle rearrangement has ceased. The mass transport mechanisms found in traditional sintering, such as grain boundary diffusion and bulk diffusion, become the dominating driving forces for densification. The rate of densification during this phase slows down to rates associated with solid-state sintering processes. Large

particles begin to coarsen at the expense of smaller particles due to surface-surface diffusion through the liquid phase<sup>26</sup>. During cooling, the liquid phase solidifies in a network surrounding the solid particles.

# 2. SINTERING AID SELECTION

## 2.1 Contributions

The individuals listed below contributed the following tasks:

• Erich Weaver: sample preparation, pressureless sintering, density measurements, polishing, optical microscopy, scanning electron microscopy, hardness testing, data analysis

#### 2.2 Introduction

There are a multitude of sintering aids for B<sub>4</sub>C that have been studied in the literature<sup>8-12,14-</sup><sup>24</sup>. These studies cover a wide variety of approaches, from low content additives to solid state sintering aids, to liquid state reactions, to composites containing 40 wt. %+ of additives<sup>8-12,14,24</sup>. However, the sintering conditions (ramp rate, ultimate sintering temperature, isothermal hold time, sintering atmosphere, pressure, etc.) are inconsistent between each study, making it difficult to compare results. In addition, the high-temperature furnaces necessary to reach the extreme temperatures required for pressureless sintering can have individual variations; between the two high-temperature furnaces used in this thesis there was an approximately 200 °C difference in the ultimate temperature required to reach the same relative density using identical compositions. While not necessarily likely, it is conceivable that such differences could persist throughout the literature. Therefore, to determine the most promising sintering aids to examine further, it is necessary to compare sintering aids under uniform conditions. Due to this dissertation's interest in low absolute weight ballistic armor, an attempt was made to keep the theoretical density of each composition low – this occasionally resulted in additive content significantly lower than previously published works.

## 2.3 Experimental Approach

#### Materials

Boron carbide powder (HS Grade, H.C. Stark, Hermsdorf, Germany) was used in this study; these powders had a company specified mean particle size ( $d_{50}$ ) of 1.1 µm and a specific surface area (SSA) of 17 m<sup>2</sup>/g. A wide variety of powders were used as sintering aids in this study: Al

powders (US Research Nanomaterials, Houston, TX) with a d<sub>50</sub> of 1 µm, Al<sub>2</sub>O<sub>3</sub> powders (A 16 SG, Almantis, Ludwigshafen, Germany) with a d<sub>50</sub> of 0.4 µm, B powders (Millipore Sigma, St. Louis, MO) with a d<sub>50</sub> of 0.9 µm, C powders (Marineland, Blacksburg, VA) with a d<sub>50</sub> of 1.5 µm, Si powders (Millipore Sigma, St. Louis, MO) with a d<sub>50</sub> of 1 µm, SiC powders (US Research Nanomaterials, Houston, TX) with a d<sub>50</sub> of 2 µm, SiO<sub>2</sub> powders (Millipore Sigma, St. Louis, MO) with a d<sub>50</sub> of 0.5 µm, Si<sub>3</sub>N<sub>4</sub> powders (H.C. Stark, Hermsdorf, Germany) with a d<sub>50</sub> of 2 µm, Ti powders (Millipore Sigma, St. Louis, MO) with a d<sub>50</sub> of <5 µm, TiB<sub>2</sub> powders (Millipore Sigma, St. Louis, MO) with a d<sub>50</sub> of 1 µm, WC powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, Y<sub>2</sub>O<sub>3</sub> powders (REacton 99.99 %, Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YSZ (3 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (3 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, SIZ (3 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (3 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (3 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (3 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (3 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (3 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (3 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (5 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (5 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (5 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (5 mol %) powders (Alfa Aesar, Tewksbury, MA) with a d<sub>50</sub> of 1 µm, YZ (5 mol %) powders (5 µm, and ZrO<sub>2</sub> powders (Millipore Sigma, St. Louis, MO) with a d<sub>50</sub> of 1 µm.

#### **Pressureless Sintering**

A powder mix for each composition was prepared by ball-milling for 24 hours. A minimum of five pellets were prepared by loading approximately 2 grams of the ceramic powder mixture into a 15 mm diameter steel pellet die, and then uniaxially pressed at 34.5 MPa for 20 seconds. Samples were then placed in a graphite crucible and sintered in a Centorr Testor Furnace (Centorr Vacuum Industries, Nashua, NH) in a flowing Ar atmosphere purified in a 2G-100-SS Centorr Gettering Furnace to less than 10<sup>-7</sup> ppm O<sub>2</sub>. Heating at a rate of 25 °C/min to 2075 °C, followed by a 1 hr. hold, was used to densify the parts.

In addition, several sintering parameters were evaluated for their effect on final sintered density: ramp rate (10- 50 °C/min, isothermal hold time (1-4 hrs.), and atmospheric conditions (Ar, Ar with a 1 hr. hold at 1350 °C, and a 1 hr. hold in vacuum at 1350 °C). The isothermal holds at 1350 °C were tested as an attempt to evaporate the layer of  $B_2O_3$  on  $B_4C$  powder to improve sintering behavior. These experiments were performed in a Carbolite Gero LHTG 200-300/30-1G Furnace (Carbolite Gero USA, Newton, PA) with an ultimate sintering temperature of 2350 °C.

## Characterization

The apparent density of each sample was determined using the Archimedes' method. The theoretical density for each composition was calculated using the rule of mixtures with densities of 2.52 g/cm<sup>3</sup>, 14.6 g/cm<sup>3</sup>, 2.70 g/cm<sup>3</sup>, 3.95 g/cm<sup>3</sup>, 2.3 g/cm<sup>3</sup>, 2.25 g/cm<sup>3</sup>, 2.33 g/cm<sup>3</sup>, 3.21 g/cm<sup>3</sup>, 2.65 g/cm<sup>3</sup>, 3.17 g/cm<sup>3</sup>, 4.50 g/cm<sup>3</sup>, 4.52 g/cm<sup>3</sup>, 4.93 g/cm<sup>3</sup>, 4.23 g/cm<sup>3</sup>, 15.63 g/cm<sup>3</sup>, 5.01 g/cm<sup>3</sup>, 6.05 g/cm<sup>3</sup>, 6.08 g/cm<sup>3</sup>, and 5.86 g/cm<sup>3</sup> used for B<sub>4</sub>C, Al, Al<sub>2</sub>O<sub>3</sub>, B, C, Si, SiC, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, Ti, Tib<sub>2</sub>, TiC, TiO<sub>2</sub>, WC, Y<sub>2</sub>O<sub>3</sub>, YSZ (3 mol %), ZrB<sub>2</sub>, and ZrO<sub>2</sub> respectively.

Samples of particular interest were mounted and polished, finishing with a 1 µm diamond suspension. Hardness testing was performed on a Wilson Hardness Tukon 1202 using a Vickers head with a test force of 9.81 N and a hold time of 10 s in accordance with ASTM C1327-15. A minimum of ten indents were optically measured for each sample. After testing, samples were optically imaged on an Olympus GX41 microscope (Olympus Corporation, Lombard, IL).

#### 2.4 Results and Discussion

#### Effects of Sintering Aid Choice on Density

A summary of the measured relative densities from B<sub>4</sub>C pellets with various sintering aids can be found in **Table 2-1**. While all sintering aids were beneficial to sintering behavior, the effects of each sintering aid under these uniform conditions were not equal. Several sintering aids were identified as candidates for further study: Al, Al<sub>2</sub>O<sub>3</sub>, WC, Y<sub>2</sub>O<sub>3</sub>, and ZrB<sub>2</sub>. TiB<sub>2</sub> and TiC were discarded because while their densities were high, there was a significant higher standard deviation when compared to other sintering aids. This is potentially due to the large d<sub>50</sub> of those powders (2  $\mu$ m for TiB<sub>2</sub> and 5  $\mu$ m for TiC). ZrO<sub>2</sub> was discarded because despite having these highest relative density in this study, the amount of additive required significantly increased the absolute density of the resulting pellets. Studies in literature see the highest sintered densities of B<sub>4</sub>C with around 25 wt. % ZrO<sub>2</sub>; this increase in weight was deemed undesirable for lightweight armor applications<sup>12</sup>.

		Most		Average	
		Effective	Theoretical	Bulk	Average
	Concentration	Concentration	Density	Density	Relative
Sintering Aid	Range (wt. %)	(wt. %)	$(g/cm^3)$	$(g/cm^3)$	<b>Density</b> (%)
Al	1-3	1	2.62	2.50	$95.5\pm0.2$
$Al_2O_3$	1-5	1	2.63	2.48	$94.4\pm0.3$
В	1-3	2	2.62	2.45	$93.7\pm0.7$
С	1-3	2	2.62	2.47	$94.2\pm0.5$
Si	1-3	2	2.62	2.47	$94.3\pm0.1$
SiC	5-15	10	2.67	2.44	$91.3\pm0.7$
$SiO_2$	1-5	3	2.62	2.42	$92.5\pm0.4$
$Si_3N_4$	1-3	3	2.64	2.48	$93.9\pm0.3$
Ti	1-3	2	2.65	2.47	$93.3\pm0.5$
$TiB_2$	1-5	5	2.68	2.52	$94.4 \pm 1.5$
TiC	1-5	5	2.69	2.56	$95.5\pm1.3$
TiO <sub>2</sub>	1-5	3	2.65	2.48	$93.6\pm0.3$
WC	5-15	5	2.74	2.59	$94.5\pm0.5$
$Y_2O_3$	5-15	10	2.77	2.59	$95.5\pm0.5$
YSZ (3 mol %)	1-5	1	2.64	2.39	$90.4\pm0.6$
$ZrB_2$	5-15	5	2.71	2.57	$95.1\pm0.5$
$ZrO_2$	5-15	15	2.82	2.71	$96.3\pm0.1$

**Table 2-1** Sintered relative densities of B<sub>4</sub>C pellets with added sintering aids.

#### In-Situ Reactions and Effects on Microstructure

Unlike many ceramics, B<sub>4</sub>C does not exist as a line compound but as variable compositions ranging from B<sub>4</sub>C to B<sub>13</sub>C<sub>2</sub>. Most industrially available B<sub>4</sub>C powder contains excess C in the form of free graphite. This graphite is clearly visible in **Figure 2-1** as spherical graphite inclusions. These inclusions have been seen in previous literature and noted to have no noticeable effect on macro-scale mechanical properties<sup>27</sup>. It is interesting to note that there are significantly more inclusions found in the microstructure sintered at 2375 °C compared to that sintered at 2350 °C. The increased grain size in the 2375 °C microstructure results in a significantly reduced grain boundary area; it is possible that free graphite segregates towards grain boundaries when they are available.



**Figure 2-1** Grain structure of B<sub>4</sub>C pellets sintered with 5 wt. % WC at different temperatures. Increasing temperature increased grain size and resulted in more carbon inclusions.

As mentioned previously, Goldstein et al. found both YB<sub>2</sub>C and YB<sub>2</sub>C<sub>2</sub> in sintered microstructures after using Y<sub>2</sub>O<sub>3</sub> as a sintering aid, indicating that Y<sub>2</sub>O<sub>3</sub> reacts with B<sub>4</sub>C during the sintering process. An additional effect of this is that Y<sub>2</sub>O<sub>3</sub> reacts with excess carbon found in commercial B<sub>4</sub>C powder, reducing the numbers of carbon inclusions in the final microstructure. **Figure 2-2** shows sintered B<sub>4</sub>C microstructures containing additions of WC and WC + Y<sub>2</sub>O<sub>3</sub>. There are significantly fewer carbon inclusions in the microstructure containing Y<sub>2</sub>O<sub>3</sub>. There is also a noticeable effect in the Vickers hardness of these materials. **Figure 2-3** shows the measured relative density and Vickers hardness of B<sub>4</sub>C pellets containing additions of WC and Y<sub>2</sub>O<sub>3</sub>. When transitioning through a WC  $\rightarrow$  WC + Y<sub>2</sub>O<sub>3</sub>  $\rightarrow$  Y<sub>2</sub>O<sub>3</sub> spectrum of sintering aids, hardness increases despite relative density increasing. This is contrary to expected behavior where hardness increases in tandem with relative density. The likely explanation is that because graphite is extremely soft compared to B<sub>4</sub>C it is reducing the measured Vickers hardness of not affect macro-scale mechanical properties of B<sub>4</sub>C, in a localized measurement like microhardness (Vickers indents on B<sub>4</sub>C are on the range of 15-25 µm) the carbon inclusions are relevant enough to have a significant effect.



Figure 2-2 Carbon inclusions in  $B_4C$  microstructures sintered with WC and WC +  $Y_2O_3$  additions.



Figure 2-3 Relative density and hardness of B<sub>4</sub>C pellets sintered with WC and Y<sub>2</sub>O<sub>3</sub> additions.

## Effects of Sintering Parameters

**Figure 2-4** shows the effect of heating rate during sintering on the final mechanical properties of  $B_4C$  pellets. When sintering  $B_4C$ , it is intuitive that a faster ramp rate should improve mechanical properties, as there is less time for grain coarsening to occur before reaching the ultimate sintering temperature. That is the case here, with the lowest sintering rate of 10 °C/min resulting in lower relative density and hardness values than higher heating rates. There was no difference between heating rates of 25 °C/min and 50 °C/min; while the heating rate doubles, the practical difference in time spent at coarsening temperature is only a few minutes. Also intuitively, increasing isothermal hold time at the ultimate sintering temperature also increases relative density (see **Figure 2-5**).



**Figure 2-4** Effect of heating rate during sintering on relative density and hardness of B<sub>4</sub>C pellets with 5 wt. % WC and 10 wt. % Y<sub>2</sub>O<sub>3</sub> additions.



**Figure 2-5** Effect of isothermal hold time on relative density of B<sub>4</sub>C pellets with 5 wt. % WC and 10 wt. % Y<sub>2</sub>O<sub>3</sub> additions.

One of the main concerns for pressurelessly sintering  $B_4C$  is the presence of  $B_2O_3$  on  $B_4C$  particle surfaces. This layer inhibits contact between  $B_4C$  particles and promotes surface-tosurface diffusion between  $B_4C$  particles below temperatures where densification mechanisms occur<sup>8,9</sup>. While there are several potential avenues for removing  $B_2O_3$  or mitigating its effects, this study explored the use of an intermediate isothermal to great effect. **Figure 2-**6 shows the relative densities of  $B_4C$  pellets sintered in different atmospheric conditions. Compared to sintering with no isothermal hold time, an isothermal hold at 1350 °C in flowing argon increased the relative density of sintered  $B_4C$  parts significantly. Additionally, pulling a vacuum during the hold increased density further and significantly increased Vickers hardness as well. Both these improvements are likely due the evaporation of  $B_2O_3$  during the hold, leading to less particle coarsening during early stages of the sintering run, as smaller particles are known to sinter to greater densities.



**Figure 2-6** Effect of atmosphere conditions on relative density and hardness of B<sub>4</sub>C pellets with 5 wt. % WC and 10 wt. % Y<sub>2</sub>O<sub>3</sub> additions.

## 2.5 Conclusions

Pellets of  $B_4C$  containing various sintering aid additives were sintered at 2075 °C for 1 hr.. Five sintering aids: Al, Al<sub>2</sub>O<sub>3</sub>, WC, Y<sub>2</sub>O<sub>3</sub>, and ZrB<sub>2</sub> were identified as additives that significantly improved relative density while keeping absolute density low. Y<sub>2</sub>O<sub>3</sub> reacted with excess carbon in commercial B<sub>4</sub>C powder which reduced the number of carbon inclusions in sintered microstructures and improved microhardness. A fast heating rate of at least 25 °C/min with a hold time of 4 hours were found to improve relative density in sintered microstructures. An intermediate hold at 1350 °C in either argon or vacuum evaporated the B<sub>2</sub>O<sub>3</sub> layer on the surface of B<sub>4</sub>C particles, improving the relative densities and microhardness of sintered parts.

# 3. MECHANICAL PROPERTIES OF ROOM-TEMPERATURE INJECTION MOLDED, PRESSURELESSLY SINTERED BORON CARBIDE

A version of this chapter has been submitted to Ceramics International. Citation: E.A. Weaver, B.T. Stegman, R.W. Trice, J.P. Youngblood, "Mechanical Properties of Room-Temperature Injection Molded, Pressurelessly Sintered Boron Carbide", Submitted to *Ceramics International* (2021).

#### 3.1 Contributions

The individuals listed below contributed the following tasks:

- Erich Weaver: Suspension preparation, suspension characterization, injection molding, binder burnout, pressureless sintering, density measurements, scanning electron microscopy, optical measurements, x-ray diffraction, flexure testing, hardness testing, grain size measurements, data analysis
- Benjamin Stegman: Suspension preparation, injection molding, density measurements, grinding and polishing, optical microscopy, optical measurements

### 3.2 Introduction

Boron carbide (B<sub>4</sub>C) is known for its high hardness (>3200 Vickers), high melting point (2450 °C), and low density (2.52 g/cm<sup>3</sup>).<sup>12</sup> It is widely used in abrasive applications such as sandblasting nozzles, grinding and polishing media, water jet cutter nozzles, and wear-resistant coatings. The high hardness of B<sub>4</sub>C also makes it an ideal material for lightweight armor applications. Due to the neutron absorption cross-section of boron, B<sub>4</sub>C is also used in nuclear reactors<sup>1</sup>. Unfortunately, the beneficial properties of B<sub>4</sub>C can only be realized using nearly porefree, fully dense bodies. However, sintering B<sub>4</sub>C is challenging due to densification mechanisms, such as grain boundary and bulk diffusion, becoming effective only at temperatures >2200 °C. Historically, the challenges associated with sintering B<sub>4</sub>C have been overcome through the addition of pressure during the sintering process, typically through hot-pressing<sup>12</sup>. The drawback to hot-pressing is that only simple geometric shapes can be produced; any complex features or internal structures will be eliminated by the high uniaxial pressures involved. To produce commercially viable B<sub>4</sub>C components with complex geometries, methods other than pressureassisted sintering must be used.

Injection molding is an appealing method for producing ceramic components due to the ability to produce many near-net shaped parts quickly at low cost<sup>4,34,35</sup>. Traditional injection molding is accomplished by heating a polymer/ceramic mixture, injecting it into a mold, then removing the heat<sup>34,35</sup>. Ceramics such as SiO<sub>2</sub>, SiC, and Al<sub>2</sub>O<sub>3</sub> have been injection molded in the past by blending up to 30 vol.% of the desired ceramic powder with a polymer<sup>34</sup>. However, this approach to injection molding requires multiple heating and cooling cycles, along with lengthy polymer burnout cycles prior to sintering. Our prior work has developed an alternative method for injection molding ceramic suspensions that removes or reduces the limitations of traditional injection molding.<sup>4,36-38</sup>

Beginning with highly loaded (>50 vol. %) water-based suspensions that are flowable at room temperature, the rheological properties of the ceramic-polymer suspension is designed to be yield-pseudoplastic. These suspensions will not flow until their yield point is reached, at which point they become shear thinning<sup>39</sup>. This unique behavior allows the suspension to both flow into the mold at room temperature and retain its shape after removal of the stress. Parts made this way are subsequently dried, and de-molded. Less than 5 vol.% polymer binder is added, greatly simplifying the burnout process<sup>6,37,38</sup>. Extensive work has been performed to develop a suspension system for  $B_4C^6$ . The suspensions are electrosterically stabilized using a combination of polyethylenimine (PEI) and hydrochloric acid (HCl) and are robust in that small amounts of sintering aids can be added without causing drastic changes in suspension rheology<sup>6</sup>. However, the challenge of densifying these parts while maintaining their complex features remains.

Even though injection molding offers a route to complex shapes, unfortunately, hotpressing to achieve high density is not a viable method in these cases. Thus, these shapes should be densified with a method such as pressureless sintering to maintain the shape. In many systems, sintering aids are a potential means of densifying a ceramic at lower temperature. Sintering aids have also been widely shown to improve the densification, microstructure, and mechanical properties of  $B_4C^{6,8,14,15}$ . Carbon has been the most widely used sintering aid for  $B_4C$  industrially. Lee and Speyer added carbon to pressurelessly sinter  $B_4C$  to produce parts of greater than 98 % theoretical density<sup>8</sup>. Bougoin and Thevenot added polycarbosilane to pressurelessly sintered  $B_4C$  to produce dense composites of  $B_4C$  and silicon carbide (SiC)<sup>17</sup>. It has been proposed that carbon

benefits densification by reacting with the layer of  $B_2O_3$  on particle surfaces, allowing earlier contact between particles<sup>8,9</sup>. Sintering aids that undergo a reaction during the sintering process to form new phases are of interest as these phases are often liquid at the sintering temperature, and have a beneficial effect on densification.

Commonly during liquid-phase sintering, particles of a distinct second phase are added to the B<sub>4</sub>C powder during green body formation. This second phase has a lower melting temperature than the bulk phase and forms a liquid during the heating process. Alternatively, as is commonly the case for B<sub>4</sub>C and its sintering aids, a reaction can occur between B<sub>4</sub>C and the sintering aid that results in a lower melting point phase forming in-situ during the sintering process. Several systems with potential for liquid-phase-forming reactions with B<sub>4</sub>C have been studied, typically either metal oxides or borides. These compounds undergo reactions with B<sub>4</sub>C and/or the thin layer of B<sub>2</sub>O<sub>3</sub> on particle surfaces to form liquid phases containing a metal, boron, and carbon. Examples include aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), yttrium oxide (Y<sub>2</sub>O<sub>3</sub>), titanium oxide (TiO<sub>2</sub>), titanium boride (TiB<sub>2</sub>) chromium carbide (Cr<sub>3</sub>C<sub>2</sub>), chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) and zirconium oxide (ZrO<sub>2</sub>)<sup>14,15,18,19,22-24,40,41</sup>.

Several studies in the literature have noted the beneficial effect of using oxide sintering aids for  $B_4C^{14,15,24,41}$ . Goldstein et al. explored a wide variety of  $B_4C$  + metal oxide composites and reported the in-situ formation of metal boride phases that formed through a reaction between the oxides and  $B_4C^{14}$ . Notably the 8 vol. %  $Y_2O_3$  composition resulted in high density while requiring a relatively small amount of metal oxide. Levin et al. directly studied the effects of both Ti and TiO<sub>2</sub> and found that TiO<sub>2</sub> was more beneficial when compared to Ti when normalized for Ti content<sup>15</sup>. This was attributed to the formation of sub-stoichiometric  $B_4C$  leading to increased carbon and boron diffusion. Mashhadi et al. used small additions of aluminum (4 wt. %) to produce parts up to 94 % dense and saw a notable increase in flexural strength<sup>20</sup>. Kim et al. hot pressed  $B_4C$  with  $Al_2O_3$  additions to nearly full density and reported an increase in hardness and flexural strength<sup>41</sup>.

In this work, room-temperature injection molding of highly loaded (51 vol. %) aqueous  $B_4C$  suspensions was investigated as a method for producing near-net shape  $B_4C$  components. Three sintering aids: Al, Al<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub> were identified for use in this study due to their ability to produce  $B_4C$  components of high density while only requiring small amounts of additives<sup>14,15,20</sup>.

The behavior of these suspensions is characterized, and the microstructure and mechanical properties of the resulting parts is observed and discussed.

#### **3.3** Experimental Approach

## Materials

Boron carbide powder (HS Grade, H.C. Stark, Hermsdorf, Germany) was used in this study; these powders had a company specified mean particle size ( $d_{50}$ ) of 1.1 µm and a specific surface area (SSA) of 17 m<sup>2</sup>/g. Y<sub>2</sub>O<sub>3</sub> powders (REacton 99.99 %, Alfa Aesar, Tewksbury, MA) with a  $d_{50}$ of 4.61 µm and a SSA of 3.8 m<sup>2</sup>/g, were used as a sintering aid. Aluminum powders (US Research Nanomaterials, Houston, TX) with a  $d_{50}$  of 1 µm were also employed in this investigation. Aluminum oxide powders used had a  $d_{50}$  of 0.4 µm and an SSA of 8.4 m<sup>2</sup>/g (A 16 SG, Almantis, Ludwigshafen, Germany).

#### Suspension Preparation and Characterization

**Table 3-1** shows a summary of the different compositions investigated in this study. Throughout the work  $Al_2O_3$  content is controlled so that after undergoing a reaction with  $B_4C$  during sintering the amount of Al remaining is equal to that found in the metallic Al samples. As an example, 1.87 wt.%  $Al_2O_3$  and 1 wt.% Al samples contain the same amount of Al. The small amount of sintering aids used both reduces the amount of variation in suspension rheology and keeps the theoretical density of final sintered parts at a minimum.

Sample Name	Sintering	Sintering Aid	WC-Co	Dispersant	HCl Contont
Sample Name	Ald	Amount	Content	Content	Content
		(wt. %)	(wt. %)	(VOI. %)	(vol. %)
$B_4C$	N/A	N/A	5	3.57	3.57
5 wt. % Y <sub>2</sub> O <sub>3</sub>	$Y_2O_3$	5	5	3.57	3.57
10 wt. % Y <sub>2</sub> O <sub>3</sub>	$Y_2O_3$	10	5	3.57	3.57
15 wt. % Y <sub>2</sub> O <sub>3</sub>	$Y_2O_3$	15	5	3.57	3.57
1 wt. % Al	Al	1	5	3.57	3.57
2 wt. % Al	Al	2	5	3.57	3.57
3 wt. % Al	Al	3	5	3.57	3.57
1.87 wt. %	$Al_2O_3$	1.87	5	3.57	3.57
$Al_2O_3$					
3.71 wt. %	$Al_2O_3$	3.71	5	3.57	3.57
Al <sub>2</sub> O <sub>3</sub>					
5.52 wt. %	$Al_2O_3$	5.52	5	3.57	3.57
Al <sub>2</sub> O <sub>3</sub>					

Table 3-1 Composition of B<sub>4</sub>C suspensions used in injection molding experiments.

Previous work has found that attrition milling  $B_4C$  powders prior to suspension preparation substantially improved suspension rheology by reducing suspension viscosity and yield points<sup>6</sup>. The B<sub>4</sub>C powder was attrition milled in ethanol for 2 hours at 50 rpm using 3 mm tungsten carbide/cobalt (WC-Co) balls as milling media. Due to the hardness difference between B<sub>4</sub>C and WC-Co, the milling media slowly wear down over time and WC is incorporated into the B<sub>4</sub>C powder. The exact amount varies between batches and was determined individually for each batch by weighing the milling media before and after attrition milling. The amount of WC-Co incorporated varied from 3-8 wt. %; individual batches were mixed to normalize the amount of WC-Co in each to have a final composition of 5 wt. % WC-Co.

Our previous study on B<sub>4</sub>C suspensions found that PEI with a molecular weight of 25,000 g/mol acts as an excellent electrostatic dispersant for B<sub>4</sub>C powders<sup>6</sup>. The ideal amount of dispersant was found to be  $1.83 \text{ mg/m}^2$  (relative to the surface area of the ceramic powder). Hydrochloric acid (HCl) was used to modify the pH of the suspensions for increased dispersion. The amounts of PEI and HCl used in this study were both 3.57 vol. %.

Suspensions were prepared by mixing the dispersant and HCl with reverse osmosis (RO) water in a dual-centrifugal speed mixer (DAC 400, Flacktek Inc., Landrum, SC).  $B_4C$  and the sintering aid were then added in small (15-20 g) increments. Mixing increments were performed for 1 minute at 800 rpm followed by 1 min at 1200 rpm, with the total mixing time taking less than

30 minutes. After mixing, five 12.5 mm WC-Co milling media were added, and the suspension was ball milled for approximately 24 hours.

The rheological properties of the suspensions were measured using a Malvern Bohlin Gemini HR Nano rheometer (Malvern Instruments Ltd., Worcestshire, UK) with a CP 4°/40 cone and plate measuring system and a 150  $\mu$ m gap size. Approximately 1 mL of suspension was used for each test with a water trap to prevent the suspension from drying out prematurely during testing. A pre-shear of 1 s<sup>-1</sup> was applied before each test to ensure each sample had an identical shear history. A logarithmic table of shears from 0.005 – 500 s<sup>-1</sup> was applied to measure the viscosity and shear stress of each sample. During room-temperature injection molding the shear rate is estimated to be 10 s<sup>-1</sup> (with a syringe diameter of 2.1 mm and an MTS crosshead speed of 25 mm/min applied to the syringe).

### **Room-Temperature Injection Molding**

**Figure 3-1** provides an overview of the room-temperature injection molding process. All injection molds were made from a polymer resin; this was possible because the suspension was designed to flow at room temperature. A mold, shown in **Figure 3-2**, was designed to produce a rectangular billet green body with dimensions of 7 x 25 x 75 mm. The middle section of the mold was created using a Form 2 (Formlabs, Somerville, MA) stereolithography (SLA) 3-D printer. The design included three 2 mm diameter vents to allow air and excess material to escape during injection molding and an injection port sized to fit a Luer-Lock syringe tip. The top and bottom sections of the mold were cut from an acrylic sheet and had a layer of PTFE tape adhered to the inner surface. Wetted ashless filter paper (Grade 40, Whatman, UK) was applied to the top and bottom sections of the mold to aid the drying process and prevent cracking.



Binder Burnout and Sintering

**Figure 3-1** Summary of the injection molding process. Suspensions are prepared by mixing water, ceramic, powder, and a polymer dispersant. They were then injection molded and allowed to dry before undergoing binder burnout and sintering.



Figure 3-2 A) Three-piece mold used for injection molding and B) assembled view.

B<sub>4</sub>C suspensions were loaded into a 50 mL syringe with a Luer-Lock tip. In an attempt to remove any potential air bubbles introduced during syringe filling, the filled syringe was attached to an empty syringe using a small hose. Air bubbles were removed by passing the suspension between the two syringes. The filled syringe tip was then inserted into the injection port on the mold, and the entire assembly placed in an MTS load frame (MTS Insight 100, MTS Systems Corporation, Eden Prairie, MN). The MTS crosshead speed was set to 25 mm/min, resulting in a total injection time of approximately 1 min. Once injected, the top acrylic plate of the mold was removed to speed the drying process and samples were allowed to air-dry for 45 min prior to carefully removing the top filter paper. Each sample was then placed in a desiccator maintained at 30 % relative humidity by a sulfuric acid and water solution. After 24 h, each sample was completely demolded and placed back in the desiccator to finish drying (approximately 96 h).

## Binder Burnout and Sintering

Once demolded and dried, samples underwent binder burnout to remove all organic compounds. Samples were placed in a tube furnace with flowing Argon (Ar) at a heating rate of 1 °C/min to 500 °C where they were held for 25 hr. A previous study showed thermogravimetric analysis (TGA) results with a complete burn-out of PEI in a flowing Ar atmosphere below 500 °C<sup>10</sup>. Samples were then placed in a graphite crucible and sintered in a Centorr Testor Furnace (Centorr Vacuum Industries, Nashua, NH) in a flowing Ar atmosphere purified in a 2G-100-SS Centorr
Gettering Furnace to less than  $10^{-7}$  ppm O<sub>2</sub>. Heating at a rate of 25 °C/min to 2075 °C, followed by a 4 hr hold, was used to densify the parts.

#### Characterization

After sintering, the triangular runner section of each billet was cut using a diamond-tipped saw blade. These sections were then mounted and polished, finishing with a 1  $\mu$ m diamond suspension. Hardness testing was performed on a Wilson Hardness Tukon 1202 using a Vickers head with a test force of 9.81 N and a hold time of 10 s in accordance with ASTM C1327-15. A minimum of ten indents were optically measured for each sample. X-ray diffraction was performed for each composition using a Bruker D-8 Focus (Bruker, Madison, WI). Scanning electron microscopy of polished samples (coated with a layer of Au/Pt) was performed on a FEI Quanta 650 SEM at 15 kV (Thermofisher Scientific, Waltham, MA)

Size B (3 x 4 x 45 mm) flexure bars were machined (Bomas Machine Specialties, Inc., Somerville, MA) from each sintered billet in accordance with ASTM C1161-18. Before testing, the relative density of each sample was measured. The apparent density of each sample was determined using the Archimedes' method. The theoretical density for each composition was calculated using the rule of mixtures with densities of 2.52 g/cm<sup>3</sup>, 14.6 g/cm<sup>3</sup>, 5.01 g/cm<sup>3</sup>, 2.70 g/cm<sup>3</sup>, and 3.95 g/cm<sup>3</sup> used for B<sub>4</sub>C, WC-Co, Y<sub>2</sub>O<sub>3</sub>, Al, and Al<sub>2</sub>O<sub>3</sub> respectively. Flexure testing was performed using an MTS machine and a 4-point semi-articulated fixture with the crosshead speed set to 0.5 mm/min. For each composition, a minimum of seven tests were performed, and the Weibull modulus and characteristic strength were calculated in accordance with ASTM C1239-13.

After testing, the tensile edge of the fracture surface of each flexure bar was optically imaged (Olympus GX41, Olympus Corporation, Lombard, IL). Using ImageJ software, each flaw along the fracture surface was measured, and an average flaw size and maximum flaw size was determined for each sample. Select bend bar fragments were mounted, polished, and electrochemically etched in a 1 % potassium hydroxide (KOH) solution (Fisher Chemical, Waltham, MA) with a DC current of 20 V for 3-5 s. The etched surfaces were optically imaged, and an average grain size was determined using the line-intercept method.

### 3.4 Results and Discussion

# Characterization of Ceramic Suspensions

The rheological behavior of suspensions used in this study is presented in Figure 3-3. A more comprehensive exploration of the rheological behavior of suspensions containing only  $B_4C$ powers (no sintering aids) was been published previously<sup>6</sup>. Colloidal processing of multiple component systems can change the rheology of suspensions, with minimum data in the literature available for the highly loaded B<sub>4</sub>C suspensions like those studied here. For this study, it is sufficient to note that sintering aid particles (even in the relatively small amounts used) did have some influence suspension rheology. Figure 3-3A shows the viscosity versus applied shear rate of a characteristic suspension for each sintering aid as well as a B<sub>4</sub>C suspension with no sintering aid, while the shear stress as a function of applied shear rate is shown in Figure 3-3B. Both the Al and Al<sub>2</sub>O<sub>3</sub> suspensions had similar yield points than the suspensions with no sintering aid, while the Y<sub>2</sub>O<sub>3</sub> suspension had a slightly higher yield point. All suspensions demonstrated yieldpseudoplastic behavior ideal for injection molding. The yield point in each suspension can be attributed to flocculation of the ceramic particles. This yield point can also be observed in the viscosity versus applied shear rate graph as a transition in the slope of the graphs at an approximate shear rate of 3 s<sup>-1</sup>. At higher shear rates (e.g. those used in the injection molding process) the flocs of ceramic particles are broken up and flow becomes much easier. Explaining the exact cause of the difference in yield point between suspensions is difficult as a wide variety of factors such as particle size, size ratios, and surface charges can affect floc size and strength<sup>42</sup>. However, all suspensions were still flowable at room temperature and behaved similarly during injection molding.



**Figure 3-3** A) Viscosity of three of the suspensions used in this study as a function of applied shear rate at room temperature. The estimated shear rate during injection molding is 10 s<sup>-1</sup>. B) The shear stress versus shear rate for the same suspensions.

# Injected Molded Sample Characterization

A summary of the mechanical properties of each composition used in this study is presented in **Table 3-2**, with the average relative density of each composition plotted in **Figure 3-4**. All samples were successfully injection molded and underwent binder burnout without cracking or other defects. The average relative density of boron carbide with no sintering aid was 92.6 %, higher than is often reported in literature<sup>14,15,20</sup>. This can be attributed to the presence of WC-Co contamination from attrition milling. WC in amounts up to 10 wt. % has been previously shown to react with boron atoms in B<sub>4</sub>C to form  $W_2B_5^{43,44}$  and improve density<sup>44</sup>. The addition of Y<sub>2</sub>O<sub>3</sub>, Al, or Al<sub>2</sub>O<sub>3</sub> statistically improved density even further, with two-tailed t-tests resulting in  $p \leq$ 0.002 for all compositions. Additions of 10 wt. % Y<sub>2</sub>O<sub>3</sub> was the most effective sintering aid overall, with an average relative density of 97.7 %. The 1 wt. % Al and 1.87 wt. % Al<sub>2</sub>O<sub>3</sub> compositions also achieved high relative densities of 96.9 % and 95.7 %, respectively.

	Maximum	Average	Vickers	Average	Characteristic	90 %		90 %	Average
<b>a</b> 1	Sintered	Sintered	Hardness	Four-	Strength	Confidence	Weibull	Confidence	Grain
Sample	Relative	Relative	(HV)	Point	(MPa)	Bounds	Modulus	Bounds	Size
Name	Density	Density		Flexural					(µm)
	(%)	(%)		Strength					
				(MPa)					• • • • •
$B_4C$	92.6	$90.0 \pm$	$2470 \pm 47$	$295.3 \pm$	322	292 – 356	8.6	3.9 - 12.1	$2.9 \pm 0.1$
		0.5		15.2					
5 wt. %	94.8	$92.7 \pm$	$2994 \pm 41$	$176.6 \pm$	184	170 - 200	9.5	4.7 - 13.2	$32.4 \pm$
$Y_2O_3$		0.5		5.7					1.1
10 wt. %	97.7	$95.5 \pm$	$3208 \pm 53$	$212.4 \pm$	218	209 - 227	18.4	9.7 - 25.2	$41.3 \pm$
$Y_2O_3$		0.5		3.6					0.7
15 wt. %	95.6	$94.8 \pm$	$3148\pm 66$	$150.0 \pm$	153	148 - 158	20.4	10.8 - 28.0	$58.7 \pm$
$Y_2O_3$		0.2		2.3					1.3
1 wt. % Al	96.9	93.5 ±	$2911\pm38$	$274.3 \pm$	285	268 - 303	11.5	6.1 - 15.8	$10.8 \pm$
		0.4		7.0					1.5
2 wt. % Al	95.1	$93.9 \pm$	$3000\pm39$	$261.3 \pm$	290	269 - 313	11.3	5.2 - 15.9	$13.2 \pm$
		0.4		13.0					1.3
3 wt. % Al	95.1	$94.2 \pm$	$3076 \pm 21$	$265.5 \pm$	276	251 - 306	9.9	4.1 - 14.2	$10.6 \pm$
		0.2		8.9					1.6
1.87 wt. %	95.7	$92.9 \pm$	$2954\pm32$	$271.3 \pm$	304	264 - 352	5.3	2.6 - 7.4	$9.5 \pm 2.3$
$Al_2O_3$		0.8		19.0					
3.71 wt. %	95.2	94.7 ±	$3004 \pm 33$	$254.9~\pm$	267	241 - 298	7.9	3.7 – 11.3	$10.4 \pm$
Al <sub>2</sub> O <sub>3</sub>		0.1		10.2					3.8
5.52 wt. %	94.1	$93.4 \pm$	$3116\pm28$	$265.1 \pm$	279	256 - 306	7.9	4.2 - 10.8	$8.1\pm1.6$
$Al_2O_3$		0.2		10.0					

**Table 3-2** Mechanical properties of sintered B<sub>4</sub>C bars of each composition used in injection molding experiments.

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**Figure 3-4** Maximum relative density of each of the compositions used in injection molding experiments. The amounts of Al<sub>2</sub>O<sub>3</sub> were chosen to correspond to the amounts of Al after a reduction during sintering.

It had been previously proposed by Levin et al.<sup>15</sup> that metal oxides acted as more efficient sintering aids than their base metals due to the oxygen atoms creating carbon vacancies to aid lattice diffusion during sintering. In this study, additions of Al<sub>2</sub>O<sub>3</sub> were normalized to match Al content. For normalized 1 and 2 wt. % Al, the relative densities were statistically similar (p=0.57 and p=0.07 respectively). For normalized 3 wt. % Al, the oxide addition was statistically less dense than the metal base (p=0.01). This difference can likely be explained by the fact that in the Ti/TiO<sub>2</sub> study, greater amounts of sintering aid (up to 25 wt. %) were used, which would cause a much larger amounts of boron depletion in the B<sub>4</sub>C microstructure than the small amounts of sintering aid (<5 wt. %) used in the present study. In fact, when small amounts of Ti/TiO<sub>2</sub> were used, the resulting density differences were much smaller, similar to those seen in the present study<sup>15</sup>.

# Effect of Sintering Aid Choice on Microstructure

A representative microstructure for each sintering aid is shown in **Figure 3-5**. All three sintering aids react with B<sub>4</sub>C at during sintering, forming a liquid, and ultimately Metal-B-C phases upon cooling<sup>14,20,24</sup>. XRD (see **Figures 3-6** and **3-7**) confirmed the presence of these phases. Specifically, the Y<sub>2</sub>O<sub>3</sub> specimens formed a composition of YB<sub>4</sub>, YB<sub>6</sub>, YB<sub>2</sub>C, and YB<sub>2</sub>C<sub>2</sub> which matched the observations made by Goldstein et al<sup>14</sup>. The Al and Al<sub>2</sub>O<sub>3</sub> specimens both formed AlB<sub>2</sub> and Al<sub>3</sub>BC, which matched the observations made by Mashhadi et al<sup>23</sup>. All secondary phases are found as multigrain aggregates between B<sub>4</sub>C grains in the as-sintered microstructures.



Figure 3-5 Representative microstructures for each of the sintering aids used in injection molding experiments. Sintering aid phases form in the areas between B<sub>4</sub>C grains. The WC-Co contamination from attrition milling forms  $W_2B_5$  platelets regardless of which sintering aid is used. (*A*) Porosity due to incomplete sintering. (*B*)  $W_2B_5$  platelet. (*C*) Secondary sintering aid phase.



Figure 3-6 XRD patterns showing phase compositions of specimens sintered using  $Y_2O_3$  as a sintering aid.



Figure 3-7 XRD pattern showing phase compositions of specimens sintered using Al and Al<sub>2</sub>O<sub>3</sub> sintering aids.

The WC-Co also undergoes a reaction during sintering to form W<sub>2</sub>B<sub>5</sub> platelets <sup>22,44</sup>. These platelets have a high aspect ratio and, interestingly, are often found at the boundary between B<sub>4</sub>C grains and other secondary phases<sup>44</sup>. Tungsten is soluble in both aluminum and yttrium at high temperatures<sup>45</sup>, suggesting that tungsten dissolves into the liquids formed during sintering and then precipitates to form W<sub>2</sub>B<sub>5</sub> platelets. This effect is most pronounced in the Y<sub>2</sub>O<sub>3</sub> samples, likely because those samples contain the largest amount of sintering aid, and therefore the highest volume fraction of liquid phases during the sintering process (see **Figure 3-8**). The high aspect ratios of many of these particles suggest an interface-controlled growth mechanism, which further supports the proposed mechanism of solution-precipitation (as diffusion through solid B<sub>4</sub>C would be significantly slower). Phases containing Co were not identifiable in any of the XRD plots,

suggesting Co is held in solid solution in one of the other phases or Co phases are present in amounts too small to be detected.



**Figure 3-8** Microstructure of a 10 wt. % Y<sub>2</sub>O<sub>3</sub> sample. Arrows indicate the location of W<sub>2</sub>B<sub>5</sub> regions at the boundary between B<sub>4</sub>C and other secondary phases.

# Effect of Sintering Aids on Mechanical Behavior

A summary of the mechanical properties of each composition used in this study is presented in **Table 3-2**. The Vickers hardness as a function of the sintering aids is shown in **Figure 3-9**. The samples with no sintering aid had hardness values significantly below that of commercially available  $B_4C$ ; this can be attributed to their lower density. There was no statistical difference between the Al and  $Al_2O_3$  sintering aids with respect to hardness values. This is as expected due to Al and  $Al_2O_3$  forming the same Metal-B-C phases during the sintering process (Figure 3-6). The best performing compositions containing Al demonstrated hardness results similar to previous work using Al as a sintering aid (the authors were unable to find reported literature values for pressurelessly sintered B<sub>4</sub>C with added Al<sub>2</sub>O<sub>3</sub>)<sup>20</sup>. Using 10 wt. % Y<sub>2</sub>O<sub>3</sub> demonstrated the highest overall hardness, with an average value of 3208 Vickers. This can be explained by the reduction of Y<sub>2</sub>O<sub>3</sub> during the sintering process. Free carbon has been shown to decrease the hardness of B<sub>4</sub>C<sup>1</sup>, and the B<sub>4</sub>C powder used in this study contained small amounts of free carbon (as do many commercially manufactured powders. During the sintering process this carbon is off-gassed as CO as Y<sub>2</sub>O<sub>3</sub> reduces. To the best of our knowledge, this is the highest hardness value for a B<sub>4</sub>C/Y<sub>2</sub>O<sub>3</sub> composite reported in the literature.



Figure 3-9 Average Vickers hardness of each of the compositions used in injection molding experiments.

The average four-point flexural strength of each composition is shown in **Figure 3-10**. All flexure bars failed in the middle of the sample, within the inner span of four-point bend fixture (See **Figure 3-11**). It was expected that as density increased with the addition of sintering aids, flexural strength would also increase. It has been widely reported in literature that sintering aids increase flexural strength, with the maximum flexural strength usually corresponding to the highest density<sup>14,15,20,40</sup>. Despite its lower average density, the flexural strength of B<sub>4</sub>C with no sintering

aids had the highest average value among all samples. The Al and Al<sub>2</sub>O<sub>3</sub> had similar flexure values when normalized for Al content, with no statistical significance between them (all p < 0.001). Y<sub>2</sub>O<sub>3</sub> samples had the lowest flexural strength overall, with 10 wt. % Y<sub>2</sub>O<sub>3</sub> having an average flexural strength of 212.4 MPa. Y<sub>2</sub>O<sub>3</sub> samples had the most consistent results, with the smallest standard deviation across all samples tested. Due to the dependence of the flexural strength of B<sub>4</sub>C on the amount and type of sintering aid used, as well as different sintering parameters, it can be difficult to compare to values in the literature. Mashhadi et al. reported a flexural strength of 270 MPa for B<sub>4</sub>C samples with 4 wt. % Al, sintered at 2150 °C to densities of approximately 95 %<sup>20</sup>. Goldstein et al. demonstrated flexural strengths ranging from 160-200 MPa for 8 vol. % Y<sub>2</sub>O<sub>3</sub> (approximately 15 wt. %) sintered at 2180 °C to 97.5 % density<sup>14</sup>.



Figure 3-10 Average four-point flexural strength for each composition used in injection molding experiments.



Figure 3-11 Example fracture specimens. The sharpie marks indicate the approximate location of the inner roller bars during testing.

The Weibull plots of flexural strength of the composition with the highest Weibull modulus for each sintering aid are shown in **Figure 3-12**. The complete Weibull parameters for each composition, along with their 90% confidence bounds, can be found in **Table 3-2**. Due to the small number of samples tested in this study, there is a high uncertainty associated with the parameter estimates that can be seen in the confidence bounds. The  $Y_2O_3$  samples had the highest Weibull modulus, indicating the lowest scatter in their flexural strengths. The 1.87 wt. % Al<sub>2</sub>O<sub>3</sub> sample had the lowest Weibull modulus of 5.3, indicating it had the largest spread in its flexural strength values.



Figure 3-12 Weibull plots of the flexural strength of B<sub>4</sub>C samples made using each type of sintering aid.

Due to the lack of obvious macro pores in any of the sample, the primary defect for Weibull analysis was initially assumed to be small pores from incomplete sintering. However, optical examination of the tensile surface of the flexure specimens revealed significant grain pullout present across all samples (see **Figure 3-13**). The stress profile of a four-point flexure test places the maximum tensile stress on a wide region of the tensile surface of the sample. It can be assumed that the largest flaw (i.e. grain pulled out) on the tensile surface is the primary cause of failure and should be present along the intersection of the tensile surface and the fracture surface. This intersection was imaged for randomly selected samples across all compositions, and the maximum flaw size on each sample was measured using ImageJ software. A plot of flexure strength vs. the inverse square root of the maximum measured flaw size is shown in **Figure 3-14**. There is a strong positive correlation between the maximum flaw size and the flexural strength, with an  $R^2$  value > 0.98. The presence of "artificially" created flaws indicates that the true flexural strength of these compositions may be higher than the values reported in this study.



Figure 3-13 Optical image of the intersection between the tensile surface and the fracture surface of a flexure specimen.



Figure 3-14 Plot of flexural strength versus the maximum flaw size measured on the intersection of the fracture face and tensile surface. Specimens were randomly selected from each composition.

If the maximum flaw size on the tensile surface is caused by grain pullout, it follows that flexure strength should be similarly correlated to grain size. While it is impossible to determine the largest grain present on the tensile surface of any given sample, the average grain size can be readily determined using the line intercept method. The average grain size vs. average flaw size for each composition is plotted in **Figure 3-15**. There is a large positive correlation between average grain size and average flaw size with an  $R^2$  value > 0.9. The Y<sub>2</sub>O<sub>3</sub> composition, which had the largest average grain sizes, also had the largest average flaw sizes while the undoped B<sub>4</sub>C samples had both the smallest average grain size and the smallest average flaw size. All the sintering aids used in this study significantly increased grain size (with the smallest increase, 1.87 wt. % Al<sub>2</sub>O<sub>3</sub>, effectively tripling the grain size), leading to larger flaws from grain pullout which explains the drop in flexural strength. Modifying the sintering parameters used in this study to reduce grain growth while maintaining high relative densities should help increase the flexural strength of samples made with these sintering aids, particularly Y<sub>2</sub>O<sub>3</sub>.



Figure 3-15 Plot of average grain size of each composition versus the average flaw size on the intersection of the fracture face and the tensile surface. Larger grain size lead to larger flaws on the tensile surface due to grain pullout.

# 3.5 Conclusions

Room-temperature injection molding was used to prepare green bodies of highly loaded (51 vol. % solids), aqueous B<sub>4</sub>C suspensions. Samples underwent binder burnout and pressureless sintering at 2075 °C without any cracking or warpage defects. Undoped B<sub>4</sub>C and three sintering aids ( $Y_2O_3$ , Al, and  $Al_2O_3$ ) were tested, with all three sintering aids leading to high relative densities (>95 %). The most promising sintering aid identified was 10 wt. %  $Y_2O_3$  due to having the highest relative density (97.7 %) and Vickers hardness values (3208 GPa). The composition also had a high Weibull modulus of 18.4, the second highest of all samples tested. The flexural strength of the samples was negatively affected by grain pullout during polishing of the tensile surfaces. This grain pullout worsened as grain size increased, indicating that modifying sintering parameters to control grain growth could mitigate these issues in future work. Room-temperature injection molding, in conjunction with pressureless sintering aids such as  $Y_2O_3$ , could expand the

use of  $B_4C$  due to its ability to produce near net shapes of high density and favorable mechanical properties.

# 4. BALLISTIC PROPERTIES OF INJECTION MOLDED SINTERED BORON CARBIDE

A version of this chapter has been submitted to the International Journal of Impact Engineering. Citation: E.A. Weaver, T.D. Marconie, C.T. Mooers, B.R. Tretheway, A.J Maisano, R.W. Trice, J.P. Youngblood, "Ballistic Properties of Injection Molded, Pressurelessly Sintered Boron Carbide", Submitted to the *International Journal of Impact Engineering* (2021).

# 4.1 Contributions

The individuals listed below contributed the following tasks:

- Erich Weaver: Suspension preparation, injection molding, binder burnout, pressureless sintering, density measurements, hardness testing, data analysis
- Tess Marconie: Suspension preparation, injection molding, density measurements, hardness testing
- Cavin Mooers: Grinding and polishing, scanning electron microscopy
- The administers of ballistic testing have requested not to be named in publication

### 4.2 Introduction

Due to its high hardness (>3200 Vickers), high melting point (2450 °C), and low density (2.52 g/cm<sup>3</sup>), boron carbide (B<sub>4</sub>C) is an excellent material for applications such as sand-blasting nozzles, grinding and polishing media, wear-resistant coatings, and lightweight ballistic armor<sup>1</sup>. However, the beneficial properties of B<sub>4</sub>C can only be realized from fully dense, nearly pore-free bodies. Sintering B<sub>4</sub>C to full density is difficult and has historically been achieved using hot-pressing<sup>12</sup>. This limits B<sub>4</sub>C components to only simple geometries like plates, as any complex feature would simply be flattened by the uniaxial pressure from hot-pressing.

Room-temperature injection molding is an attractive method for producing complex shaped ceramic green bodies. Injection molding allows many parts to be produced quickly at low cost and in a wide variety of geometries<sup>4,34,35</sup>. Our prior work has developed a method of injection molding that can be adapted for a wide range of ceramics including  $B_4C^{6,37,38,46,47}$ . The method uses a highly loaded (>50 vol. %) aqueous suspension that is designed to be yield-pseudoplastic; the suspension has a yield point and will not flow until that yield point is reached, at which point

it becomes a shear thinning fluid. This unique behavior means that the suspension can both flow into the mold during injection molding and can retain its shape after it is removed from the mold, all at room temperature. The suspensions use far less polymer binder (<5 vol. %) than a typical ceramic injection molding suspension, which makes the binder burnout process greatly simplified<sup>6,34,47</sup>. In addition, the suspensions are robust and can support the additions of sintering aids without large changes in suspension rheology, which is important for the pressureless sintering process needed to densify these parts<sup>47</sup>.

Sintering aids are important when pressurelessly sintering B<sub>4</sub>C and have been shown to improve densification, microstructure, and mechanical properties<sup>6,14,15,47</sup>. Density and hardness are important for good ballistic performance, so sintering aids are necessary for injection molded parts that cannot be hot-pressed like traditional B<sub>4</sub>C components. Our previous work has shown that adding yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) and tungsten carbide (WC) to B<sub>4</sub>C suspensions significantly improved their sintered density and mechanical properties<sup>47</sup>.

Depth of penetration (DOP) testing is one of the most widely used test methods for the ballistic performance of ceramic materials<sup>48-51</sup>. A ceramic tile is tightly confined in front of a metal backing block (usually aluminum). The depth of penetration into the backing block is compared to that in a reference block with no ceramic tile sample. While this test method is widely used, there are few studies in the literature concerning the ballistic performance of B<sub>4</sub>C, and these studies focus on testing parameters. Many factors can affect the differential efficiency of a ballistic tile including tile thickness, type of confinement, projectile velocity, and material properties<sup>51-56</sup>.

In this study, we investigate the use of room-temperature injection molding highly loaded slurries as a method of producing  $B_4C$  for ballistic armor. Five formulations (undoped  $B_4C$ , 5 wt. % WC, 5 wt. % WC + 10 wt. % Y<sub>2</sub>O<sub>3</sub>, 10 wt. % Y<sub>2</sub>O<sub>3</sub>, 10 wt. % ZrB<sub>2</sub>) were identified for testing due to their ability to produce high density and high hardness components. The density, hardness, microstructure, and ballistic performance of these formulations is observed and discussed.

# 4.3 Experimental Approach

#### Materials

The B<sub>4</sub>C powder used in this study (HS Grade, H.C. Starck, Germany) had a company-specified mean particle size ( $d_{50}$ ) of 1.1 µm and a specific surface area (SSA) of 17 m<sup>2</sup>/g. The WC powders

(US Research Nanomaterials, Houston, TX) had a company-specified  $d_{50}$  of 150-200 nm and a SSA of 1.3-2.0 m<sup>2</sup>/g. Y<sub>2</sub>O<sub>3</sub> powders (REacton 99.99 %, Alfa Aesar, Tewksbury, MA) used as a sintering aid had a  $d_{50}$  of 4.6 µm and a SSA of 3.8 m<sup>2</sup>/g. ZrB<sub>2</sub> powders (B Grade, H.C. Starck, Germany) had a company-specified  $d_{50}$  of 1.5-3.0 µm.

### Suspension Preparation and Characterization

A summary of the compositions used in this study is shown in **Table 4-1**. A previous study has shown that ethanol washing B<sub>4</sub>C powders prior to preparing them in a suspension improved suspension rheology by lowering the yield point and viscosity<sup>6</sup>. For all compositions, the B<sub>4</sub>C and sintering aid powders were mixed to match each final composition and washed in ethanol using a ball mill and 12.5 mm WC-Co milling media for 24 hours at 50 rpm. The powders were then dried using a rotary evaporator and pressed through a 42 mesh (465  $\mu$ m) sieve.

	Sintering	Sintering Aid	Dispersant		Solids	Sintering
Sample Name	Aid	Amount	Content (vol. %)	pН	Loading	Temperature
		(wt. %)			(%)	(°C)
B <sub>4</sub> C	N/A	N/A	3.5	7.5	51.5	2350
5 wt. % WC	WC	5	3.5	7.5	51.5	2350
5 wt. % WC +	WC +	5 + 10	3.5	7.5	51	2350
10 wt. % Y <sub>2</sub> O <sub>3</sub>	$Y_2O_3$					
10 wt. % Y <sub>2</sub> O <sub>3</sub>	$Y_2O_3$	10	3.5	7.5	51/52	2350
10 wt. % ZrB <sub>2</sub>	$ZrB_2$	10	3.5	7.5	52	2375

**Table 4-1** Composition of B4C suspensions used in this ballistic properties experiments. Sintering aid selections were made based on preliminary studies for density and hardness.

Previous work has shown that 25,000 g/mol polyethylenimine (PEI) acts as a good electrostatic dispersant for B<sub>4</sub>C suspensions<sup>6</sup>. 1.83 mg/m<sup>2</sup> of PEI (relative to the surface area of B<sub>4</sub>C powder) was found to be the best amount of dispersant for suspension stabilization. In addition, HCl was used to adjust the pH of suspensions to increase dispersion further. Due to small batch-to-batch variations in suspension viscosity, small adjustments to each suspension were required.

A particle loading of 51.5 vol. % solids and a pH of 7.5 were initially used as a base. From there, particle loading was adjusted in 0.5 vol. % steps until a viscosity suitable for injection molding weas achieved. The final particle loading of each composition can be found in **Table 4-1**. Throughout the study, the small variations in particle loading suspension viscosity did not lead to noticeable changes in final part density or microstructure.

Suspensions were prepared by first mixing the PEI and HCl with reverse osmosis (RO) water in a dual-centrifugal speed mixer (DAC 400, Flacktek Inc., Landrum, SC). Next, ceramic powders (B<sub>4</sub>C and the relevant sintering aid) were added in 15-20 g increments. Each increment of mixing was performed at 800 rpm for 1 minute followed by 1200 rpm for 1 minute. The total mixing time was less than 30 minutes. After mixing was complete, five 12.5 mm diameter WC-Co milling media were added, and the suspension was ball milled for approximately 24 hours.

# **Room-Temperature Injection Molding**

An overview of the injection molding process can be found in **Figure 4-1**. 3-D printed molds, shown in **Figure 4-2a** and **4-2b**, were designed to produce green bodies with dimensions of 49 mm diameter x 10 mm height (with the desired final sintered dimensions being 40 mm diameter x 7 mm height). In addition, to demonstrate the viability of using injection molding to produce non-standard geometries, a separate mold with a small amount of curvature was designed (see **Figure 4-2c**). The main section of the molds was produced using a Form 2 (Formlabs, Somerville, MA) stereolithography (SLA) 3-D printer. The mold was designed with an injection port fitted for a Luer-Lock syringe tip and air vents to allow air and excess suspension to escape during injection molding. The top and bottom portions of the mold were made of acrylic sheet and coated with PTFE tape to prevent the green body from sticking. Wetted ashless filter paper (Grade 40, Whatman, UK) was adhered to both the top and bottom sections of the mold to help prevent the part from sticking and to aid the drying process.



**Figure 4-1** Summary of the injection molding process. Suspensions are prepared by mixing water, ceramic, powder, and a polymer dispersant. They are then injection molded and allowed to dry before undergoing binder burnout and sintering.



Figure 4-2 (A) Injection mold features, (B) three-piece mold used for injection molding, (C) mold used for injection molding a curved part.

After being removed from the ball mill, suspensions were vacuum mixed (Twister Evolution, Renfert, Hilzingen, Germany) at 200 rpm for 5 minutes in order to remove any air entrapped during the suspension preparation process. They were then loaded into a 50 mL Luer-Lock syringe that was undergoing vibration to prevent the formation of new air bubbles. The filled syringe was inserted into the mold, and both together were placed in an MTS load frame (MTS Insight 100, MTS Systems Corporation, Eden Prairie, MN). Injection molding occurred at room-temperature, with a crosshead speed of 25 mm/min with a total injection time of approximately 90 seconds. After injection, the top acrylic plate was removed, and the green body was allowed to dry for 45 minutes in room-temperature conditions. The top filter paper was then carefully removed, and the green body and mold were placed in either a humidity oven set to 35 °C and 95 % relative humidity. After approximately 24 hours the green body was removed completely from the mold and placed back into the humidity oven or desiccator to complete drying (approximately 72 hours).

# Binder Burnout and Sintering

After drying was complete, each green body underwent binder burnout to remove the organic polymer binder. A previous study showed complete burnout of PEI in a flowing Ar atmosphere below 500 °C<sup>8</sup>. Samples were placed in a tube furnace under a flowing Ar atmosphere with a heating rate of 1 °C/min to 500 °C with a hold time of 25 hours. Samples were then sintered in a Carbolite Gero LHTG 200-300/30-1G Furnace (Carbolite Gero USA, Newton, PA) with a heating rate of 50 °C/min, a 1 hour hold in vacuum at 1350 °C, an ultimate sintering temperature of up to 2350 °C (except for the ZrB<sub>2</sub> samples, which had an ultimate temperature of 2375 °C), a hold time of 4 hours, and a flowing argon atmosphere.

#### *Characterization*

After sintering, each sample was leveled using a diamond grinding wheel on a Kent USA surface grinder (Kent Industrial, Tustin, CA). The apparent density of each sample was measured using the Archimedes method. The theoretical density of each sample was calculated using the rule of mixtures and densities of 2.52 g/cm<sup>3</sup>, 15.63 g/cm<sup>3</sup>, 5.01 g/cm<sup>3</sup>, and 6.08 g/cm<sup>3</sup> for B<sub>4</sub>C, WC, Y<sub>2</sub>O<sub>3</sub>, and ZrB<sub>2</sub>, respectively. For hardness testing, a small pellet of each composition was prepared and then cut, mounted, and polished, finishing with a 1 µm diamond suspension. Hardness testing was performed in accordance with ASTM C1327-15 using a Wilson Hardness Tukon 1202 using a Vickers head with a test force of 9.81 N and a hold time of 10 seconds. A minimum of ten indents were measured for each sample. Scanning electron microscopy (SEM) was performed on polished samples using a Scios Dual Beam SEM/FIB (ThermoFisher Scientific, Waltham, MA).

# **Ballistic Testing**

A schematic diagram of the configuration used for DOP testing is shown in **Figure 4-3**. The 40mm diameter boron carbide discs were mounted tightly in 102 mm x 102 mm x 102 mm aluminum backing blocks using a fast curing epoxy (Devcon, Milpitas, CA). A conical projectile with a weight of 117.41 g was fired at the center of each ceramic tile at a velocity of 762 m/s. For comparison, a set of commercially-produced boron carbide pucks were purchased. These parts underwent testing identical to the testing performed on injection molded parts.



**Figure 4-3** Schematic diagram of A) reference depth of penetration in the aluminum backing block (side view), B) residual depth of penetration in the aluminum backing material (side view), and C) ceramic tile embedded in the aluminum backing block.

The depth of penetration of each test was measured using an X-ray computerized tomography (CT) scan. The differential efficiency factor (DEF) was calculated according to the equation:

$$DEF = \frac{\rho_b \times (P_0 - P_b)}{\rho_c \times t}$$

where  $\rho_b$  is the density of the aluminum backing material,  $\rho_c$  is the density of the ceramic material,  $P_0$  is the reference depth of penetration (DOP),  $P_b$  is the residual DOP in the backing material, and t is the thickness of the ceramic tile.

### 4.4 Results and Discussion

### Effect of Composition on Density and Microstructure

A sintered boron carbide disc and a curved boron carbide sample are shown in **Figure 4-4a** and **Figure 4-4b** respectively. Initial attempts at injection molding a curved part resulted in the green body slumping towards the center of the sample. A decrease in pH, leading to higher viscosity, resulted in a green body that retained its shape during the drying process. To the best of the authors' knowledge, this is the first time a curved, non-standard geometry part has been produced using injection molding and pressureless sintering. **Table 4-2** provides a summary of the mechanical properties of each of the compositions used in this study. It was expected that, as is widely reported in literature, the additions of sintering aids would increase the sintered density of the B<sub>4</sub>C components. However, the composition with no sintering aid had the highest sintered density. One possible explanation is that at the high sintering temperatures used in this study (2350 °C), several of the sintering aids (notably Y<sub>2</sub>O<sub>3</sub>) undergo reactions with B<sub>4</sub>C and form liquid phases. While these phases are beneficial for sintering at lower temperatures<sup>47</sup>, at high temperatures they could cause B<sub>4</sub>C grains to quickly coarsen before densification mechanisms become truly active. This is supported by the fact that sintering aids that do not undergo reactions that form liquids, namely ZrB<sub>2</sub> and WC, the highest average densities were 95.2 and 93.5 % respectively. The two compositions containing Y<sub>2</sub>O<sub>3</sub> had the lowest relative densities, specifically 92.7 % for the 10 wt. % Y<sub>2</sub>O<sub>3</sub> composition and 91.7 % for the 5 wt. % WC + 10 wt. % Y<sub>2</sub>O<sub>3</sub> composition.



**Figure 4-4** (A) A sintered boron carbide disc used for ballistic testing and (B) a successfully pressurelessly sintered curved piece of boron carbide.

		Average	Sintered	Vickers	Average	Average	Average
	Theoretical	Measured	Relative	Hardness	Tile	Depth of	Differential
Sample	Density	Bulk Density	Density	(HV)	Thickness	Penetration	Efficiency
Name	(g/cm <sup>3</sup> )	(g/cm <sup>3</sup> )	(%)		(mm)	(mm)	
B <sub>4</sub> C	2.52	2.42	$96.0\pm0.3$	N/A	$7.08\pm0.05$	$53.3\pm3.8$	$3.7 \pm 0.7$
5 wt. % WC	2.63	2.46	$93.5\pm1.3$	$3107 \pm 127$	$6.29\pm0.05$	$56.2\pm2.3$	$3.6\pm0.5$
5 wt. % WC	2.76	2.53	$91.7\pm0.1$	$3284 \pm 107$	$9.76\pm0.12$	$48.0\pm5.9$	$2.9\pm0.6$
+ 10 wt. %							
$Y_2O_3$							
10 wt. %	2.65	2.46	$92.7\pm0.5$	$3458\pm76$	$6.95\pm0.07$	$55.9 \pm 4.6$	$3.3\pm0.7$
Y <sub>2</sub> O <sub>3</sub>							
10 wt. %	2.68	2.55	$95.2\pm1.0$	$3359 \pm 186$	$6.65\pm0.07$	$56.3\pm3.0$	$3.4\pm0.4$
$ZrB_2$							
HP Com.	2.50	2.49	$99.8\pm0.1$	N/A	7.0	$56.1\pm0.8$	$3.1\pm0.2$
Ref. 1							

**Table 4-2** Mechanical properties and test parameters of each composition used in ballistic properties experiments.

Two representative B<sub>4</sub>C microstructures are shown in **Figure 4-5**. In **Figure 4-5a** a sintering aid that does not form a liquid during sintering (WC) is shown. WC reacts with B<sub>4</sub>C to form  $W_2B_5^{42}$  in a solid-state reaction during sintering, which can be seen in small particles or platelets throughout the microstructure. **Figure 4-5b** shows a sintering aid that does form a liquid during sintering (WC + Y<sub>2</sub>O<sub>3</sub>). Capillary action forces the liquid into the small regions between grains of B<sub>4</sub>C, resulting in more irregularly shaped secondary phase particles<sup>47</sup>. Tungsten is soluble in the liquid formed by Y<sub>2</sub>O<sub>3</sub>, which results in the formation of many more W<sub>2</sub>B<sub>5</sub> platelets at the boundary between the yttrium containing phase and B<sub>4</sub>C<sup>47</sup>.



**Figure 4-5** Representative microstructures for two of the sintering aids used in ballistic properties experiments. Sintering aid phases form in the areas between B<sub>4</sub>C grains and show up as lighter colored areas in the SEM image. (A) 5 wt. % WC composition, where no liquid phases form during sintering. (B) 5 wt. % WC + 10 wt. % Y<sub>2</sub>O<sub>3</sub> composition, where Y<sub>2</sub>O<sub>3</sub> reacts to form a liquid during sintering. Image courtesy of Cavin Mooers.

# Effect of Composition on Hardness and Differential Efficiency

The Vickers hardness of each composition used in this study is shown in **Table 4-2**. It was expected that higher density would result in higher hardness, but that was not the case. 10 wt. %  $Y_2O_3$  had the highest hardness value of 3458 Vickers, followed by 10 wt. %  $ZrB_2$  with 3359 Vickers. We were unable to measure the hardness of the undoped B<sub>4</sub>C samples, despite had the highest relative density, due to their tendency to crack and fracture near the indent location. In samples we were able to measure, when hardness is plotted in relation to density (**Figure 4-6**) there is no correlation between the two. One explanation for this is that Vickers hardness is a very local measurement. Successful indents are made in areas containing little local porosity and may not best represent the mechanical behavior of a macro-scale sample like those used in a ballistic test and so induce a selection bias.



Figure 4-6 Hardness values as a function of relative density for each composition used in ballistic properties experiments.

The depth of penetration and differential efficiency of each composition used in this study, as well the reference commercially hot-pressed undoped B<sub>4</sub>C composition, is listed in **Table 4-2**. It was expected that differential efficiency would generally follow hardness trends, as has been shown in previous studies<sup>52-55</sup>. The undoped B<sub>4</sub>C composition had the highest differential efficiency of the compositions prepared during this study at 3.7. All samples except 5 wt. % WC + 10 wt. % Y<sub>2</sub>O<sub>3</sub> had higher differential efficiency than the commercial reference, which can be explained by the low average relative density of the 5 wt. % WC + 10 wt. % Y<sub>2</sub>O<sub>3</sub> composition. Despite this, the 5 wt. % WC + 10 wt. % Y<sub>2</sub>O<sub>3</sub> samples had the lowest average depth of penetration, likely due to having the largest thickness. Undoped B<sub>4</sub>C had the highest differential efficiency overall, with a value of 3.7.

Mechanical properties like hardness have been widely noted to affect ballistic performance in  $B_4C^{57-59}$ , but the authors were unable to find any studies noting the effects of relative density (likely due to ballistic tests being performed on exclusively hot-pressed specimens). It would be expected that as hardness tends to increase with density, then as relative density increases, differential efficiency would increase as well. **Figure 4-7a** shows the relationship between relative density and differential efficiency for the compositions in this study, and the relationship is as expected with differential efficiency increasing with density. However, **Figure 4-7b**, which shows the relationship between hardness and differential efficiency, does not show the same trend. While this is surprising, it is likely due to the previous anomalous uncorrelation of hardness with density that is likely related to the previously mentioned selection bias with microhardness testing. In a hot-pressed sample, where all regions of the part are equally dense, there would be no discrepancy between hardness and ballistic behavior. But for pressurelessly sintered samples, where fully dense parts are difficult to achieve, mechanical properties on the micro-scale do not necessarily fully represent behavior on the macro-scale.



Figure 4-7 (A) Differential efficiency as a function of relative density for each of the compositions used in ballistic properties experiments. (B) Differential efficiency as a function of hardness for each of the compositions used in ballistic properties experiments.

#### 4.5 Conclusions

Highly loaded (51-52 vol. % solids) aqueous B<sub>4</sub>C suspensions were used to produce green bodies in a room-temperature injection molding process. Samples underwent binder burnout to remove polymer processing additives and were then pressurelessly sintered at 2350 °C for 4 hours in a flowing Ar atmosphere. Five compositions were studied: undoped B<sub>4</sub>C, 5 wt. % WC, 5 wt. % WC + 10 wt. % Y<sub>2</sub>O<sub>3</sub>, 10 wt. % Y<sub>2</sub>O<sub>3</sub>, and 10 wt. % ZrB<sub>2</sub>. All compositions resulted in relative densities > 91.5 %, with undoped B<sub>4</sub>C having the highest average relative density of 96.0 %. 10 wt. % Y<sub>2</sub>O<sub>3</sub> demonstrated the highest hardness value of 3284 Vickers. All compositions had comparable or better differential efficiencies to the commercial B<sub>4</sub>C during DOP testing, with undoped B<sub>4</sub>C having the highest value of 3.7. The differential efficiencies of the samples with sintering aids were negatively affected by their lower densities despite their high hardness values. Future work to adjust degassing processes and sintering parameters could improve the sintered relative densities of these compositions, potentially leading to further improved ballistic performance exceeding that of commercial armor. Room-temperature injection molding and pressureless sintering are a viable option for producing B<sub>4</sub>C ballistic components in a wide variety of near-net complex geometries, such as the curved parts produced in this study.

# 5. BONDING OF PRESSURELESSLY SINTERED BORON CARBIDE

# 5.1 Contributions

The individuals listed below contributed the following tasks:

• Erich Weaver: Suspension preparation, casting, pressureless sintering, x-ray diffraction, grinding and polishing, optical microscopy, data analysis

# 5.2 Introduction

During the process of developing a room-temperature injection molding process for  $B_4C$ , it became clear that there was a maximum thickness that could be produced before all green bodies would crack, regardless of other conditions. The critical cracking thickness of the aqueous  $B_4C$  suspensions used in the previous chapters was approximately 18 mm (which translates to a 12 mm sintered part). This limits the part geometries that can be produced significantly. While there are methods to increase the critical cracking thickness of suspensions, another economic approach is to produce multiple, thinner green bodies and join them together, either during the sintering process or after.

Efforts in the literature to join  $B_4C$  are scarce. There have been some efforts to bond sintered boron carbide parts using metals as an interlayer<sup>60-62</sup>. Cockeram was able to achieve good layer adhesion using titanium and molybdenum foils as an interlayer using a post-sinter heat treatment at 1500 °C<sup>60</sup>. Sekine et al. achieved four-point bending strength similar to that of dense  $B_4C$  using thin sheets of aluminum in a low temperature joining process<sup>61</sup>. Vosughi et al. showed that Cu interlayer would diffuse into surface roughness on  $B_4C$  bodies during a heat treatment process at 900 °C<sup>62</sup>. All these studies were performed post-sintering using metal foils; to the best of the authors knowledge there have been no attempts in the literature to bond  $B_4C$  green bodies in-situ during the sintering process or using powders.

While efforts to join B<sub>4</sub>C have been limited, there has been no shortage of attempts to bond SiC, another common armor material. A wide variety approaches have been tested, ranging from metals like Ti<sup>63</sup>, Mo<sup>64</sup>, and Ni<sup>65</sup>, to ceramic interlayers like TiC<sup>66</sup>, TiB<sub>2</sub><sup>67</sup>, and YSZ<sup>68</sup>. Of particular note is Si-C reaction bonding<sup>69</sup>. A mixture of SiC, Si, and graphite powder is placed in between two SiC bodies and surrounded by pellets of excess Si. At elevated temperatures, the Si melts and

infiltrates into the gap between the two parts, reacting with the graphite to form a bond containing a mixture of SiC and Si. This technique is promising because it forms a bond with excellent adhesion, can be performed at relatively low temperatures for B<sub>4</sub>C (<1700 °C), and can be performed without the use of external pressure<sup>69</sup>.

### 5.3 Experimental Approach

# Materials

Boron carbide powder (HS Grade, H.C. Stark, Hermsdorf, Germany) was used in this study; these powders had a company specified mean particle size ( $d_{50}$ ) of 1.1 µm and a specific surface area (SSA) of 17 m<sup>2</sup>/g. Y<sub>2</sub>O<sub>3</sub> powders (REacton 99.99 %, Alfa Aesar, Tewksbury, MA) with a  $d_{50}$ of 4.61 µm and a SSA of 3.8 m<sup>2</sup>/g, were used as a sintering aid. Aluminum powders (US Research Nanomaterials, Houston, TX) with a  $d_{50}$  of 1 µm were also employed in this investigation. Silicon carbide powders used had a  $d_{50}$  of 600 nm (US Research Nanomaterials, Houston, TX). Silicon powders had a  $d_{50}$  of 1 µm (US Research Nanomaterials, Houston, TX). Carbon black powders had a  $d_{50}$  of 150 nm (US Research Nanomaterials, Houston, TX). Table 5-1 shows a summary of the different compositions investigated in this study.

	B4C	Y2O3	SiC		С	Al
	Content	Content	Content	Si Content	Content	Content
Sample Name	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)
Sintered B <sub>4</sub> C	90	10	N/A	N/A	N/A	N/A
Y <sub>2</sub> O <sub>3</sub> Bonding	0-100	0-100	N/A	N/A	N/A	N/A
SiC Bonding	N/A	N/A	70	5	25	N/A
SiC Bonding w/ Al	N/A	N/A	63.6	4.5	22.7	9.1

 Table 5-1 Composition of powder mixes used in bonding experiments.

# Y<sub>2</sub>O<sub>3</sub> Bonding – Pellet Casting and In-Situ Bonding

Pellets used for initial bonding studies were prepared by loading approximately 2 grams of the ceramic powder mixture into a 15 mm diameter steel pellet die, and then uniaxially pressed at 34.5 MPa for 20 seconds.

In order to facilitate bonding between pellets during the sintering process, a thin layer of loose powder was applied to the top of the bottom pellet using a flour sifter. The amount of powder applied was calculated (using basic density calculations) to form a layer of 100 µm thickness and was verified using a scale after application. Samples were then sintered in a Carbolite Gero LHTG 200-300/30-1G Furnace (Carbolite Gero USA, Newton, PA) with a heating rate of 50 °C/min, a 1 hour hold in vacuum at 1350 °C, an ultimate sintering temperature of up to 2350 °C, a hold time of 4 hours, and a flowing argon atmosphere.

### SiC Bonding – Suspension Preparation

Suspensions were prepared by mixing the dispersant and HCl with reverse osmosis (RO) water in a dual-centrifugal speed mixer (DAC 400, Flacktek Inc., Landrum, SC). B<sub>4</sub>C and the sintering aid were then added in small (15-20 g) increments. As in injection molding experiments detailed in previous chapters, the amounts of PEI and HCl used in suspensions in this study were both 3.57 vol. %. Mixing increments were performed for 1 minute at 800 rpm followed by 1 min at 1200 rpm, with the total mixing time taking less than 30 minutes. After mixing, five 12.5 mm WC-Co milling media were added, and the suspension was ball milled for approximately 24 hours.

# SiC Bonding – Billet Casting

After being removed from the ball mill, suspensions were vacuum mixed (Twister Evolution, Renfert, Hilzingen, Germany) at 200 rpm for 5 minutes in order to remove any air entrapped during the suspension preparation process. The suspensions were then casted into an injection molding die with the top acrylic plate removed. During the casting process, the mold was subjected to constant vibration to prevent the formation of new air bubbles. The green body and mold were then placed in either a humidity oven set to 35 °C and 95 % relative humidity or a desiccator containing a sulfuric acid/water solution tuned to maintain approximately 95 % relative humidity. After approximately 24 hours the green body was removed completely from the mold and placed back into the humidity oven or desiccator to complete drying (approximately 48 hours).

# SiC Bonding - Binder Burnout and Sintering

Once demolded and dried, casted samples underwent binder burnout to remove all organic compounds. Samples were placed in a tube furnace with flowing Argon (Ar) at a heating rate of 1 °C/min to 500 °C where they were held for 25 hr. A previous study showed thermogravimetric analysis (TGA) results with a complete burn-out of PEI in a flowing Ar atmosphere below 500 °C<sup>10</sup>. Samples were then sintered in a Carbolite Gero LHTG 200-300/30-1G Furnace (Carbolite Gero USA, Newton, PA) with a heating rate of 50 °C/min, a 1 hour hold in vacuum at 1350 °C, an ultimate sintering temperature of up to 2350 °C, a hold time of 4 hours, and a flowing argon atmosphere.

#### SiC Bonding - Post-Sintering Bonding

After sintering, the surfaces of each pellet or billet were leveled using a diamond wheel on a Kent USA surface grinder (Kent Industrial, Tustin, CA). Then a thin layer of an SiC powder mixture was applied using a flour sifter. As with the Y<sub>2</sub>O<sub>3</sub> bonding process, the amount of powder added was targeted to form a layer of 100  $\mu$ m thickness and verified by weight. In addition, small, sacrificial pellets of Si were prepared and placed alongside samples. The samples and Si pellets were then sintered in a Carbolite Gero LHTG 200-300/30-1G Furnace (Carbolite Gero USA, Newton, PA) with a heating rate of 50 °C/min, a 1 hour hold in flowing argon at 1590 °C.

# *Characterization*

After sintering, samples were sectioned, mounted and polished, finishing with a 1  $\mu$ m diamond suspension. Each section was optically imaged using an Olympus GX41 optical microscope (Olympus Corporation, Lombard, IL). For the Y<sub>2</sub>O<sub>3</sub> bonded samples, an area analysis was performed using ImageJ software to determine the distribution of sintering aid phases.

# 5.4 Results and Discussion

# Y<sub>2</sub>O<sub>3</sub> Bonding

It was expected that the presence of an yttrium-based liquid phase during sintering would permit the formation of a strong, solid bond region between two B<sub>4</sub>C pellets. However, the location

and distribution of these bonds depended largely on the composition of the powder mixture placed between the pellets. **Figure 5-1** shows vertical cross sections of bonds formed with a variety of powder compositions. For low  $Y_2O_3$  concentrations (<25 wt. %), the bonds formed between pellets were continuous, and voids, while more common in the bonding region, are on the same scale as voids found in the bulk pellets. For higher concentrations of  $Y_2O_3$ , the small bridges formed between the two pellets and bonding was incomplete along the remaining interface. As the concentration of  $Y_2O_3$  increases, it would be expected that larger amounts of liquid would form at the bonding interface. While the presence of liquid during sintering has been thus far beneficial to sintering, there is a critical value of liquid (and therefore, of  $Y_2O_3$ ) where the B<sub>4</sub>C particle network is unable to maintain structural integrity and collapses into the liquid phase.



**Figure 5-1** B<sub>4</sub>C pellets bonded with (A) 5 wt. % Y<sub>2</sub>O<sub>3</sub>, (B) 10 wt. % Y<sub>2</sub>O<sub>3</sub>, (C) 20 wt. % Y<sub>2</sub>O<sub>3</sub>, (D) 30 wt. % Y<sub>2</sub>O<sub>3</sub>, (E) 50 wt. % Y<sub>2</sub>O<sub>3</sub>, and (F) 70 wt. % Y<sub>2</sub>O<sub>3</sub> powder.

**Figure 5-2** shows a representative optical microscopy image of a bond formed using a  $Y_2O_3$  powder mixture. While it can be difficult to assess the presence of various phases due to grain pullout, the concentration of  $Y_2O_3$  in the bonded region is approximately equivalent to that of the bulk pellets. However, the  $Y_2O_3$  found in the bonded region is found in larger pockets than that in the bulk pellets. It is likely that the looser packing of the B<sub>4</sub>C powder of the bonded region (which was not pressed like the bulk pellets) allow for the formation of larger pockets of  $Y_2O_3$ 

liquid during the sintering process, as capillary action is not as strong as it would be in the pellets, where many  $B_4C$  particles are making contacts with one another.



Figure 5-2 Optical microscopy image of a bond formed between B<sub>4</sub>C pellets using a B<sub>4</sub>C-Y<sub>2</sub>O<sub>3</sub> powder mixture.

# SiC Bonding

Initial studies on small pellets bonded with the SiC layer appeared promising. The silicon pellets was consumed during a reaction with the loose powder in the bonding layer, forming a mixture of SiC and Si. This was confirmed using XRD analysis (see **Figure 5-3**). **Figure 5-4** shows an optical microscopy image of a SiC/Si bond between two  $B_4C$  components. The bond region has excellent adhesion to the  $B_4C$  interface. However, there is significant cracking throughout the microstructure. These cracks originate in the  $B_4C$  bulk and the penetrate cleanly into the SiC/Si bond. This indicates a strong bonding interface between the  $B_4C$  and Si/C bonding region. **Figure**
**5-5** shows two parts bonded using the SiC powder mixture. In smaller parts, these cracks are hairline cracks and only visible upon inspection under a microscope (**Figure 5-5A**). However, in larger parts, these cracks are much larger in scale and visible to the naked eye (**Figure 5-5B**). While the string bond between SiC/Si region and B<sub>4</sub>C is desirable for joining parts, the causes of cracking need to be identified and mitigated.



Figure 5-3 XRD plot of SiC bonding region after sintering.



Figure 5-4 Optical microscopy image of SiC powder mixture bonding layer after sintering.



**Figure 5-5** (A) 15 mm pellets bonded using SiC powder mixture and (B) 50 mm billet bonded with SiC powder mixture.

Due to the differences in coefficient of thermal expansion between  $B_4C$  and the bonding region, significant stresses can build during cooling. For two layers of dissimilar material, the stress in each individual phase due a coefficient of thermal expansion mismatch can be calculated using the equation:

$$\sigma_{phase}^{A} = \frac{-\Delta \alpha * \Delta T * E^{A}}{1 - v^{A}} \left[ 1 + \left(\frac{t^{A}}{t^{B}}\right) \left(\frac{\frac{E^{A}}{1 - v^{A}}}{\frac{E^{B}}{1 - v^{B}}}\right) \right]^{-1}$$

Where  $\Delta \alpha$  is the difference in coefficients of thermal expansion,  $\Delta T$  is the change in temperature, *E* is Young's modulus of each phase, *t* is the thickness of each phase, and *v* is the poisson ratio of each phase. For this study, 5.87, 2.77, and 2.56 x 10<sup>-6</sup> K<sup>-1</sup> were used for the coefficients of thermal expansion for B<sub>4</sub>C<sup>70</sup>, SiC<sup>71</sup>, and Si<sup>72</sup>, respectively, It is also necessary to consider that bonding region is comprised of a mixture of SiC and Si phases. A rough estimate of the coefficient of thermal expansion for the bond can be obtained using the rule of mixtures. Using ImageJ area analysis techniques, it was determined that the phase composition of the bond is 68.5 % Sic and 31.5 % Si, which results in a combined CTE of 2.7 x 10<sup>-6</sup> K<sup>-1</sup>. When cooling from the heat treatment temperature of 1590 °C, there is an estimated tensile stress of 191.2 MPa place on the B<sub>4</sub>C phases. Reports on the tensile strength of B<sub>4</sub>C range from 150-300 MPa, so it is likely the cracking is due to thermal expansion mismatch<sup>73,74</sup>.

In an attempt to reduce the coefficient of thermal expansion mismatch, the addition of other materials with high coefficients of thermal expansion were explored. Due to its high coefficient of thermal expansion and previous use as a sintering aid, 10 wt. % Al was added to the existing SiC mixture. Theoretically this addition would lower the resulting stress significantly to 124.6 MPa. However, when attempted experimentally, there was still significant cracking in samples with added aluminum. This could be due to the aluminum reacting with either Si, C, or B to form a new phase with a lower coefficient of thermal expansion, or due to it leaving the bonding region completely due to liquid transport mechanisms. Another potential method to reduce the thermal expansion mismatch stress would be to reduce the thickness of the bonding layer. However, current techniques using Si pellets result in imprecise control over the thickness of the bonding layer, and would need to be improved in future studies.

### 5.5 Conclusions

Powder mixtures of  $B_4C-Y_2O_3$  and SiC-C-Si with Si infiltration were used to join isostatically pressed pellets and pre-sintered boron carbide components, respectively.  $B_4C$  joined with powder mixtures containing low concentrations of  $Y_2O_3$  developed bonds with similar microstructure similar to that of  $B_4C$  pellets but contained increased concentration of voids. Large concentrations of  $Y_2O_3$  led to incomplete bonding between pellets. The SiC-C-Si powder mixture with Si infiltration resulted in a SiC-Si bonding region with strong adhesion to  $B_4C$  at the interface. However, differences in the coefficient of thermal expansion between  $B_4C$  and the bonding layer result in the  $B_4C$  cracking upon cooling. Attempts to modify the CTE of the bonding region with additions of Al were unsuccessful, but more precise control of the bonding region thickness could reduce the mismatch stress and lead to crack free components.

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# **PUBLICATIONS**

## **Submitted Articles**

- E.A. Weaver, B.T. Stegman, R.W. Trice, J.P. Youngblood, "Mechanical Properties of Room-Temperature Injection Molded, Pressurelessly Sintered Boron Carbide", Submitted to *Ceramics International* (2021).
- E.A. Weaver, T.D. Marconie, C.T. Mooers, B.R. Tretheway, A.J Maisano, R.W. Trice, J.P. Youngblood, "Ballistice Properties of Injection Molded, Pressurelessly Sintered Boron Carbide", Submitted to the *International Journal of Impact Engineering* (2021).

### VITA

Erich Addison Weaver was born in Kennewick, WA, and grew up in Columbus, OH and Middletown, MD. He attended Middletown High School before traveling south to attend the University of Alabama in Tuscaloosa, AL, earning a bachelor's degree in Metallurgical and Materials Engineering. During his undergraduate career he worked on several materials research projects, including silicon wafer masking and magnetostricting alloys of cobalt and nickel. During the summer of his sophomore year he worked as an undergraduate research assistant in the University of Alabama Micro-Fabrication Facility. During the summer of his junior year he worked as undergraduate research assistant at the Naval Surface Warfare Center in Carderock, MD. While at the University of Alabama, Erich was also an inaugural member of the Metallurgical Engineering department's Materials Bowl team. After graduating, he joined the Materials Engineering Graduate Program at Purdue University, with Dr. Rodney Trice and Dr. Jeffrey Youngblood serving as his primary advisors. During his time at Purdue, Erich was a member of the American Ceramic Society's President's Council of Student Advisors (ACerS PCSA) and Material's Engineering program's Graduate Student Association (MSEGSA) where he served as the social chair for several years. During his graduate studies, Erich was awarded the National Defense Science and Engineering Graduate (NDSEG) fellowship. Outside of the lab, Erich enjoys lifting weights, reading, and competitive gaming.