Summer 2008

Modeling and measurement of thermal residual stresses and isotope effects on thermo physical properties of ZrB₂-SiC ceramics

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MODELING AND MEASUREMENT OF THERMAL RESIDUAL STRESSES AND ISOTOPE EFFECTS ON THERMO PHYSICAL PROPERTIES OF ZrB$_2$-SiC CERAMICS

by

MICHAEL PHILLIP TEAGUE

A THESIS

Presented to the Graduate Faculty of the MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree MASTER OF SCIENCE IN MATERIALS SCIENCE AND ENGINEERING

2008

Approved by

Dr. Gregory E. Hilmas, Advisor
Dr. William G. Fahrenholtz
Dr. K. Chandrashekhara
The Introduction and Background sections provide information about the thesis topic and summarize the manuscripts. Pages 48 to 66 of this thesis have been prepared in the style used for publication in the *32nd International Conference & Exposition on Advanced Ceramics & Composites Proceedings*. The manuscript titled “FINITE ELEMENT MODELING OF INTERNAL STRESS FACTORS FOR ZrB₂ – SiC CERAMICS,” was accepted for publication on March 26, 2008. The manuscript titled “PROCESSING AND THERMAL PROPERTIES OF ZRB₂-SIC CERAMICS MADE WITH ISOTOPICALLY PURE ¹¹BORON” is pending review at Oak Ridge National Laboratory before final submission to the *Journal of the American Ceramic Society*. 
ABSTRACT

Commercially available finite element modeling software (ABAQUS) was used to investigate the internal residual stresses that develop as a result of cooling from processing temperatures in ZrB₂-SiC ceramics. The size and shape of the SiC particles were varied to evaluate their effect on the residual stresses. Results were compared to experimental data and showed similar trends, where increasing SiC particle size increased tensile stress and also decreased strength. Models were used to analyze benefits of novel shaped SiC inclusions and also better understand the shortcomings of the composites.

An attempt to validate the models using neutron diffraction to measure residual stress led to the fabrication of ZrB₂-SiC composites made using isotopically pure $^{11}\text{B}$ and a reaction hot pressing technique. Natural boron in conventional ZrB₂ ceramics had to be replaced with the $^{11}\text{B}$ (0.0055 barns) due to the high thermal neutron absorption of natural boron (767 barns). Neutron diffraction experiments were successfully performed at Argonne National Laboratory, however, stress free reference samples for ZrB₂ and SiC must still be measured to complete the residual stress analysis.

ZrB₂-SiC ceramics made from $^{11}\text{B}$ were characterized to confirm a complete reaction and full density. The microstructure was compared to natural B ZrB₂-SiC ceramics to confirm equivalent grain size. Effects on the thermal properties by the $^{11}\text{B}$ isotope were studied by measuring thermal diffusivity of both natural boron and $^{11}\text{B}$ containing ZrB₂-SiC specimens at Oak Ridge National Laboratory. The thermal conductivity and thermal expansion were both determined to be lower for the $^{11}\text{B}$ containing materials.
ACKNOWLEDGEMENTS

I would like to express my appreciation to my advisors Dr. Greg Hilmas and Dr. Bill Fahrenholtz for taking a chance on a Mechanical Engineering graduate and for having the patience not to fire me while I slowly and stubbornly learned how to become a materials engineer. By providing me this opportunity, not only was a whole new world opened to me for my studies, but also doors were opened for my employment pursuits.

Dr. KC for taking the time to be on my committee and support my thesis.

I’d like to acknowledge the Air Force Office of Scientific Research for funding my research under contract FA9550-06-01-0125.

I must convey the deepest appreciation to my wife, Melissa. Without her love and support, I would have almost certainly failed. Thank you for helping me struggle along trying to learn the material and never letting me give up. I love you.

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I would like to extend my appreciation to everyone in the Ultra High Temperature group. Sean “Shaq” Landwehr and Jeremy Watts provided extensive support with all my research tasks, taking the time to teach this slow minded individual how to use most of the equipment (often several times). Many thanks to Harlan Brown-Shaklee for boosting my spirits in down times. I would also like to acknowledge: Jim Zimmerman, Andrew Buchheit, Adam Chamberlain, Sumin Zhu, Matt “Shaq Jr.” Thompson, Xiaohong Zhang.

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In memory of my best little friend Smalls, who was taken well before her time. We will miss you. (Sept 11, 2002 – April 11, 2008)
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUBLICATION THESIS OPTION</td>
<td>iii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
</tr>
<tr>
<td>SECTION</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 PURPOSE OF THIS THESIS</td>
<td>1</td>
</tr>
<tr>
<td>1.2 REFERENCES</td>
<td>2</td>
</tr>
<tr>
<td>2. BACKGROUND</td>
<td>3</td>
</tr>
<tr>
<td>2.1 ULTRA HIGH TEMPERATURE MATERIALS</td>
<td>3</td>
</tr>
<tr>
<td>2.2 ZIRCONIUM DIBORIDE BASED MATERIALS</td>
<td>3</td>
</tr>
<tr>
<td>2.2.1 Conventional Hot Pressing</td>
<td>5</td>
</tr>
<tr>
<td>2.2.2 Reactive Hot Pressing</td>
<td>6</td>
</tr>
<tr>
<td>2.2.3 Pressureless Sintering</td>
<td>6</td>
</tr>
<tr>
<td>2.2.4 Other Processing Techniques</td>
<td>8</td>
</tr>
<tr>
<td>2.3 SILICON CARBIDE PARTICLE SIZE EFFECT</td>
<td>8</td>
</tr>
<tr>
<td>2.4 RESIDUAL STRESSES</td>
<td>10</td>
</tr>
<tr>
<td>2.5 MEASUREMENT TECHNIQUES</td>
<td>12</td>
</tr>
<tr>
<td>2.5.1 Neutron Diffraction</td>
<td>15</td>
</tr>
<tr>
<td>2.5.2 Fluorescence Spectroscopy</td>
<td>19</td>
</tr>
<tr>
<td>2.6 MODELING</td>
<td>20</td>
</tr>
<tr>
<td>2.7 REFERENCES</td>
<td>26</td>
</tr>
<tr>
<td>PAPERS</td>
<td></td>
</tr>
<tr>
<td>I. FINITE ELEMENT MODELING OF INTERNAL STRESS FACTORS FOR ZRB₂–SIC CERAMICS</td>
<td>35</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>35</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>36</td>
</tr>
</tbody>
</table>
3.3 THERMAL EXPANSION MEASURED BY NEUTRON DIFFRACTION .................................................................64
3.4 HEAT CAPACITY ........................................................................................................................................66
3.5 THERMAL DIFFUSIVITY ............................................................................................................................66
3.6 THERMAL CONDUCTIVITY .........................................................................................................................67
4. CONCLUSIONS ..............................................................................................................................................68
5. REFERENCES ..................................................................................................................................................69
6. FIGURES ........................................................................................................................................................73
7. TABLES ..........................................................................................................................................................79

SECTION
3. CONCLUSIONS .............................................................................................................................................83
4. FUTURE WORK ................................................................................................................................................86

APPENDICES
A. FINITE ELEMENT MODELING ..........................................................................................................................88
B. NEUTRON DIFFRACTION ...............................................................................................................................107
VITA .....................................................................................................................................................................111
LIST OF ILLUSTRATIONS

Fig 2.1: Thermally etched cross section of ZrB$_2$-30\% SiC,\textsuperscript{7} finer grained materials, which should result in higher strengths.\textsuperscript{7} ........................................5

Fig 2.2: Four-point bend strength of hot pressed ZrB$_2$-SiC vs SiC grain size.\textsuperscript{39} ....... 10

Fig 2.3: Strain measured from different lattice reflections during heating of MgO/SiC nanocomposites. A representative error bar is inset.\textsuperscript{72} ...............18

Fig 2.4: Average hydrostatic stress measured during heating and cooling of MgO-SiC nanocomposites. A representative error bar is inset.\textsuperscript{72} ...............19

Fig 2.5: Hydrostatic stresses as a function of SiC percentage measured by fluorescence spectroscopy (■) and compared to neutron\textsuperscript{77} (●) and x-ray\textsuperscript{76} (▲) results. (a) Al$_2$O$_3$ matrix, (b) SiC particles. .............................................20

Fig 2.6: Comparison of longitudinal (a) and transverse (b) residual stresses in TMP’d SCS-6/Ti-6-3-2 using X-rays, neutrons and FEM.\textsuperscript{79} .........................22

Fig 2.7: Illustration of how the constrained strain ($e^c$) is calculated from the misfit strain ($e^{T*}$). (a) Isotropic misfit strain $e^{T*}$ of 0.19, (b) strain of ‘ghost’ inclusion $e^T$ obtained from Eq 10, (c) $e^c$ obtained from Eq 12.\textsuperscript{81} ..... 23

Fig 2.8: ABAQUS model prepared for solving showing applied boundary conditions.\textsuperscript{93} ................................................................................. 26

PAPER I

Fig. I.1: Spiral architecture meshed by OOF2. Red highlights SiC section.............41

Fig. I.2: Round SiC particles in a ZrB$_2$ matrix showing SiC particles in compression and the matrix in tension. .................................................................46

Fig. I.3: Plot showing stresses predicted in the ZrB$_2$ matrix (●) and SiC particles (○) compared to measured flexure strengths reported in recent literature..................................................46

Fig. I.4: Neutron diffraction pattern for Zr$^{11}$B$_2$-SiC .........................................48

Fig. I.5: ISAW output showing peak shifts as a function of temperature. The full diffraction pattern for 25°C is displayed at the bottom.\textsuperscript{34} .................49
PAPER II

Fig. II.1: SEM micrographs of ZrB$_2$-30vol% SiC (a), and Zr$_{11}$B$_2$-30vol% SiC (b) showing nearly identical microstructures...........................................73

Fig. II.2: Thermal expansion curves for ZrB$_2$-SiC and Zr$_{11}$B$_2$-SiC......................74

Fig. II.3: Comparison of thermal expansion of ZrB$_2$, SiC, and ZrB$_2$-30vol% SiC, as determined by dilatometry, neutron diffraction, and calculated from published CTE data. All ZrB$_2$ materials were made using $^{11}$B. .........75

Fig. II.4: Heat capacity of ZrB$_2$-30vol% SiC and Zr$_{11}$B$_2$-30vol% SiC measured by DSC. ............................................................76

Fig. II.5: Thermal diffusivity of ZrB$_2$-SiC (nB) and two Zr$_{11}$B$_2$-SiC (B11-1 & B11-2) samples as a function of temperature. ..............................................77

Fig. II.6: Thermal conductivity of ZrB$_2$-SiC (nB) and two Zr$_{11}$B$_2$-SiC (B11-1 & B11-2) samples as a function of temperature. ..............................................78
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Summary of Some Properties of ZrB$_2$</td>
<td>4</td>
</tr>
<tr>
<td>2.2</td>
<td>RT Mechanical Properties of ZrB$_2$-SiC Ceramics</td>
<td>4</td>
</tr>
</tbody>
</table>

**PAPER I**

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.1</td>
<td>RT mechanical properties of ZrB$_2$-SiC ceramics</td>
<td>37</td>
</tr>
<tr>
<td>I.2</td>
<td>Material properties and modeling parameters</td>
<td>39</td>
</tr>
<tr>
<td>I.3</td>
<td>Sizes of SiC particles for shape models</td>
<td>41</td>
</tr>
<tr>
<td>I.4</td>
<td>Comparison of mechanical properties of Zr$^{11}$B$_2$-SiC to other ZrB$_2$-SiC materials</td>
<td>48</td>
</tr>
</tbody>
</table>

**PAPER II**

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>II.1</td>
<td>CTE and thermal conductivity of ZrB$_2$, ZrB$_2$-SiC, B, boron isotopes, and B$_4$C (natural and isotope enriched)</td>
<td>79</td>
</tr>
<tr>
<td>II.2</td>
<td>Batching amounts and average starting particle sizes of constituents</td>
<td>80</td>
</tr>
<tr>
<td>II.3</td>
<td>Density results of the 3 dilatometry specimens</td>
<td>81</td>
</tr>
<tr>
<td>II.4</td>
<td>Percentage changes in thermophysical property values over the temperature range of 500 K to 1500 K for ZrB$_2$-SiC prepared from naturally occurring boron (nB) and isotopically purified $^{11}$B (B11-1 and B11-2)</td>
<td>82</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

1.1 PURPOSE OF THIS THESIS

The goal of the work for this thesis was to create a modeling process that could be used to improve ZrB$_2$-SiC ceramics. These materials are being developed for use in ultra high temperature applications that require high thermal and chemical resistance.\textsuperscript{1} ZrB$_2$ has been studied because of its high melting temperature (3250°C), high hardness (23 GPa) and a high strength (>500 MPa).\textsuperscript{2} SiC has been added to lower densification temperatures and to improve oxidation resistance.\textsuperscript{3} There is still a need, however, to improve upon the strength of these materials. A modeling effort was created in an effort to investigate residual stresses and their role in the strength of a ZrB$_2$ matrix containing uniformly distributed SiC particles. The goal was to create a model capable of not only analyzing the residual stresses that develop as a result of cooling from processing temperatures, but that could also be used to predict new microstructures that could reduce these stresses.

Born out of the desire to validate the models using neutron diffraction to measure the residual stresses, was the replacement of natural boron with the $^{11}$B isotope in the ZrB$_2$. The high neutron absorption characteristics of natural boron required that $^{11}$B be substituted into the ceramics, which then led to a study on the effects of the $^{11}$B isotope on the thermal properties of ZrB$_2$-SiC ceramics. Previous research indicated that isotopically pure boron materials had different thermal conductivities than the natural materials.\textsuperscript{4-7} As a result, the focus of the thesis work shifted towards the study of the Zr$^{11}$B$_2$-SiC ceramics and the impact of $^{11}$B on thermal conductivity and thermal expansion.
1.2 REFERENCES


2. BACKGROUND

2.1 ULTRA HIGH TEMPERATURE MATERIALS

In the continued pursuit of hypersonic flight the materials currently available for the thermal protections systems (TPS) will be insufficient to survive the environments required. Current carbon-carbon systems are coated with silicon carbide but are only useful up to around 1600°C \(^1\), above which temperature there is rapid oxidation and a significant decrease in mechanical strength. New materials with melting temperatures in excess of 3000°C, known as ultra high-temperature ceramics (UHTCs), are currently being researched for use as future TPS materials. Out of the potential choice of materials the carbides and refractory metals have shown poor oxidation characteristics.\(^2,3\) This has promoted further research of the diborides, which have superior oxidation resistance compared to other UHTCs and refractory metals. Of the UHTCs and refractory metals, zirconium diboride (ZrB\(_2\)) has the lowest theoretical density (6.09 g/cm\(^3\)), meaning that similar parts made from ZrB\(_2\) weigh less than those made from current refractory materials or the other UHTCs. Because saving weight will always be of the utmost concern for any flight application, this lower density has further prompted research into the diboride class of materials.

2.2 ZIRCONIUM DIBORIDE BASED MATERIALS

Zirconium diboride has been studied for many years, and many of its properties have been characterized, some of which are summarized in Table 2.1.\(^4-8\) The combination of high melting temperature, high thermal and electrical conductivity, as well as the relatively low density makes ZrB\(_2\) promising for many aerospace applications.
Table 2.1: Summary of Some Properties of ZrB₂.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>6.119</td>
<td>4</td>
</tr>
<tr>
<td>Melting temperature °C</td>
<td>3245</td>
<td>5</td>
</tr>
<tr>
<td>Young's modulus (GPa)</td>
<td>489</td>
<td>6</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>215</td>
<td>6</td>
</tr>
<tr>
<td>Vicker's Hardness (GPa)</td>
<td>23</td>
<td>6</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (K⁻¹)</td>
<td>5.9 x 10⁻⁶</td>
<td>7</td>
</tr>
<tr>
<td>Heat capacity at 25°C (J/(mol · K))</td>
<td>48.2</td>
<td>8</td>
</tr>
<tr>
<td>Thermal conductivity (W/(m*K))</td>
<td>60</td>
<td>7</td>
</tr>
</tbody>
</table>

One of the issues with ZrB₂, is that it has a relatively low strength (300-400 MPa) and poor strength retention at elevated temperatures.⁹,¹⁰ Other materials, such as silicon carbide and silicon nitride, have been added to improve strength, lower densification temperatures and produce fine grained (2-4 μm) microstructures.⁷,¹¹,¹² Use of SiC as an additive has been shown to promote oxidation resistance¹³⁻¹⁶ and improve room temperature mechanical properties as shown in Table 2.2.

Table 2.2: RT Mechanical Properties of ZrB₂-SiC Ceramics.⁷

<table>
<thead>
<tr>
<th>SiC Content (vol %)</th>
<th>Modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>Strength (MPa)</th>
<th>Toughness (MPa*m¹/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>489</td>
<td>23 ± 0.9</td>
<td>565 ± 53</td>
<td>3.5 ± 0.3</td>
</tr>
<tr>
<td>10</td>
<td>450</td>
<td>24 ± 0.9</td>
<td>713 ± 48</td>
<td>4.1 ± 0.3</td>
</tr>
<tr>
<td>20</td>
<td>466</td>
<td>24 ± 2.8</td>
<td>1003 ± 94</td>
<td>4.4 ± 0.2</td>
</tr>
<tr>
<td>30</td>
<td>484</td>
<td>24 ± 0.7</td>
<td>1089 ± 152</td>
<td>5.3 ± 0.5</td>
</tr>
</tbody>
</table>
2.2.1 Conventional Hot Pressing. Several methods are widely used to densify ZrB$_2$-SiC composites. Hot pressing using commercially available ZrB$_2$ and SiC powders is the most widely used process. For one widely reported process, the powders are comminuted and mixed using an attrition mill with WC media. After the powder is dried by rotary evaporation it is packed into a graphite die and hot pressed at 1900°C and 32MPa to densify the final part. This processing method allows full densification at temperatures below the melting temperatures of ZrB$_2$ and SiC, and can produce microstructures with grain sizes approaching 1 µm as seen in Fig 2.1. Unfortunately, this process is not attractive commercially. Hot pressing limits the size and shape of billets and expensive diamond tooling is required to machine the billets into complex shapes.

![Fig 2.1: Thermally etched cross section of ZrB$_2$-30% SiC.](image)
2.2.2 **Reactive Hot Pressing.** Another fabrication method is ‘in situ’ reactive hot pressing. Reactive hot pressing has been studied in an effort to reduce the processing temperature, which should result in even finer grain sizes, and to reduce impurity content, which should improve strength at elevated temperatures. By processing at lower temperatures the expectation is for finer grained materials, which should result in higher strengths. Thermodynamically favorable reactions can be used to produce the desired products, but only thermodynamically stable products can be produced. The powders are mixed using a ball milling process and then hot pressed to form the final part. Several reactions, shown below, have been used to synthesize ZrB\(_2\)-based ceramics.

\[
\begin{align*}
2\text{Zr} + \text{Si} + \text{B}_4\text{C} &\rightarrow 2\text{ZrB}_2 + \text{SiC} \quad (1) \\
2\text{ZrH}_2 + \text{B}_4\text{C} + \text{Si} &\rightarrow 2\text{ZrB}_2 + \text{SiC} + 2\text{H}_2 \quad (2) \\
\text{Zr} + \text{B} + \text{SiC} &\rightarrow \text{ZrB}_2 + \text{SiC} \quad (3)
\end{align*}
\]

Small amounts of B\(_4\)C were added to Reaction 3 to promote the removal of ZrO\(_2\) during an isothermal hold at 1650ºC. All of these methods have been shown to produce nearly fully dense (>95%) parts containing ~30 vol% SiC, at or below 1900ºC.

2.2.3 **Pressureless Sintering.** A third densification technique, pressureless sintering, has recently been applied to ZrB\(_2\)-SiC ceramics. In this process no uniaxial load is applied to densify the part, only heat. This technique is attractive for manufacturing ZrB\(_2\)-SiC ceramics because of the ability to produce near net-shape parts with complex shapes. Early efforts to densify ZrB\(_2\) using this method required the addition of sintering aids including BN, AlN, SiC and B\(_4\)C. Based on a report that a
smaller starting particle size in TiB₂ ceramics improved densification, an attempt was made to densify ZrB₂ ceramics without additives.²⁶ Commercially available ZrB₂ powder was attrition milled using WC media to reduce the starting particle size.²⁷ This powder was pressed into pellets and sintered to nearly full density at 2150ºC for 9 hours. ZrB₂ with a relative density of 98% was produced without additional sintering aids; although some WC was incorporated into the powder due to wear of the milling media. Building on that work, efforts to improve density and lower densification temperature have focused on reacting additives. The addition of B₄C, along with reduced starting particle sizes, led to densities >98% at sintering temperatures as low as 1850ºC.²⁸ Further studies have shown that sintering at 1900ºC with the addition of 2 wt% B₄C and 1 wt% C improved relative density to >99% by further removing the B₂O₃ and ZrO₂ from the ZrB₂ surfaces.²⁹,³⁰

Following these studies, densification of ZrB₂-SiC using pressureless sintering techniques were also investigated.³¹,³² It was found that a borosilicate liquid phase present on the particle surfaces had to be eliminated before the onset of coarsening. B₂O₃ on ZrB₂ and SiO₂ on SiC reacted to form a borosilicate liquid which promoted coarsening of the ZrB₂ grains. Carbon additions along with B₄C combined to react with and remove the borosilicate liquid, thus allowing for parts to be sintered to near full density at temperatures from 1950-2000ºC. This process produced ZrB₂-SiC composites with mechanical properties similar to those obtained from hot pressing except for flexural strength, which was lower (~1089 MPa for the hot pressed grade versus ~460 MPa for the pressureless sintered material).
2.2.4 Other Processing Techniques. Other methods that have been used to densify ZrB$_2$ and ZrB$_2$-SiC include reactive sintering and spark plasma sintering. Reactive sintering is similar to reactive hot pressing where zirconium metal is combined with crystalline boron, silicon and carbon. The mixture is then heated to initiate the reaction with no applied load.\textsuperscript{33} More recently, spark plasma sintering (SPS) has also been investigated to densify ZrB$_2$ and ZrB$_2$-SiC. This process is similar to hot pressing in that a uniaxial load is applied during heating. However, in SPS the heat is produced by a direct or pulsed electric current through the die and powder. Due to the direct heating method, parts can be heated to the sintering temperature and densified more rapidly than through other means, having a total processing time of about 3 hours compared to \~6 hours for conventional hot pressing. Further, rapid heating can reduce grain growth and produce fully dense (>99\%) parts without the used of sintering aids.\textsuperscript{34,35} As with other processing techniques, SPS has also been paired with reactive processing to produce parts at lower temperatures with reduced levels of impurities.\textsuperscript{36} With so many options for the densification of ZrB$_2$-SiC composites, there is great potential for producing any necessary part as future applications dictate.

2.3 SILICON CARBIDE PARTICLE SIZE EFFECT

Throughout the research of ZrB$_2$-SiC composites, studies were conducted to investigate the effect of SiC particle size on properties of the resulting ceramics. Results indicated that the SiC controlled the growth of ZrB$_2$ grains, which had a direct impact on the resulting properties.\textsuperscript{17} Subsequent investigations on the addition of ultra fine SiC (~0.8 µm on average) to ZrB$_2$ showed improved sinterability and mechanical properties
of ZrB$_2$-SiC composites compared to the addition of larger SiC particles (~11.6 µm on average). In these studies, the sub-micron SiC particles were thought to consume more fracture energy due a higher density of energy consuming sites (SiC particles) along the crack path. The increased crack deflection and bridging in these materials led to enhanced fracture toughness and flexural strength compared to materials with coarser SiC particles. The use of ultra fine SiC also allowed ZrB$_2$-SiC composites with only 10 or 15 percent SiC to be sintered to greater than 99% density. The latter result had been impossible without other sintering additives that had been reported in previous work.

More detailed investigations focused on the effect of SiC particle size in composites with 30 volume percent SiC. The grain size of the ZrB$_2$ and SiC was changed by using two different particle sizes of ZrB$_2$ (2 and 6 µm) with the same SiC (0.7 µm) while varying the processing temperature and hold time. The results showed that the strength was affected by the SiC particle size; while the hardness and modulus of elasticity were unaffected. Smaller starting ZrB$_2$ particle size, combined with a shorter processing time, produced the highest strength materials (1063 MPa versus 720 MPa for the larger particle size ZrB$_2$). It was shown that the SiC grain size and the critical flaw size, calculated using the Griffith criterion, were nearly equivalent. Given this, it was concluded that the SiC particle size was most likely the strength limiting flaw in ZrB$_2$-SiC ceramics free of other defects.

Building on this research, experiments were conducted to specifically examine the effect of SiC particle size on the same composites. Varying the starting SiC particle size, while keeping all other processing parameters constant, it was shown (Fig 2.2) that as SiC particle size decreases, the strength increases.
ZrB$_2$-SiC composites with the finer SiC particle size also showed improved densification, possibly due to smaller SiC particles pinning grain boundaries and preventing grain growth as indicated by a smaller ZrB$_2$ grain size when the SiC particles were smaller. This research showed that in order to improve the strength of ZrB$_2$-SiC composites, SiC particle size must be minimized.

### 2.4 RESIDUAL STRESSES

Interest in residual stresses in composite materials, and how they impact mechanical properties, has increased in recent years. As researchers continue to push materials closer to their performance limits it has become more important to understand and control their failure. Residual stresses are important to understand because when
combined with applied stresses they can lead to structural failure. Therefore, the ability to limit residual stresses could improve the performance of a material. Residual stresses in multi-phase materials can come from differences in coefficients of thermal expansion (CTE), yield strengths, or stiffness’ of the phases. Stresses also come in two forms, macro and micro. Macro stresses typically occur in composites as a result of multiple components being joined for an engineering application, such as when two parts are misfit and interact, or as a result of a welding operation. Micro stresses occur in composite materials as a result of different properties of the various phases that constitute the microstructure.

Residual stresses can also be used to improve the static and fatigue loading capabilities of a brittle material. Typically, this is done by creating a compressive residual stress at the surface of the material. Generally, failure cracks originate on the tensile surface of a material; therefore, by preloading the surface in compression it takes more tensile force to initiate a crack. A common example of this is tempered glass where the surface of the glass is cooled rapidly, in relation to the center of the glass, resulting in a compressive surface stress. Residual stresses can act to put compressive stresses on critical flaws; therefore, increasing the critical load required to propagate the crack. However, the downside to this process is that a residual tensile stress is produced near the center of the glass, and once a crack penetrates through the surface, it will run rapidly through the stressed region, shattering the glass violently. In the case of fatigue life, processes such as shot-peening can be used to produce a residual compressive stress on the surface, which can improve the fatigue life.
Understanding how residual stresses develop and how they affect the material is only half of the battle. Residual stresses must be measured and modeled in order to control their impact on designs. Measurement of the stresses, through experimental methods like x-ray diffraction, can be used to understand how processing and material selection can impact the overall strength of a material as well as to validate modeling efforts. Whereas stress measurements can only take place after materials have been produced, modeling can be used to predict residual stresses before a part is ever made, saving time, money and resources. The application of both techniques in combination can lead to improved material design while saving both time and money.

### 2.5 MEASUREMENT TECHNIQUES

A wide variety of techniques are available for the determination of residual stresses in materials, and most of the available non-destructive options are diffraction based. Diffraction techniques can be used to measure changes in interplanar spacing, \( d \), that when used with Bragg’s Law, can be used to calculate lattice strains. When the incident wavelength is known, as well as changes in the scattering angle \( 2\theta \), the change in \( d \) can be determined as shown in Equation 4. The strain can then be calculated from Equation 5 and the resulting stress can be determined using Equation 6.\(^{44}\)

\[
\lambda = 2d \sin \theta \tag{4}
\]

\[
\varepsilon_{ij} = \frac{\Delta d_{ij}}{d_o} = \frac{d_{ij} - d_o}{d_o} \tag{5}
\]
\[
\sigma_{ij} = \frac{E}{1 + \nu} \varepsilon_{ij} + \frac{vE}{(1 + \nu)(1 - 2\nu)} \delta_{ij} (\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33})
\]
\[
\delta_{ij} = 1 \rightarrow i = j
\]
\[
\delta_{ij} = 0 \rightarrow i \neq j
\]

In the equations above, \( \varepsilon \) is the strain, \( d \) is the d-spacing, \( E \) is Young’s modulus, \( \nu \) is Poisson’s ratio, and \( \delta \) is the Kronecker delta function.

Diffraction results can be affected by grain orientations causing peak shifts due to two different types of stresses. The first type of stress, macrostress, is caused by misfits between different regions of a material, which can cover a relatively large area. The second stress type, microstress, is on the same scale as the grain size, and these stresses are always present in polycrystalline materials as a result of different thermal and elastic properties between neighboring grains that are either oriented differently or are simply a different material. This peak shift can be used to determine both macro and micro stresses in composite materials by solving equations 7-9 simultaneously.\(^{43}\)

\[
^{'}\sigma^M_{ij} = m^{'}\sigma^M_{ij} + ^{'}\mu^{'}\sigma^M_{ij} \quad (7)
\]
\[
^{'}\sigma^P_{ij} = m^{'}\sigma^P_{ij} + ^{'}\mu^{'}\sigma^P_{ij} \quad (8)
\]
\[
(1 - f)^{'}\sigma^M_{ij} + f^{'}\sigma^P_{ij} = 0 \quad (9)
\]

Where \( t \) signifies the total stress calculated from Equation 6, \( M \) represents the matrix, \( P \) represents the particulate reinforcement, \( m \) the macro stress, \( \mu \) the micro stress, and \( f \) is the volume fraction of the particulate.
X-ray diffraction (XRD) is the most widely available diffraction method, and can be used to determine residual stresses. The standard wavelength for an x-ray is typically between 0.1 and 0.2 nm, which can penetrate only a small distance (<50 µm) into a specimen.\(^{44}\) XRD is typically considered a surface sensitive technique as a result of this shallow penetration depth.\(^{45}\) Stresses formed by hot rolling a metal plate, shot-peening, or stresses formed during machining can all be measured with XRD. Another strength of XRD is its ability to obtain high local resolution, such as in the area near welds.\(^{46}\) For stress measurements using XRD there is an assumption of plane strain at the surface so the stresses are determined directly using the \(\sin^2 \Psi\) method.\(^{47-49}\) Stress is then related to changes in interplanar spacing by an elastic constant.\(^{45}\)

The limitations for standard XRD experiments are in the measurement of residual stresses in the bulk material. With normal XRD, the small penetration depth limits the measurement of the stresses to those on the surface. Therefore, with normal XRD one must assume that the surface stresses are representative of the bulk stresses which is not necessarily true. To improve the penetration depth, high energy x-ray diffraction (HEXRD) systems have been developed that operate around 100keV.\(^{50-52}\) This method uses a rotating anode and a particle accelerator to create the higher energy x-rays required to penetrate several mm into the bulk. Comparisons between HEXRD and neutron diffraction, which is typically used to evaluate bulk stresses, have shown similar stress values proving the method’s functionality.\(^{53}\)

Despite these limitations, XRD has been used effectively over the years to determine residual stresses in a wide variety of materials. Specifically surface residual stresses have been of interest, due to the fact that the surface is often the initial source for
failure. Taking advantage of the low penetration depth, XRD can be used to determine only those stresses at the surface. XRD systems can also be packaged into portable systems which can evaluate a material in place which is an invaluable resource in the prediction and prevention of failure of materials in use in industry.

2.5.1 Neutron Diffraction. Where XRD is limited in its penetration depth and in its resolution for lighter elements such as oxygen, neutron diffraction is able to fill those voids. Neutrons have wavelengths comparable to atomic spacing, which result in penetration depths of several centimeters. The greater penetration depth allows for the measurement of bulk stresses within parts. Neutron diffraction requires a neutron source, such as a nuclear reactor, or a spallation source, neither of which are widely available. This fact makes neutron diffraction a more difficult and expensive experimental option. Therefore, XRD options are typically explored first. Also due to its complexity, neutron diffraction can not be performed as routinely as XRD. It has been suggested that neutron diffraction and XRD should not be considered competing techniques, but rather complementary techniques that should be used alongside each other during residual stress measurements.

As previously mentioned, there are two options for obtaining neutrons, and they represent two different experimental techniques. A reactor source, which relies on nuclear fission, is required for conventional $\theta/2\theta$ scanning. This method uses a continuous beam source with a constant wavelength to determine $\Delta\theta$ shifts and is better suited for analysis of limited angular segments of the diffraction pattern. A spallation source is used in the time of flight (TOF) neutron diffraction method and is better suited for complete diffraction patterns. With TOF measurements the Bragg angle $\theta$ is held
constant, typically $2\theta = 90^\circ$, while the wavelength of the neutrons changes.\textsuperscript{56} This change is modulated using the spallation source where pulses of neutrons are released having a wide variety of energies which result in different wavelengths, with the most energetic neutrons arriving first. To take advantage of the varying energies, TOF systems such as the Intense Pulsed Neutron Source (IPNS)\textsuperscript{57} at Argonne National Laboratory uses choppers to regulate the incoming wavelengths by periodically interrupting the source (30Hz). This prevents the more energetic neutrons from later pulses from catching up to slower neutrons from previous pulses and, in the case of IPNS, allows for a range of neutron wavelengths from 0.2 – 5.7 Å.\textsuperscript{58,59}

One complication in the measurement of bulk stresses by neutron diffraction is that the plane stress assumption used in XRD measurements is no longer valid. As a result, a stress free standard must be used in combination with the stressed sample to accurately evaluate the residual stresses.\textsuperscript{60,61} The most common source for measurement of a stress free sample in composite materials are fine powders of the starting constituents of the composite.\textsuperscript{62} These measurements can be made using either neutron diffraction or XRD as penetration depth does not affect the results of the stress free powder samples. This is one example of the complementary use of neutron diffraction and XRD.

Neutron diffraction has been used to determine residual stresses in various materials for more than twenty years. Some of the early experiments focused on understanding residual stresses in metals. The stresses resulting from welding operations were one of the most important early investigations that used neutron diffraction.\textsuperscript{63} Neutron diffraction was particularly useful because it was a non-destructive method and provided superior penetration depth to more completely study the weld effects. Other
early applications included studies of the effect of shot-peening metals.\textsuperscript{64,65} Neutron diffraction studies were performed in order to determine the magnitude and coverage of the good residual stress in the materials due to the shot-peening. The studies were able to determine the depth of material affected by this process and were able to better understand the widely used fatigue limiting method. Other uses of neutron diffraction included analysis of the stresses developed in train rails over time,\textsuperscript{66} analysis of overloading materials for fatigue resistance,\textsuperscript{67} analysis of pressure vessels and the impact of being autofrettaged,\textsuperscript{68-69} as well as the analysis of stress fields that develop in two phase materials such as duplex steel.\textsuperscript{70}

Neutron diffraction has also proven invaluable in the study of ceramic composite materials. Due to the depth of penetration and low absorption coefficients for most ceramics, full diffraction peaks for all components of a composite can be resolved. This allows for the use of Rietveld analysis,\textsuperscript{71} which can yield a wealth of information about a material including residual stresses.\textsuperscript{57} A recent study examined the development of residual stresses during thermal cycling of MgO-SiC nanocomposites.\textsuperscript{72} The parts were fabricated by hot pressing in an inert gas atmosphere similar to the processing of ZrB\textsubscript{2}-SiC composites described earlier. A sample of MgO-SiC was oriented such that scattering information from crystallographic planes perpendicular and parallel to the part surface could be recorded. Using the shift in the corresponding peaks, the strains for the material along specific crystallographic planes as well as for directions perpendicular and parallel to the hot pressing direction were determined for the matrix and the particulates. As temperature increased, the strain was reduced towards zero for both the matrix and the particulates. Hydrostatic stresses were then determined for each phase and results
showed the matrix to be in tension while the SiC particulates were in compression. Again, as temperature increased, the stresses returned to zero indicating that the material achieved a ‘stress free’ state at around 1500°C (Fig 2.3 and Fig 2.4). The research concluded that the difference in the coefficients of thermal expansion between the two constituents led to development of residual stresses during cooling from the densification temperature. The work also cited diffusion as a mechanism for stress relaxation, where the grains are able to move to relieve stress at high enough temperatures, which explained why the material would be stress free above 1500°C. The work would not have been possible without the use of neutron diffraction, and the work proved the capabilities of neutron diffraction in the study of residual stresses in composite materials.

Fig 2.3: Strain measured from different lattice reflections during heating of MgO/SiC nanocomposites. A representative error bar is inset.\(^{72}\)
2.5.2 **Fluorescence Spectroscopy.** One non-diffraction method currently being used to measure residual stresses is known as fluorescence piezospectroscopy. This method detects changes in characteristic Raman or fluorescence luminescence lines that shift linearly with differences in hydrostatic stress. The key advantage to this method is that it is cheaper and faster than the diffraction techniques making it superior for routine measurements that require less detail. However, the penetration depth is limited to around ~10 µm, but it can still provide some details about the bulk material. Silicon carbide is known as a material that gives good Raman spectra, so this method could be useful for characterizing ZrB$_2$-SiC materials. Using optical microscopy spectral shifts can be observed and measured. This method has been used to study fiber composites and has provided information about stresses along the fibers.

In more recent studies, Cr$^{3+}$ fluorescence probes have been used to explore residual stresses in Al$_2$O$_3$-SiC nanocomposites. One study used fluorescence probes to determine the residual stresses in the matrix and in the particles, and then compared the data to previous measurements made by neutron and x-ray diffraction. The results
showed that the fluorescence measurements agreed with the previous data (Fig 2.5).

Another study on the effects of indentations and scratches on Al₂O₃-SiC nanocomposites also used Cr³⁺ fluorescence to determine residual stresses, which further showed the power of this technique. The study was done to show that during machining, a residual compressive stress formed on the surface, giving parts unexpectedly high strength. Surface effects were evaluated using fluorescence and the results were compared to polycrystalline alumina to better understand residual stresses and their effect on the properties.⁷⁸

![Graph](image)

Fig 2.5: Hydrostatic stresses as a function of SiC percentage measured by fluorescence spectroscopy (■) and compared to neutron⁷⁷ (●) and x-ray⁷⁶ (▲) results. (a) Al₂O₃ matrix, (b) SiC particles.

### 2.6 MODELING

As mentioned previously, measuring residual stresses is one part of a broader strategy to understand and control residual stresses. Modeling, both analytically and
computer-based, can provide insight into the interactions that cause stresses and aid in the prediction of stresses in parts before they are manufactured. Finite element modeling (FEM) has been used to predict stresses and strains in titanium matrix composites\textsuperscript{79,80} and the results have been compared to x-ray and neutron diffraction results (Fig 2.6).

Generally, neutron diffraction results agreed with FEM results better than XRD due to the ability of neutron diffraction to measure bulk properties. These experiments showed the relationship between modeling and measuring residual stresses, especially that experimental measurements can be used to validate models.

Computational modeling of thermal residual stresses, while the standard now, owes its beginning to J. D. Eshelby and his work during the middle of the 20\textsuperscript{th} century. His work to evaluate misfit stresses that developed between ellipsoidal particles in a matrix has become known as the Eshelby model.\textsuperscript{81}

Misfits can arise from a difference in thermal expansion coefficients between the two materials, causing one to expand more than the other, which produces a misfit strain between the two materials. Throughout his research, Eshelby formulated a mathematical approach for determination of the stresses that formed as a result of these ellipsoidal inclusions.\textsuperscript{82,83} For the case of a misfit strain caused by thermal contraction (Fig 2.7), Eshelby’s equations can be used to determine the transformation strain, $\varepsilon^T$, and stress, $\sigma_1$, that result due to difference in thermal expansion (Equations. 10 & 11). The constrained strain of the inclusion is shown in Equation 12.
Fig 2.6: Comparison of longitudinal (a) and transverse (b) residual stresses in TMP’d SCS-6/Ti-6-3-2 using X-rays, neutrons and FEM.²⁹

\[
\varepsilon^T = \left[ (C_I - C_M)S + C_M \right]^{-1} C_I (\alpha_I - \alpha_M) \Delta T
\]  
\hspace{2cm} (10)

\[
\sigma_I = C_M (S - I) \varepsilon^T
\]  
\hspace{2cm} (11)

\[
\varepsilon^c = S \varepsilon^T
\]  
\hspace{2cm} (12)

In the equations, the subscripts \( I \) and \( M \) represent the inclusion and matrix respectively, \( C \) is the stiffness tensor, \( S \) is the Eshelby tensor, \( \alpha \) is the coefficient of thermal expansion, and \( I \) is the identity matrix. These equations, and others formulated by Eshelby, have been used to calculate stresses in various composite materials over the years⁸⁴-⁸⁷, and the Eshelby method has proven a valuable tool in the determination of residual stresses.

The Eshelby model can approximate strains, but it is not the only mathematical approach to evaluating residual stresses. Finite difference methods (FDM) and finite element methods (FEM) both use partial differential equations to solve for stress and strain.⁸¹ These methods divide the part into many small sections known as elements.
The resulting group of elements, known as the mesh, can then be evaluated individually allowing for solutions for each small area, as well as the interactions between those areas.

Fig 2.7: Illustration of how the constrained strain ($e^c$) is calculated from the misfit strain ($e^{T*}$). (a) Isotropic misfit strain $e^{T*}$ of 0.19, (b) strain of ‘ghost’ inclusion $e^T$ obtained from Eq 10, (c) $e^c$ obtained from Eq 12.81

Both methods solve the general two-dimensional second order equation (13), and break the part into smaller elements, but FDM must use rectangular elements while FEM can use almost any element type, typically providing a more accurate result.

$$a \frac{\partial^2 \phi}{\partial x^2} + b \frac{\partial^2 \phi}{\partial x \partial y} + c \frac{\partial^2 \phi}{\partial y^2} + d \frac{\partial \phi}{\partial x} + e \frac{\partial \phi}{\partial y} + f \phi + g + a \frac{\partial \phi}{\partial t} = 0$$ (13)
While FDM is typically simpler, FEM is better suited to solving steady-state problems and complex geometries making it the more widely used option for modeling of systems like metal matrix composites. FEM uses basic starting equations, such as \( F = K a \), for steady-state stress analysis where \( F \) is a force vector, \( K \) is a stiffness vector and \( a \) is a vector of displacements and other unknowns. The general solution method for FEM problems can be broken down into several steps.

- Selection of the partial differential equation
- Meshing the part
- Evaluation of \( K \) and \( F \) for each element. This can be done using variational and weighted residual methods. This step represents the core of FEM solutions.
- Assembly and solution of a simultaneous set of equations.

Finite element methods can be used to solve for multiple fields at one time, such as heat transfer and displacement.\(^88\) These problems, known as coupled thermo-mechanical problems, are used to solve for the stresses that result from thermal expansion differences between adjacent cells.

While FEM can be solved by hand for a small number of elements, the solution of more complex problems requires computer software. Programs such as ABAQUS\(^89\), ANSYS\(^90\), and many others are widely used to run finite element simulations. Computational modeling technology is often paired with computer aided design (CAD) tools, which allows the engineers to analyze any part that can be drawn. This technology is now used in thermomechanical modeling and has become more important in the engineering process and a key design tool for composite materials.\(^91\)
Commercially available FEM packages all use the same basic three step process: pre-processing, solver, and post-processing. During pre-processing the model is created, material properties are applied, and boundary conditions are implemented. During this step the mesh will also be created and the geometry prepared for solving. Fig 2.8 shows an example of a model prepared for solving.

Once ready, the solver is prepared and the relevant solution technique, i.e. displacement or heat transfer, is selected. After solving, the results are analyzed during the post-processing step. Typically graphical interfaces display the results of the simulation, and individual variables (stress, strain, heat flux, etc.) can be selected and displayed. Results can also be graphed with one variable displayed as a function of another or exported to spreadsheets for use in other calculations.

Various software packages have been used to simulate residual stresses in materials. Much of the work with the modeling software has focused on metals as they are the most widely used engineering materials. Residual stresses resulting from processing in steel disks,\textsuperscript{92} stresses from thermal cycling in Al-SiC\textsubscript{p} composites,\textsuperscript{93} and thermal strains in titanium matrix composites\textsuperscript{79,80} have all been explored using computer FEM. One study used finite element simulations to investigate the residual stresses that develop in Mo- and FeAl- toughened Al\textsubscript{2}O\textsubscript{3} after hot pressing.\textsuperscript{94} The simulation applied both a compressive load boundary condition to simulate the pressing, and a thermal load decrease to the part to represent cooling. The analysis also explored thermal expansion effects. Another simulation explored the effects of residual stress on the strength and toughness of TiN-Si\textsubscript{3}N\textsubscript{4} composites.\textsuperscript{95} The effect of the size and spacing of the dispersed particles (TiN) on the residual stresses, crack propagation and crack deflection were
investigated both experimentally and by finite element simulation. With the simulations, the researchers were able to show a relationship between particle sizes and strength and toughness, with increasing particle size decreasing strength but increasing toughness. All the various studies show the great potential of computational finite element modeling to play an important role in the future design and analysis of materials.

2.7 REFERENCES


I. FINITE ELEMENT MODELING OF INTERNAL STRESS FACTORS FOR ZRB$_2$ – SIC CERAMICS

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ABSTRACT

Commercial finite element modeling software (ABAQUS and OOF2) was used to calculate the internal stresses produced during cooling after hot pressing of ZrB$_2$ – SiC ceramics. The size and shape of the SiC inclusions was varied to determine their effect on the residual stresses. Alternate SiC particle shapes designed to limit residual tensile stresses were modeled to minimize residual thermal stresses. Models were validated by measuring actual residual stresses by neutron diffraction. Due to the high neutron absorption of the more common boron isotopes, ZrB$_2$-SiC parts were fabricated by reactive hot pressing using isotopically pure $^{11}$Boron for these experiments. Characterization of the $^{11}$B materials confirmed similar microstructure and material properties (hardness, Young’s modulus and flexure strength) to parts made using powders containing naturally occurring boron. While exact residual stresses for the ZrB$_2$-SiC composites have yet to be determined, models to investigate the trends in SiC particle size and shape effects, and a method to create neutron diffraction compatible materials, have been accomplished.
1. INTRODUCTION

Materials for thermal protection systems for hypersonic flight and re-entry vehicles were the focus of research in the past (1960’s to 70’s) and again in more recent years (2000 to present). Zirconium diboride (ZrB$_2$), from the family of ultra-high temperature materials, has been studied for use in applications that require high thermal and chemical resistance.\(^1\) ZrB$_2$ has a high melting temperature (3250ºC), high hardness (23 GPa) and a high strength (>500 MPa).\(^2\) Silicon carbide (SiC) is commonly added to ZrB$_2$ to reduce processing temperatures, control grain size, and improve the mechanical properties and oxidation resistance.\(^3\) A wide variety of processing methods have been used to synthesize these materials such as hot pressing, reactive hot pressing, and pressureless sintering. Reactive hot pressing has shown promise due to the reduced processing temperatures and for the ability to use phase pure starting components such as Zr and Si instead of using commercially available ZrB$_2$ and SiC powders.\(^4-6\) Equations 1-3 list some of the reactions that have been used to synthesize ZrB$_2$-SiC composites.

\[
\begin{align*}
2\text{Zr} + \text{Si} + \text{B}_4\text{C} & \rightarrow 2\text{ZrB}_2 + \text{SiC} \\
2\text{ZrH}_2 + \text{B}_4\text{C} + \text{Si} & \rightarrow 2\text{ZrB}_2 + \text{SiC} + 2\text{H}_2 \\
\text{Zr} + \text{B} + \text{SiC} & \rightarrow \text{ZrB}_2 + \text{SiC}
\end{align*}
\]

The addition of up to 30 vol% SiC has been shown to markedly improve the strength of ZrB$_2$-SiC over monolithic ZrB$_2$ (Table I.1). Further, the addition of ultra fine (submicron) SiC particles improved sinterability in ZrB$_2$-SiC composites,\(^7,8\) while providing improved fracture toughness and flexural strength. In other studies, SiC particles were determined to be the strength limiting flaw, and, thus, decreasing SiC particle size resulted in an increase in the strength of ZrB$_2$-SiC ceramics.\(^9,10\)

A side effect of the use of a second phase with markedly different linear coefficients of thermal expansion (CTEs) is the residual stresses that are generated during cooling from the processing temperature. Residual stresses in composite materials, and how they impact mechanical properties, have become an increasingly important subject in materials research in recent years.\(^11\) As researchers continue to push materials closer
to their property limits, it has become more important to understand and control failure. Residual stresses are important because, when combined with applied stresses, they can lead to premature structural failure. Thus, the ability to limit residual stresses could improve the thermo-structural capabilities of a material. These stresses in multi-phase materials such as ZrB$_2$-SiC, arise from the difference in the CTE of the phases (for ZrB$_2$ CTE = 6.7 x 10$^{-6}$ K$^{-1}$; for SiC CTE = 4.7 x 10$^{-6}$ K$^{-1}$).

To attempt to accommodate residual stresses in engineering designs, several modeling and measurement techniques have been investigated. The majority of the modeling techniques used to predict residual stresses fall into two main categories, Eshelby-type and finite element models. Analytical models derived from Eshelby type analysis can be used to predict the stresses using simple mathematical relations, but are often only valid for mean phase stresses.\textsuperscript{12,13} Finite element models can be used to model complex constitutive laws, but are often limited by idealist unit cell representations.\textsuperscript{14} Finite element analysis (FEA) programs have the ability to run the complicated equations on microstructures built with computer aided design (CAD) software. Programs such as ABAQUS\textsuperscript{15} and Object Oriented Finite Element Analysis (OOF2)\textsuperscript{16} have proven useful for this type of analysis.\textsuperscript{17-19} Other programs have also been used to model thermal residual stresses, and in some cases to attempt to relate those stresses back to strength and fracture toughness.\textsuperscript{20-24}

Experimental techniques for measuring residual stresses in materials can be used to validate the models. The primary non-destructive methods for determining residual stresses are X-ray and neutron diffraction. X-ray diffraction is the least expensive and more widely available testing method; however, due to its low depth of penetration (< 50

<table>
<thead>
<tr>
<th>SiC Content (vol %)</th>
<th>Modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>Strength (MPa)</th>
<th>Toughness (MPa*m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>489</td>
<td>23 ± 0.9</td>
<td>565 ± 53</td>
<td>3.5 ± 0.3</td>
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<td>450</td>
<td>24 ± 0.9</td>
<td>713 ± 48</td>
<td>4.1 ± 0.3</td>
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<tr>
<td>20</td>
<td>466</td>
<td>24 ± 2.8</td>
<td>1003 ± 94</td>
<td>4.4 ± 0.2</td>
</tr>
<tr>
<td>30</td>
<td>484</td>
<td>24 ± 0.7</td>
<td>1089 ± 152</td>
<td>5.3 ± 0.5</td>
</tr>
</tbody>
</table>
µm) it is only effective for measuring residual stresses near external surfaces. Neutron diffraction, in contrast, is more promising because of improved penetration due to a wavelength closer to atomic spacing. Use of neutron diffraction has been limited by cost and access to pulsed neutron sources. Another limiting factor for neutron diffraction is the neutron absorption characteristics of the elements being tested. The thermal neutron absorption for a typical, commercial grade boron (B) is around 770 barns, based on the volumetric contributions of the boron isotopes (20 vol% $^{10}$B, 3835 barns; 80 vol% $^{11}$B, 0.0055 barns). A neutron absorption of ~100 barns is too high for use in a neutron diffraction experiment. A high absorption cross section results in low scattered intensity, which is detrimental to neutron diffraction analysis. Detectors in the system pick up scattered neutrons to create diffraction patterns, so a higher scattering ability (low neutron absorption) is required. Therefore, isotope $^{11}$B was used in the current study, along with Zr and SiC, to fabricate ZrB$_2$-SiC materials for residual stress testing.

The objective of this study was to model residual stresses in ZrB$_2$-SiC ceramics that result from the CTE mismatch. SiC particle size and shape were varied to determine their impact on the resultant stresses. ZrB$_2$-SiC parts produced using the $^{11}$B isotope were fabricated so that the residual stresses could be measured by neutron diffraction analysis to validate the models.

2. EXPERIMENTAL PROCEDURE AND MODEL DEVELOPMENT

2.1 MODEL CREATION AND SETUP

Using a commercially available finite element analysis program, ABAQUS, models representing SiC particulates in a ZrB$_2$ matrix were created. The SiC phase was modeled as a round particle in a two dimensional (2D) ZrB$_2$ matrix. Material properties were assumed to be isotropic for both the ZrB$_2$ and the SiC after initial modeling efforts indicated only small changes in stress fields as a result of the anisotropic properties of the $\alpha$-SiC (hexagonal polytype). The material properties used in the models, as well as other key model input variables, are included as Table I.2.
The first step was to build a 2D matrix measuring 15µm square. The SiC particles were set on a grid system to limit random interaction and overlap and were from 4 (2x2 grid) to 400 (20x20 grid) in number. The phases were sized such that there was always ~30 vol% SiC in the composite. These particles were assigned to a section with SiC material properties, while the matrix was assigned another section with ZrB$_2$ properties. Next, boundary conditions were applied to simulate the heating and cooling conditions that are typical of the hot pressing cycle for ZrB$_2$-SiC ceramics. To accomplish this, the part had to be heated without creating any stress or expansion. This was accomplished by using a field condition that set the initial temperature without altering the microstructure in any way. The cooling boundary condition was setup using a surface film condition. The surface film condition cools the part according to equation 4,

$$q = -h \times (T - T_o)$$

(4)

where $q$ is the heat flux, $h$ is the surface film coefficient and $T_o$ is the temperature of the surrounding material, which is also known as the sink temperature. The sink temperature allowed for the cooling rate of all four sides to be adjusted individually to account for the

<table>
<thead>
<tr>
<th>Material Properties</th>
<th>ZrB$_2$</th>
<th>SiC</th>
<th>Modeling Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus$^{33}$ (GPa)</td>
<td>489</td>
<td>430</td>
<td>Surface Film Coefficient</td>
</tr>
<tr>
<td>Thermal Conductivity$^{33}$ (W/m•K)</td>
<td>64.4</td>
<td>110</td>
<td>Sink Temperature</td>
</tr>
<tr>
<td>CTE$^{33}$ (µm/µm•K)</td>
<td>6.80 x $10^{-6}$</td>
<td>4.50 x $10^{-6}$</td>
<td>Initial Temperature</td>
</tr>
<tr>
<td>Density$^2$ (g/cm$^3$)</td>
<td>6.26</td>
<td>3.18</td>
<td>Mesh Seeding Size</td>
</tr>
<tr>
<td>Specific Heat$^{33}$ (J/g•K)</td>
<td>0.5</td>
<td>0.67</td>
<td>Step Size</td>
</tr>
<tr>
<td>Poisson’s Ratio$^{33}$</td>
<td>0.15</td>
<td>0.17</td>
<td>Time Period</td>
</tr>
</tbody>
</table>
location of the model within a larger part. Because the models were a local/global approximation, it was important that the model be able to predict different behavior based on the sample being either completely within a larger part or located near the edge of a billet.

With all the material properties and boundary conditions set, the part was then meshed. A coupled temperature-displacement element type was used, which allowed for static stress/strain relationships to be run along with thermal stress/strain and heat fluxes. The model was given a step size of 0.004 seconds with a maximum allowable temperature change per step of 50°C. This created steps that allowed examination of the stresses at nearly any temperature during the cooling process. Post processing was performed using the system available in ABAQUS and was used to determine the stresses in the material.

2.2 MODELING SIZE AND SHAPE EFFECTS

With the modeling process, an effort was made to model ZrB₂-SiC ceramics with different microstructures. Shape effects were explored by modeling different SiC shapes and sizes using the same grid pattern used in the earlier size effect models (Table I.3). Squares, hexagons, and peanut shapes were all modeled to further explore the size effects and any effect the shape of the SiC particle might have on the residual stresses. The peanut shape was created in an attempt to minimize the addition of stresses from neighboring particles. The particles were aligned such that each particle was rotated 90° relative to its neighbors such that a convex side on one particle always faced a concave side of its neighbors.

A spiral shaped particle was also explored. Based on a spiral shape created in earlier research in Al₂O₃ – ZrO₂ systems, SiC particles were formed into spiral shapes allowing ZrB₂ to penetrate between each layer of the spiral as shown in Fig. I.1.
Table I.3: Sizes of SiC particles for shape models.

<table>
<thead>
<tr>
<th>Grid</th>
<th>Hexagon Leg (µm)</th>
<th>Square Side (µm)</th>
<th>Circle Diameter (µm)</th>
<th>Peanut Radius (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2x2</td>
<td>2.549</td>
<td>4.108</td>
<td>4.635</td>
<td>1.554</td>
</tr>
<tr>
<td>3x3</td>
<td>1.699</td>
<td>2.739</td>
<td>3.090</td>
<td>1.036</td>
</tr>
<tr>
<td>4x4</td>
<td>1.274</td>
<td>2.054</td>
<td>2.318</td>
<td>0.777</td>
</tr>
<tr>
<td>5x5</td>
<td>1.019</td>
<td>1.643</td>
<td>1.854</td>
<td>0.621</td>
</tr>
<tr>
<td>6x6</td>
<td>0.850</td>
<td>1.369</td>
<td>1.545</td>
<td>0.518</td>
</tr>
<tr>
<td>7x7</td>
<td>0.728</td>
<td>1.174</td>
<td>1.324</td>
<td>0.444</td>
</tr>
<tr>
<td>8x8</td>
<td>0.637</td>
<td>1.027</td>
<td>1.159</td>
<td>0.389</td>
</tr>
<tr>
<td>9x9</td>
<td>0.566</td>
<td>0.913</td>
<td>1.030</td>
<td>0.345</td>
</tr>
<tr>
<td>10x10</td>
<td>0.510</td>
<td>0.822</td>
<td>0.927</td>
<td>0.311</td>
</tr>
</tbody>
</table>

Fig. I.1: Spiral architecture meshed by OOF2. Red highlights SiC section.

2.3 OOF2

In addition to ABAQUS, the program Object Oriented Finite Element Analysis (OOF2; freeware available from the National Institute for Standards and Technology) was used to model an actual ZrB$_2$-SiC microstructure from micrograph obtained by scanning electron microscopy (SEM). The micrograph was imported into the program, and using image enhancement tools, was enhanced such that the contrast between the darker SiC phase and the lighter ZrB$_2$ phase was a large as possible. OOF2’s image
selection tools were then used to select all of the SiC using a combination of the ‘burn method,’ which selects other equivalent neighboring colors according to set contrast values, and individual pixel selection to improve boundaries between the materials. Once selected, the pixels representing the SiC and ZrB$_2$ were assigned to groups and given material properties.

The most complicated process in OOF2 was the creation of the skeleton. The skeleton is the backbone by which the mesh is created and the boundary conditions are assigned. Starting with four square elements, the skeleton was refined until the homogeneity of the elements was better than 99%. Initially the elements contained some SiC pixels and some ZrB$_2$ pixels, resulting in poor homogeneity (approximately 40%). The program provided extensive tools to split the initial elements into smaller elements, move them along boundary conditions, and to pin them in certain locations in order to obtain the best possible skeleton. Individual elements were also selected on the basis of their homogeneity and modified to create a finer mesh at the boundaries while allowing for larger elements within larger sections of one material or the other. Once completed, the program created a mesh over top of the skeleton. Boundary conditions could then be applied using OOF2, but to maintain the original modeling conditions, the skeleton, mesh, and material sections were exported into ABAQUS using a program called OOF2ABAQUS. This allowed the model created in OOF2 to have the exact same boundary conditions applied as the other models and the same processor and post-processing to be run on the OOF2-based model. Using OOF2, it was then possible to compare idealized models to actual microstructures.

2.4 POWDER PROCESSING

ZrB$_2$-SiC composites were fabricated using the $^{11}$Boron ($^{11}$B) isotope so the residual stresses could be measured by neutron diffraction. Crystalline $^{11}$B (Isotopically 99.65 At% $^{11}$B, >99.99 wt% phase pure) with an average starting particle size of around 10µm was donated by EaglePicher, LLC. The boron powder was ball milled in hexane using tungsten carbide media for 17 hours to reduce the particle size to ~1µm. The powder was separated from the hexane by rotary evaporation (Model Rotavapor R-124, Buchi, Flawil, Germany) at a temperature of 70ºC, a vacuum of ~30 kPa, and a rotation
speed of 140 rpm. The $^{11}$B powder was then combined with other commercial powders ZrH$_2$ (Grade C, Chemetall, Frankfurt, Germany) and SiC (UF-25, H.C. Starck, Newton, MA) to produce a ZrB$_2$-30 vol% SiC composite according to equation 5, and based on previous reaction processing studies.\textsuperscript{3-5}

$$ZrH_2 + ^{11}B_2 + SiC \rightarrow Zr^{11}B_2 + SiC + H_2(g)$$  \hspace{1cm} (5)

After batching, the powder was attrition milled (Model HD-01; Union Process, Akron, OH) in hexane at 600 rpm for 240 min in a fluoropolymer coated bucket using tungsten carbide media and a tungsten carbide spindle to reduce the starting particle sizes. The powder was again dried by rotary evaporation.

The composites were then densified using a reaction hot pressing process. The powder was loaded into a graphite die lined with BN-coated graphite foil, and was compacted at a 30 MPa uniaxial pressure. The temperature of the graphite die was monitored using an infrared pyrometer (Model OS 3708, Omega Engineering, Stamford, CT). From room temperature to 1650°C, the furnace was heated under a vacuum of ~20 Pa. At 1650°C the chamber was backfilled with argon and a flowing argon atmosphere was maintained through the rest of the hot pressing cycle. The furnace was heated at a rate of ~5°C/min up to 1000°C, the temperature at which all of the H$_2$ gas had been released, as indicated by a decreased vacuum pressure. After release of the H$_2$, the heating rate was increased to ~20°C/min. When the furnace reached 1900°C, a uniaxial pressure of 32 MPa was applied for 45 min after which the furnace was turned off and allowed to cool. The pressure was released at 1700°C. The resulting billets were nominally 4.625 mm in diameter x 3 mm thick after hot pressing.

2.5 CHARACTERIZATION

Several characterization experiments were performed to compare the composite made with $^{11}$B to those produced with natural B consisting of mixed B isotopes. The microstructures of polished cross sections were examined using a scanning electron microscope (SEM; Model S4700 Hitachi, Tokyo, Japan). The bulk density of each part was measured using the Archimedes method with distilled water as the immersing
medium. Vickers’ microhardness measurements (Model V-1000-A2, Leco, St. Joseph, MI) were performed using a test load of 2 kg and a dwell time of 10 sec. Flexural strength was determined using a 4-point bend test according to ASTM standard C1161-02a using size A bend bars (nominally 1.5 mm by 2 mm by 25 mm). According to ASTM Standard C1259-01, Young’s modulus was measured by impulse excitation (Model MK4-I Grindosonic, J.W. Lemmens, St. Louis, MO). X-ray diffraction (XRD: Scintag, XDS 2000, Cupertino, CA) analysis was used to confirm the phase composition of the material after reaction hot pressing.

2.6 NEUTRON DIFFRACTION

Neutron diffraction was performed on three samples to determine residual stresses at the Intense Pulsed Neutron Source (IPNS) facility of Argonne National Laboratory. Using the general purpose powder diffractometer (GPPD), flexure bars of ZrB$_2$-SiC were loaded onto the alumina holder in a molybdenum furnace and placed under vacuum. Data was gathered for 2 hours at temperatures ranging from room temperature (~25ºC) up to 1200ºC (using 100ºC increments to 700ºC, and then 50ºC increments to 1200ºC). Powder diffraction studies, which are required for calculation of residual stresses, have not been completed, but will be reported in a subsequent publication.

3. RESULTS AND DISCUSSION

3.1 MODELING EFFORTS

3.1.1 Size Effect

Finite element models based on ZrB$_2$-30 vol% SiC composites containing idealized round SiC particles, predicted compressive residual stresses in the dispersed SiC particles while the ZrB$_2$ matrix immediately surrounding each particle was in tension. Previously an Eshelby analysis shown in equation $6^{30}$, had been used to predict radial compressive stresses as high as 2.1 GPa within the ZrB$_2$ matrix and tangential tensile stresses of 4.2 GPa at the ZrB$_2$-SiC boundaries.$^3$
\[ \sigma_{\text{radial}} = -2 \times \sigma \tan = \frac{(\alpha_m - \alpha_i)\Delta T}{(1-2\nu)E_i + (1-\nu_m)(2E_m)} \left( \frac{R}{r + R} \right)^3 \]  \hspace{1cm} (6)

Equation 6 assumes round SiC inclusions of radius R, and predicts the stress at a distance \( r \) from the interface where \( m \) denotes matrix, \( i \) denotes inclusion, \( \alpha \) represents CTE, \( \nu \) is Poisson’s ratio, and \( E \) is Young’s modulus.

Stress fields were also observed to overlap between particles, resulting in larger tensile stress fields as shown in Fig. I.2. The maximum and minimum stresses for each model were recorded and plotted alongside experimental results for flexural strength vs. SiC particle size (Fig. I.3). The results showed that as particle size decreased, the magnitude of the tensile stresses in the matrix decreased, while the magnitude of the compressive stresses in the particles increased. This corresponded to an increase in strength as the particle size decreased. While the exact magnitudes of the residual stresses are unknown, the data demonstrates a strong correlation between the magnitude of the residual stresses and measured strength. The compressive stresses in the SiC particles, as well as the tensile stresses surrounding them, are consistent with a higher propensity to deflect cracks. Crack deflection would force the crack into a different mode and that energy consuming effect would improve the strength of the material, which agrees with findings in previous studies.\(^7,8\) The smaller particles also reduced the size of the areas in the matrix that were under the most severe tensile load, decreasing the probability that a critical flaw would form within those areas.

3.1.2 Shape Effect

Models containing 30 vol% SiC, having square or hexagonal shapes, showed a similar trend to the round SiC particles where decreasing SiC particle size decreased the magnitude of the tensile stresses in the matrix and increased the magnitude of the compressive stresses in the inclusions. However, the data overlap made it difficult to determine if one or more of the shapes might be superior in terms of the strength of an as-processed ceramic. One conclusion that can be drawn from the models is that sharp points on the SiC particles (with increasing sharpness going from round to hexagonal to square) increased the residual tensile stresses in the ZrB\(_2\) at the ZrB\(_2\)-SiC interfaces. The sharp corners acted as stress concentrators, an effect observed in other, similar modeling
Fig. I.2: Round SiC particles in a ZrB$_2$ matrix showing SiC particles in compression and the matrix in tension.

Fig. I.3: Plot showing stresses predicted in the ZrB$_2$ matrix ($\bullet$) and SiC particles ($\circ$) compared to measured flexure strengths reported in recent literature.
A final result of this initial study was that the square particles showed a reduced combined stress affected area in the matrix. The peanut shape was then developed as a way to enhance this effect. The peanut shape would, theoretically, provide no sharp corners and so that the highest stress point on each particle, the convex ends, would be facing the lowest tensile face of the neighboring particle, which was the concave middle. The models concluded that even though there was a high stress point at the end of each particle, there was little combined stress effect between the particles due to their specific orientations.

After the initial results of the SiC particle studies, the spiral architectures were developed. Early results of spiral shaped SiC inclusions exhibited a smaller stress gradient between the matrix and particles indicating a promising microstructure. While the overall magnitudes of the tensile stresses were not significantly lower than other shapes, it was theorized that a smaller stress gradient would lead to fewer micro cracks during cooling and improve the overall strength of macroscopic parts. Subsequent fabrication of ceramics containing novel SiC particle shapes in a ZrB$_2$ matrix resulted in much lower strengths (~150 MPa) than was expected based on the original models. Returning to the models and using OOF2 to model actual microstructures, it was determined that due to the large size of the SiC inclusions (~100 µm in diameter) the volume affected by the residual tensile stresses was much greater than originally modeled leading to a greater probability of containing a critical flaw within those areas, which would account for lower strengths.

### 3.2 11Boron / Neutron Diffraction

A ZrB$_2$-30 vol% SiC composite was fabricated from $^{11}$B, ZrH$_2$, and SiC by reaction hot pressing. Archimedes analysis revealed the parts to be ~99% of their theoretical density, assuming that approximately 1 wt% WC was picked up from the milling media during attrition milling. Comparison of known diffraction patterns for ZrB$_2$ and SiC to a neutron diffraction pattern collected from the reaction hot pressed parts confirmed that a ZrB$_2$-SiC composite had formed (Fig. I.4). Vickers’ microhardness results, along with results from strength testing, were compared to values found in the literature to confirm that the material was similar to those produced using
powders containing naturally occurring boron (Table I.4). Hardness values ranged from 27 GPa (ZrB$_2$-SiC) to 20.5 (Zr$^{11}$B$_2$-SiC) and Young’s modulus numbers ranged from 510 (ZrB$_2$-SiC) to 412 (Zr$^{11}$B$_2$-SiC), while the strength numbers were less than half of previous values of 1089 and 800 MPa. Visual comparison of the micrographs for ZrB$_2$-SiC and Zr$^{11}$B$_2$-SiC showed that the $^{11}$B material appeared to have grains roughly twice the size of the higher strength materials. According to previous work, larger SiC grains lead to decreased strength, which may explain the lower strength in the materials containing $^{11}$B. However, the strength results are based on a small sample set (3) of flexure bars, so further testing must be conducted to determine an accurate flexure strength value.

Fig. I.4: Neutron diffraction pattern for Zr$^{11}$B$_2$-SiC.

Table I.4: Comparison of mechanical properties of Zr$^{11}$B$_2$-SiC to other ZrB$_2$-SiC materials.

<table>
<thead>
<tr>
<th></th>
<th>HP$^2$ ZrB$_2$-SiC</th>
<th>RHP$^6$ ZrB$_2$-SiC</th>
<th>RHP$^6$ Zr$^{11}$B$_2$-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (GPa)</td>
<td>484</td>
<td>510</td>
<td>412</td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>1089 ± 152</td>
<td>800 ± 115</td>
<td>373 ± 110</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>24 ± 0.7</td>
<td>27 ± 2.2</td>
<td>20.5 ± 0.6</td>
</tr>
</tbody>
</table>
Although not all of the experiments needed to determine residual stresses have been completed, some useful data has been gathered. As temperature increased, the diffraction peaks shifted to lower two theta values, indicating an increase in d-spacing correlating to thermal expansion of the composite material. (Fig. I.5) Once analysis of the powder samples is complete, the inherent thermal expansion of each phase can be calculated, which will allow the strains to be determined for each phase in the composite material. The diffraction patterns from the experiments also provided evidence that the use of $^{11}$B to produce the parts made neutron diffraction possible. The patterns were visible within the first few minutes of data acquisition, which indicated the excellent scattering from the material.

![Fig. I.5: ISAW output showing peak shifts as a function of temperature. The full diffraction pattern for 25°C is displayed at the bottom.](image)

4. CONCLUSIONS

Using commercially available finite element analysis software (ABAQUS), models were constructed to represent ZrB$_2$-30 vol.% SiC ceramics. The models, while unverified, provided insight into the nature of the residual stresses that develop during
cooling from the final processing temperature as a result of the thermal expansion mismatch between the constituents of the composite. Stress values were compared to strength data taken from the literature and indicate trends that agree with published experimental data. Modeling has also been used to help explain low strengths measured for ZrB$_2$ containing novel SiC inclusions by focusing on the large areas under high tensile load due to the large size of the SiC inclusions.

Fully dense (~99%) ZrB$_2$-SiC parts were successfully fabricated by reaction hot pressing of $^{11}$B isotope, ZrH$_2$ and SiC powders. The material had comparable hardness (20.5 to 27 GPa) and Young’s modulus (412 to 510 GPa) to published data, for similar materials made from commercially available powders, respectively. Strength values were less than half of the values reported from previous work, but more complete experiments must be run to confirm the strength of this material. Samples cut from these parts have been tested and successfully examined using the pulsed neutron diffraction sources at Argonne National Laboratory. Subsequent experiments will be used to confirm the magnitude of residual thermal stresses.

5. ACKNOWLEDGEMENTS

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The authors would also like to thank EaglePicher, LLC. for the generous donation of $^{11}$B for this research, Shuangmei Zhao of Missouri S&T for extensive support with the Abaqus modeling, Steve Langer at NIST for help installing and learning OOF2, and Joe Fieramosca and Ryoji Kiyanagi at Argonne National Laboratory for running the Neutron Diffraction experiments as well as help with processing the data.
6. REFERENCES


II. PROCESSING AND THERMAL PROPERTIES OF ZRBO$_2$-SIC CERAMICS MADE WITH ISOTOPICALLY PURE $^{11}$BORON

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ABSTRACT

Thermal properties were measured for two different ZrB$_2$-30 vol% SiC ceramics made by reaction hot pressing. One ceramic was made using natural boron and the other was prepared from isotopically pure (99%) $^{11}$B. Thermal expansion was measured using dilatometry and compared to values calculated from lattice expansion measured by elevated temperature neutron diffraction and calculated from published data. Thermal diffusivities were measured using the laser flash method. The natural boron sample had a thermal diffusivity of 0.2689 cm$^2$/s at room temperature, double the diffusivity of the two samples made from $^{11}$B (0.1331 and 0.1274 cm$^2$/s). Thermal conductivity was then calculated using the measured thermal diffusivities, calculated heat capacity values, and densities calculated as a function of temperature. The specimens prepared from $^{11}$B had a thermal conductivity of only 30 W/m•K at room temperature while the thermal conductivity of the specimens prepared using natural boron were twice that value (~62 W/m•K). The effect of the $^{11}$B isotope in the ZrB$_2$-SiC materials on these thermal properties were consistent with isotope effects observed for other ceramics.
1. INTRODUCTION

Zirconium diboride (ZrB$_2$) based composites have been investigated for use in high temperature (T>2000ºC) structural applications. Potential applications for these materials include leading and trailing edges of hypersonic vehicles, which will also require high strength, toughness and oxidation resistance.$^{1,2}$ Silicon carbide (SiC) has been added to ZrB$_2$ and the resultant composite materials have shown increases in strength, fracture toughness and oxidation resistance.$^{3-7}$ Recent research has also concluded that the SiC particle size in these composites controls strength.$^{8,9}$

Based on these results, a computer modeling effort was initiated to understand the strength characteristics of ZrB$_2$-SiC composites. The model focused on the effects of SiC particle size and shape on the thermal residual stresses that form during cooling from the processing temperatures due to the mismatch in the coefficients of thermal expansion of ZrB$_2$ and SiC.$^{10}$ Initial models agreed qualitatively with trends in the measured strength, but could not be quantified until the actual residual stresses were measured.$^{11}$

Bulk residual stresses can be measured using neutron diffraction techniques. However, the naturally occurring boron (80 at% $^{11}$B and 20 at% $^{10}$B) in standard ZrB$_2$-SiC composites has a high thermal neutron absorption (767 barns) due to the $^{10}$B (3835 barns), which makes neutron diffraction impossible.$^{12}$ As a result, materials were synthesized in which the natural boron was replaced with isotopically pure $^{11}$B, which has a thermal neutron absorption of only 0.0055 barns. In addition to the residual stress studies that are reported separately, the mechanical and thermal properties of the ceramics prepared using the $^{11}$B isotope were measured.
Isotope effects on thermal properties have been documented in several systems. Research on isotopically enriched single crystals of diamond indicated that removal of $^{13}$C from the diamond increased the room temperature thermal conductivity by around 30%.$^{13-17}$ Similar studies of single crystal germanium found increased thermal conductivity for materials where the $^{76}$Ge was removed.$^{18}$ Natural silicon contains $^{28}$Si (92 at%), $^{29}$Si (5 at%), and $^{30}$Si (3 at%), and research has shown that an isotopically pure $^{28}$Si exhibited a higher thermal conductivity than the natural silicon.$^{19}$

In addition to the broader studies, isotope effects have been studied for boron compounds. Boron carbide, made from either $^{10}$B or $^{11}$B, has been researched.$^{20,21}$ Boron nitride nanotubes made from natural boron and $^{11}$B have also been investigated.$^{22}$ For both materials, natural B materials exhibited higher thermal conductivities, with the values decreasing as the $^{11}$B content increased. Another study explored the isotope effects on the specific heat of boron crystals and found that between 5 and 100 K, the isotopes had no effect.$^{23}$ In a thorough study of $^{10}$B, $^{11}$B and natural $\beta$-boron materials, thermal conductivity results again showed that values decreased as $^{11}$B content increased.$^{24}$ The authors also reported the effect of isotope on the thermal expansion coefficient, where $^{10}$B was found to have a higher expansion than $^{11}$B.

Contrary to most studies that have found that purified ceramics containing the lighter isotope have higher thermal conductivity, a study of polycrystalline boron carbide found that the natural boron materials had a higher thermal conductivity than either $^{10}$B or $^{11}$B enriched boron carbide.$^{21}$ The authors accounted for this by explaining that the phonons were scattered by the grain boundaries of the polycrystalline material.
Thermophysical properties for ZrB$_2$ and ZrB$_2$-30 vol% SiC made using natural boron and standard hot pressing techniques have been reported.$^{25}$ Some published thermal properties of ZrB$_2$-SiC composites, as well as various boron isotopes and ceramics fabricated using the isotopes, are included in Table II.1.

The goal of this research was to evaluate the effect of replacing natural boron with $^{11}$B on certain thermal properties of ZrB$_2$-SiC ceramics.

2. EXPERIMENTAL PROCEDURE

2.1 POWDER PROCESSING

Two different ZrB$_2$-SiC ceramics were fabricated for this study. One was produced from crystalline boron powder (SB99, Reade Materials, Reno, NV) and the other from isotopically pure crystalline $^{11}$B (99.65 At% $^{11}$B, >99.99 wt%) that was donated by EaglePitcher, LLC. Both composites were prepared using ZrH$_2$ (Grade C, Chemetall, Frankfurt, Germany) and SiC (UF-25, H.C. Starck, Newton, MA) that were batched in the amounts described in Table II.2. The compositions were designed to produce ZrB$_2$-SiC composites containing 30 vol% SiC.

In the case of the composites fabricated from natural boron, the starting powders were combined in a fluoropolymer coated bucket and attrition milled (Model HD-01; Union Process, Akron, OH) in hexane for 2 hours at 600 rpm using tungsten carbide milling media. The hexane was removed from the powder using rotary evaporation (Model Rotavapor R-124, Buchi, Flawil, Germany) at a temperature of 70°C, a vacuum of ~30 kPa, and a rotation speed of 140 rpm.
The composites fabricated using $^{11}$B were produced using a similar process. However, an extra ball milling step was required to reduce the starting particle size of the $^{11}$B. The crystalline $^{11}$B was ball milled in hexane using tungsten carbide milling media for 17 hours to reduce the starting particle size from ~100 µm to ~1 µm. The hexane was removed using rotary evaporation as described previously. The resulting $^{11}$B powder was then mixed with the other starting powders and was processed as described above. The composites were produced according to reactions (1) and (2), respectively.

\[
\text{ZrH}_2 + \text{B}_2 + \text{SiC} \rightarrow \text{ZrB}_2 + \text{SiC} + \text{H}_2(g) \tag{1}
\]

\[
\text{ZrH}_2 + ^{11}\text{B}_2 + \text{SiC} \rightarrow \text{Zr}^{11}\text{B}_2 + \text{SiC} + \text{H}_2(g) \tag{2}
\]

### 2.2 REACTIVE HOT PRESSING

The composites were densified using a reaction hot pressing process used in previous studies.\(^{27-30}\) The powder was loaded into a graphite die lined with BN-coated graphite foil, and was compacted at a 30 MPa uniaxial pressure before loading into the hot press. The temperature of the graphite die was monitored using an infrared pyrometer (Model OS 3708, Omega Engineering, Stamford, CT). From room temperature to 1650°C, the furnace was heated under a vacuum of ~20 Pa, with a one hour hold at 1450°C and a second hour long hold at 1650°C to remove volatile species. Above 1650°C, the chamber was backfilled with argon and a flowing argon atmosphere was maintained through the rest of the hot pressing cycle. The furnace was heated at a rate of ~5°C/min up to 1000°C, the temperature at which all of the H\textsubscript{2} gas had been released, as indicated by a
decreased vacuum pressure. After release of the H₂, the heating rate was increased to ~20ºC/min. When the furnace reached 1900ºC, a uniaxial pressure of 32 MPa was applied for 45 minutes after which the furnace was turned off and allowed to cool. The pressure was released at 1700ºC. The resulting billets were nominally 4.6 cm in diameter by 3 mm thick after hot pressing.

2.3 SAMPLE PREPARATION

After hot pressing, billets were ground to remove surface impurities and any remaining graphite foil using an automated surface grinder (Model FSG-3A818, Chevalier Machinery, Inc., Santa Fe Springs, CA). Three thermal diffusivity samples, one from the natural boron sample (nB) and one each from two separate ¹¹B samples (B11-1 & B11-2), were cut out of billets using a 15.9 mm (0.625in) diamond core drill and then ground to 12.7 mm (0.5 in) diameter. Rectangular bars that were 2 mm x 2 mm x 25 mm were cut and ground from the billets for use in thermal expansion experiments. The remaining pieces of the billet were ground with a mortar and pestle and then sifted through a 325 mesh sieve to ensure particle sizes no larger than ~40 µm for additional characterization studies.

2.4 CHARACTERIZATION

Bulk density of hot pressed billets was measured using the Archimedes’ method. Measurements were made at room temperature (~20ºC) using distilled water as the immersion fluid. The bulk density of each billet was measured and used in thermal conductivity calculations. Phase compositions after reaction hot pressing were
determined using X-ray diffraction (XRD; XDS 2000, Scintag, Cupertino, CA) analysis. The microstructures were examined using a scanning electron microscope (SEM; Model S4700 Hitachi, Tokyo, Japan) to explore any potential effects of microstructure on the thermal conductivity.

2.5 LINEAR THERMAL EXPANSION

Linear thermal expansion was measured for ZrB$_2$-30 vol% SiC and Zr$^{11}$B$_2$-30 vol% SiC using a single push-rod dilatometer (Model 1600, Orton, Westerville, OH). The measurements were made under flowing argon from 50 to 1200ºC relative to a sapphire standard. Measurements were collected every 1ºC while the sample was heated and then cooled at a rate of 5ºC/min.

2.6 LATTICE THERMAL EXPANSION BY NEUTRON DIFFRACTION

Neutron diffraction experiments were performed using the general purpose powder diffractometer (GPPD) instrument at the intense pulsed neutron sources (IPNS) facility of Argonne National Laboratory. Samples of Zr$^{11}$B$_2$, SiC, and Zr$^{11}$B$_2$-30vol% SiC were tested. Four bars measuring 2mm x 2mm x 25mm were grouped together for each test and heated using a molybdenum furnace in vacuum drawn by an ion pump (~5•10$^{-4}$ Pa) from 25ºC to 1200ºC. Diffraction patterns were acquired every 100ºC from 100ºC up to 800ºC and every 50ºC from 800ºC to 1200ºC. A separate powder sample of Zr$^{11}$B$_2$-30vol% SiC was run at room temperature (~25ºC) to determine the lattice parameters for Zr$^{11}$B$_2$ and SiC.
2.7 HEAT CAPACITY

Differential scanning calorimetry (DSC 404C, Netzsch, Selb, Germany) was used to determine the constant pressure heat capacity ($c_p$) according to ASTM E 1269. Measurements were taken using powder samples between 65 and 1200°C in a flowing argon atmosphere.

2.8 THERMAL DIFFUSIVITY

Thermal diffusivity ($D$) was measured using the laser flash technique according to ASTM E 1461-01 at Oak Ridge National Laboratory. Room temperature measurements were obtained using a Xenon flash diffusivity system. An alumina laser flash apparatus (Netzsch LFA 427, Netzsch, Selb/Bavaria, Germany) was used for temperatures between 200 and 600°C, and a graphite furnace (Anter Flashline 5000, Anter Corp, Pittsburgh, PA) was used for measurements between 600°C and 1200°C. Three samples were measured, one ZrB$_2$-SiC sample (nB) and two Zr$_{11}$B$_2$-SiC samples (B11-1, B11-2). Measurements were taken approximately every 100°C during heating, as well as at one point (~800°C) during cooling in an argon gas environment. The experiment consisted of flashing the front surface of the material using a short (<1 µsec) laser pulse and measuring the back surface using an IR detector.

2.9 THERMAL CONDUCTIVITY

Thermal conductivity was calculated from the measured thermal diffusivity ($D$), density as a function of temperature ($\rho(T)$), and heat capacity ($c_p$) using Equation (3). The effect of thermal expansion was taken into account when calculating density using Equation (4).
where RT represents the room temperature measurements and $\Delta l(T)$ is the linear thermal expansion.

$$k = D \cdot \rho(T) \cdot c_p$$  \hspace{1cm} (3)

$$\rho(T) = \rho_{RT} \cdot \left[1 + \frac{\Delta l(T)}{l_{RT}}\right]^{-3}$$  \hspace{1cm} (4)

3. RESULTS & DISCUSSION

3.1 CHARACTERIZATION

The room temperature bulk densities were 5.257 g/cm$^3$ for the ZrB$_2$-SiC and 5.273 and 5.213 g/cm$^3$ for the two Zr$^{11}$B$_2$-SiC billets (Table II.3). The results for the natural boron material were similar to published results for materials prepared by the same method.$^{3, 9, 25, 28, 29}$ The results indicate that the reactions went to completion for both processes. Previous research has shown that the attrition milling process introduces approximately 3 wt% WC in the system, which was accounted for the increase in the density measurements relative to the theoretical density.$^3$ The nB sample had a slightly higher relative density (%TD, >99%) than the B11-1 and B11-2 samples (%TD >98%). ZrB$_2$ made with $^{11}$B had a slightly higher theoretical density (6.147 g/cm$^3$) than standard ZrB$_2$ (6.128 g/cm$^3$) due to the heavier $^{11}$B and slightly lower unit cell parameters as determined by Rietveld analysis of diffraction data from powder samples.

X-ray diffraction analysis confirmed that ZrB$_2$ was formed by the reactive processing of ZrH$_2$ and B or $^{11}$B. ZrB$_2$, SiC and WC were all detected in the hot pressed materials. SEM analysis of each thermal diffusivity specimen confirmed that all of the materials had
similar microstructures (Fig. II.1). The results indicated that the SiC (dark phase) was dispersed uniformly throughout the ZrB$_2$ matrix (light gray phase) and that little or no porosity was present, confirming the inferences from the density measurements. The grain sizes appeared to be in the range of 1-5µm, and were nearly equivalent for each of the specimens.

3.2 THERMAL EXPANSION

Linear thermal expansion was measured by dilatometry and the resultant thermal strains ($\Delta L/L_0$) were plotted as a function of temperature (Fig. II.2) for bulk ZrB$_2$-SiC and Zr$^{11}$B$_2$-SiC. A linear fit was used to determine the average coefficient of thermal expansion (CTE) over the temperature range. The natural B sample had a CTE of 6.71 x 10$^{-6}$ K$^{-1}$, which is in agreement with the previously reported value (6.8 x 10$^{-6}$ K$^{-1}$).$^{25}$ Similar to previous work involving the boron isotopes, the sample containing $^{11}$B had a lower thermal expansion compared to the sample containing some $^{10}$B,$^{24}$ with an average CTE of 6.17 x 10$^{-6}$ K$^{-1}$. Third order polynomials were fit to the expansion curves to relate thermal expansion to temperature. The curves, given by equations (5) and (6), had $R^2$ values of 0.999 and 0.998, respectively.

$$\left(\frac{\Delta L(T)}{L_0}\right)_{ZrB_2-SiC} = -1.1064e^{-4} + 2.7992e^{-6} \times T + 5.4251e^{-9} \times T^2 - 2.0956e^{-12} \times T^3$$ \hspace{1cm} (5)

$$\left(\frac{\Delta L(T)}{L_0}\right)_{Zr^{11}B_2-SiC} = -2.9863e^{-4} + 3.124e^{-6} \times T + 4.0398e^{-9} \times T^2 - 1.4659e^{-12} \times T^3$$ \hspace{1cm} (6)
Equations (5) and (6) were then combined with equation (4) to calculate the density of each material as a function of temperature. The density of each material decreased by about 0.1 g/cm$^3$ between 25 and 1200ºC due to the expansion of the lattice.

### 3.3 THERMAL EXPANSION MEASURED BY NEUTRON DIFFRACTION

Neutron diffraction patterns were collected on bulk specimens of Zr$^{11}$B$_2$-30 vol% SiC, Zr$^{11}$B$_2$, and SiC at temperatures ranging from 25 to 1200ºC. A powder sample of Zr$^{11}$B$_2$-30 vol% SiC was also evaluated at room temperature. EXPGUI$^{33}$, a freely available software package for diffraction pattern refinement using GSAS (LANCE, Los Alamos, NM), was used to perform Rietveld analysis on the neutron diffraction patterns. Lattice parameters were determined for each material at the measurement temperatures. Thermal expansion coefficients were calculated by plotting the average of the $a$ and $c$ lattice parameters (Equation 7) as a function of temperature (Fig. II.3).

$$\frac{\Delta L_{\text{avg}}}{L_o} = \frac{\left(2a + c - \frac{2a_o + c_o}{3}\right)}{\frac{2a_o + c_o}{3}}$$

(7)

The thermal expansion coefficients for SiC and ZrB$_2$ were calculated using equations (8) and (9), respectively.$^{34}$ The room temperature lattice parameters, which were used to calculate $a_o$, were calculated using neutron diffraction patterns collected at room temperature for the powder sample of Zr$^{11}$B$_2$-SiC.
In the equations above, \( a(T) \) represents the temperature dependent lattice parameter. The equations were determined for the thermal expansion of a polycrystalline sample, thus the strain in both the \( a \) and \( c \) crystallographic directions is the same. That strain was determined from the calculated lattice parameters using Equation (7), and plotted as a function of temperature. The thermal expansions measured for each of the materials by dilatometry and high temperature diffraction are compared to values calculated from published CTE data in Fig. II.3.

For Zr\(^{11}\)B\(_2\) in the bulk ceramic, it was observed that the thermal expansion calculated from published CTE data was higher than the thermal expansion measured using neutron diffraction. This can be attributed to the fact that the published value was for phase pure Zr\(^{11}\)B\(_2\), while the neutron diffraction results were measured from a ceramic containing 30 vol.% SiC. Hence, ZrB\(_2\) in a ZrB\(_2\)-SiC composite develops a compressive strain during cooling due to the thermal expansion mismatch between ZrB\(_2\) and SiC. The SiC has a lower CTE than the Zr\(^{11}\)B\(_2\) and, as a result, reduces the apparent the thermal expansion of the Zr\(^{11}\)B\(_2\) in the composite. Similarly, the values calculated for SiC based on its inherent CTE differ from the measured values for SiC in the composite by neutron diffraction. In this case, the calculated values were higher than the measured values due to the higher CTE of ZrB\(_2\), which induces a tensile strain on the SiC lattice in the
composite. The thermal expansion for the Zr\textsuperscript{11}B\textsubscript{2}-SiC measured by dilatometry falls between the values calculated for ZrB\textsubscript{2} and SiC because the materials have a combined affect on the thermal expansion of the bulk ceramic.

3.4 HEAT CAPACITY

Heat capacity values were measured by DSC from 65ºC to 1200ºC. Results indicated that the \textsuperscript{11}B isotope in the ZrB\textsubscript{2}-SiC composites had no effect on heat capacity (Fig. II.4). However, possible oxidation during the DSC run prevented the use of measured values in the thermal conductivity calculations. Instead, \( C_p \) values calculated from published data (Equation (10)) were used to calculate thermal conductivity.\textsuperscript{25}

\[
C_p = 0.62246 + 0.0001 \times T - 19834 \times T^{-2}
\]  

3.5 THERMAL DIFFUSIVITY

Room temperature (25ºC) thermal diffusivity values were measured for the three ZrB\textsubscript{2}-SiC billets. The nb sample had a thermal diffusivity value (0.2689 cm\textsuperscript{2}/s) which was more than double the values measured for B11-1 and B11-2 (0.1331 and 0.1274 cm\textsuperscript{2}/s) as shown in Fig. II.5. The thermal diffusivity decreased with increasing temperature for both materials. However, the nB sample had a much larger decrease, than B11-1 and B11-2. By 1200ºC, the thermal diffusivity of all three samples appeared to be approaching constant values of about 0.15 for the nB sample, and 0.10 for \textsuperscript{11}B.
3.6 THERMAL CONDUCTIVITY

The thermal conductivities were calculated as a function of temperature (Fig. II.6). The conductivity of the nB sample was similar to reported values, where the thermal conductivity decreased from ~60 W/m•K at 300 K to ~52 W/m•K near 1500 K. Both the B11-1 and B11-2 samples had room temperature thermal conductivities (29.7 and 28.5 W/m•K) that were about half of the value calculated for the nB sample. Similar to the nB sample, the $^{11}$B samples exhibited an increase in thermal conductivity up to ~500 K. However, unlike the nB sample, which exhibited a decrease in thermal conductivity of ~15 W/m•K with increasing temperature, the thermal conductivity for the $^{11}$B materials was relatively constant with temperature and even continued to increase slightly up to a value of ~40 W/m•K at 1500 K.

Boron isotope effects have been studied previously and it has been observed that increasing the $^{11}$B content of a material reduces the thermal conductivity. The materials tested in this research exhibited the same effect, where the pure $^{11}$B ZrB$_2$ materials had a lower thermal conductivity than the natural boron containing ZrB$_2$ materials. The change in thermal conductivity has been attributed to variations in the phonon-velocity caused by the isotopic mass. Phonon-velocity is proportional to $M^{-1/2}$, where M is the isotopic mass. So, as M increases, phonon velocity decreases, lowering the thermal conductivity.

The apparent increase in thermal conductivity for the $^{11}$B materials appears to be due to thermal diffusivity values. Starting with the points above 500 K, where the thermal conductivity starts to decrease for the normal boron material, the percent change in thermal diffusivity, specific heat and densities were determined (Table II.4). The decrease in thermal conductivity is due mostly to the decrease in thermal diffusivity, which is not as great for the $^{11}$B materials. The B11-2 sample has a nearly constant
thermal diffusivity, and as a result, the increase in heat capacity drives the thermal conductivity increase. There was some discrepancy in the two $^{11}$B samples measured, so to facilitate a better understanding, more samples should be run to create a better average.

If the isotope effects shown in single crystal studies of a variety of materials translate to ZrB$_2$ ceramics, isotopic content of ceramics could be manipulated to control thermal properties. This would be of tremendous value to the UHTC community. The use of $^{11}$B could lower the coefficient of thermal expansion, which could reduce thermal stresses that result due to the CTE mismatch between ZrB$_2$ ($6.8 \times 10^{-6}$ K$^{-1}$) and SiC ($4.6 \times 10^{-6}$ K$^{-1}$). The isotopes could also be used to tailor the thermal conductivity, where $^{10}$B could be used to increase thermal conductivity, which would be expected to improve thermal shock resistance for slow shock applications. In situations where a specific thermal expansion or thermal conductivity is desired, the isotopes could be mixed in specified amounts to design materials to meet these requirements.

4. CONCLUSIONS

ZrB$_2$-30vol% SiC and Zr$^{11}$B$_2$-30vol% SiC ceramics were fabricated by reactive hot pressing from ZrH$_2$ and crystalline boron powders. All materials were greater than 98% relative density and X-ray diffraction analysis indicated the desired products formed. SEM analysis of the samples machined for thermal diffusivity experiments confirmed that the microstructures were similar for all the materials.

Linear thermal expansion was measured for both ceramics. The material prepared from natural boron had a higher average CTE ($6.71 \times 10^{-6}$ K$^{-1}$) than the ceramic made using $^{11}$B ($6.17 \times 10^{-6}$ K$^{-1}$). The CTE of the natural boron ceramic was similar to reported
values and isotope enrichment decreased CTE as reported for other materials.\textsuperscript{24} Changes in the lattice parameters of ZrB\textsubscript{2} and SiC, measured by neutron diffraction, were also used to calculate CTE values. Results revealed the impact of each material on the CTE of the particulate composites, and were an indicator of the residual thermal stresses that can develop in particulate composite materials due to CTE mismatch.

Thermal diffusivity was measured at Oak Ridge National Laboratory on two samples made with \textsuperscript{11}B and one made using natural boron. That data was combined with temperature dependent density values and with calculated constant pressure specific heat values to calculate the thermal conductivity of each material. Again, the natural boron material had a thermal conductivity (60 W/m•K), similar to reported values. In contrast, the room temperature thermal conductivity of the \textsuperscript{11}B material (~29 W/m•K) was only half that of the natural boron material, which was consistent with reported trends.\textsuperscript{21-24} A steady decrease in thermal conductivity with increasing temperature was observed for the natural boron composite, which decreased to ~50 W/m•K at 1500 K. Meanwhile, values for the \textsuperscript{11}B composites increased slightly, to ~40 W/m•K at 1500 K, because thermal diffusivity did not change significantly with temperature, which allowed the increasing heat capacity to control the thermal conductivity at elevated temperatures.

5. REFERENCES


6. FIGURES

Fig. II.1: SEM micrographs of ZrB$_2$-30vol% SiC (a), and Zr$_{11}$B$_2$-30vol% SiC (b) showing nearly identical microstructures.
Fig. II.2: Thermal expansion curves for ZrB$_2$-SiC and Zr$^{11}$B$_2$-SiC.
Fig. II.3: Comparison of thermal expansion of ZrB$_2$, SiC, and ZrB$_2$-30vol% SiC, as determined by dilatometry, neutron diffraction, and calculated from published CTE data. All ZrB$_2$ materials were made using $^{11}$B.
Fig. II.4: Heat capacity of ZrB$_2$-30vol% SiC and Zr$_{11}$B$_2$-30vol% SiC measured by DSC.
Fig. II.5: Thermal diffusivity of ZrB$_2$-SiC (nB) and two Zr$^{11}$B$_2$-SiC (B11-1 & B11-2) samples as a function of temperature.
Fig. II.6: Thermal conductivity of ZrB$_2$-SiC (nB) and two Zr$^{11}$B$_2$-SiC (B11-1 & B11-2) samples as a function of temperature.
Table II.1: CTE and thermal conductivity of ZrB$_2$, ZrB$_2$-SiC, B, boron isotopes, and B$_4$C (natural and isotope enriched).

<table>
<thead>
<tr>
<th>Sample</th>
<th>CTE (ppm / K)</th>
<th>Thermal Conductivity (W/m•K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB$_2$</td>
<td>-</td>
<td>83.8 (298K) 81.8 (1273K)</td>
<td>26</td>
</tr>
<tr>
<td>ZrB$_2$ - 6.8 (300-1300K) 8.4 (1300-1675 K)</td>
<td>53 (298 K) 65 (1200 K)</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>ZrB$_2$ - 20vol% SiC</td>
<td>-</td>
<td>99.2 (298 K) 79.0 (1273 K)</td>
<td>26</td>
</tr>
<tr>
<td>ZrB$_2$ - 30 vol% SiC</td>
<td>6.8 (300-1300K) 7.8 (1300-1675 K)</td>
<td>62 (298 K) 56 (1200 K)</td>
<td>25</td>
</tr>
<tr>
<td>Natural B</td>
<td>-</td>
<td>410 (40 K)</td>
<td>23</td>
</tr>
<tr>
<td>Natural B</td>
<td>-</td>
<td>18 (298 K)</td>
<td>24</td>
</tr>
<tr>
<td>$^{10}$B (93.2at% 10B)</td>
<td>-</td>
<td>570 (40 K)</td>
<td>23</td>
</tr>
<tr>
<td>$^{10}$B</td>
<td>3 (100 K) 9.5 (800 K)</td>
<td>22 (298 K)</td>
<td>24</td>
</tr>
<tr>
<td>$^{11}$B</td>
<td>1 (100 K) (800 K)</td>
<td>16 (298 K)</td>
<td>24</td>
</tr>
<tr>
<td>B$_4$C</td>
<td>-</td>
<td>14.8 (360 K)</td>
<td>21</td>
</tr>
<tr>
<td>$^{10}$B$_4$C</td>
<td>-</td>
<td>15.6 (360 K)</td>
<td>21</td>
</tr>
<tr>
<td>$^{11}$B$_4$C</td>
<td>-</td>
<td>13.3 (360 K)</td>
<td>21</td>
</tr>
</tbody>
</table>
Table II.2: Batching amounts and average starting particle sizes of constituents.

<table>
<thead>
<tr>
<th></th>
<th>ZrH₂</th>
<th>SiC</th>
<th>B</th>
<th>¹¹B</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB₂-30 vol% SiC</td>
<td>73.31 g</td>
<td>20.04 g</td>
<td>17.0 g</td>
<td>-</td>
</tr>
<tr>
<td>Zr¹¹B₂-30 vol% SiC</td>
<td>72.07 g</td>
<td>19.77 g</td>
<td>-</td>
<td>17.0 g</td>
</tr>
<tr>
<td>Average Starting</td>
<td>45</td>
<td>0.7</td>
<td>0.1</td>
<td>~100 (as received)</td>
</tr>
<tr>
<td>Particle Size (µm)</td>
<td></td>
<td></td>
<td></td>
<td>~1 (after ball milling)</td>
</tr>
</tbody>
</table>
Table II.3: Density results of the 3 dilatometry specimens.

<table>
<thead>
<tr>
<th>Sample (name)</th>
<th>ZrB$_2$-SiC (nB)</th>
<th>Zr$^{11}$B$_2$-SiC#1 (B11-1)</th>
<th>Zr$^{11}$B$_2$-SiC #2 (B11-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Density (g/cm$^3$)</td>
<td>5.270</td>
<td>5.326</td>
<td>5.326</td>
</tr>
<tr>
<td>Bulk Density (g/ cm$^3$)</td>
<td>5.257</td>
<td>5.273</td>
<td>5.213</td>
</tr>
<tr>
<td>%TD (g/ cm$^3$)</td>
<td>99.3%</td>
<td>99.0%</td>
<td>98.9%</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>2.611</td>
<td>2.194</td>
<td>2.626</td>
</tr>
<tr>
<td>Unit Cell (Å)</td>
<td>a = 3.168</td>
<td>a = 3.166</td>
<td>a = 3.166</td>
</tr>
<tr>
<td></td>
<td>c = 3.530</td>
<td>c = 3.524</td>
<td>c = 3.524</td>
</tr>
</tbody>
</table>
Table II.4: Percentage changes in thermophysical property values over the temperature range of 500 K to 1500 K for ZrB$_2$-SiC prepared from naturally occurring boron (nB) and isotopically purified $^{11}$B (B11-1 and B11-2).

<table>
<thead>
<tr>
<th>Change 500 - 1500K</th>
<th>nB</th>
<th>B11-1</th>
<th>B11-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusivity</td>
<td>-38.28%</td>
<td>-22.97%</td>
<td>-3.84%</td>
</tr>
<tr>
<td>Cp</td>
<td>+ 28.57%</td>
<td>+ 28.57%</td>
<td>+ 28.57%</td>
</tr>
<tr>
<td>Density</td>
<td>-1.98%</td>
<td>-1.83%</td>
<td>-1.83%</td>
</tr>
<tr>
<td>Conductivity</td>
<td>-22.22%</td>
<td>-2.77%</td>
<td>+ 21.38%</td>
</tr>
</tbody>
</table>
3. CONCLUSIONS

Finite element models were created using the commercially available program, ABAQUS, to analyze thermal residual stresses that result from CTE mismatch between the ZrB$_2$ matrix and the SiC particulates. Size effect models were created and the results exhibited comparable trends to published experimental results. As SiC particle size increased, the modeled tensile stresses in the ZrB$_2$ increased, while the experimental strength of the material decreased. Several shapes were also modeled which led to the creation of SiC particles shapes designed to limit residual stresses. A peanut shaped particulate was modeled and exhibited lower residual stresses between the particulates. Finally the freely available finite element program, OOF2, was successfully used to create a mesh on images of SEM micrographs. This mesh was then imported into ABAQUS to be solved using identical boundary conditions as the idealized models, providing a useful tool for validation of the models as well as a valuable tool for future analysis.

ZrB$_2$-SiC and Zr$^{11}$B$_2$-SiC ceramics consisting of 30vol% SiC were successfully fabricated from ZrH$_2$ and crystalline boron powders by reactive hot pressing. All samples were densified to ~99% of the theoretical density, while SEM analysis confirmed equivalent microstructures. The $^{11}$B materials had comparable hardness (20.5 to 27 GPa) and Young’s modulus (412 to 510 GPa) to published data for similar materials made from commercially available powders (27 GPa and 510 GPa, respectively). Limited results for flexure strength for the $^{11}$B materials were lower than anticipated, but additional testing is still required to confirm these results.
Neutron diffraction studies from room temperature up to 1200°C on Zr\textsuperscript{11}B\textsubscript{2}-SiC, Zr\textsuperscript{11}B\textsubscript{2}, and SiC ceramics were completed at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. EXPGUI, a graphical interface for GSAS, was used to complete Rietveld analysis of the diffraction patterns for each material. Lattice parameters were determined and used to determine the thermal expansion for the Zr\textsuperscript{11}B\textsubscript{2} and SiC in the composite as well as in the monolithic ceramics. Residual stresses for the ZrB\textsubscript{2}-SiC composite will be determined from this data once the stress free reference standards are measured.

The effects of the isotope \textsuperscript{11}B on several thermophysical properties were determined for ZrB\textsubscript{2}-SiC ceramics. Thermal expansion was measured for ZrB\textsubscript{2}-SiC and Zr\textsuperscript{11}B\textsubscript{2}-SiC ceramics with 30vol\% SiC using a single push-rod dilatometer. Thermal expansions of Zr\textsuperscript{11}B\textsubscript{2} and SiC based on lattice expansion were determined using neutron diffraction data of Zr\textsuperscript{11}B\textsubscript{2}-SiC, Zr\textsuperscript{11}B\textsubscript{2}, and SiC bars, and compared to the dilatometer results as well as values calculated from published data. The materials made with \textsuperscript{11}B (6.17·10^-6 ppm/K\textsuperscript{-1}) exhibited a lower coefficient of thermal expansion than those made from natural boron (6.71·10^-6 ppm/K\textsuperscript{-1}). Thermal diffusivity of one ZrB\textsubscript{2}-SiC sample and two Zr\textsuperscript{11}B\textsubscript{2}-SiC samples was measured by laser flash method at Oak Ridge National Laboratory. The natural boron sample exhibited a higher room temperature thermal diffusivity (0.2689 cm\textsuperscript{2}/s) but saw a steady decrease with increasing temperature, while the two \textsuperscript{11}B samples exhibited a lower room temperature diffusivity (0.1331 and 0.1274 cm\textsuperscript{2}/s) with little decrease as temperature increased up to around 1200°C. Heat capacity was assumed to be the unaffected by the isotope based on published work. Thermal conductivity was calculated from thermal diffusivity, heat capacity, and density
calculated as a function of temperature. The natural boron material exhibited twice the room temperature conductivity (60 W/m·K) compared to the $^{11}$B samples (29.7 and 28.5 W/m·K). The increased thermal conductivity was accounted for by mass variance in the samples, where the higher mass of the $^{11}$B atom lead to slower phonons resulting in a lower thermal conductivity.
4. FUTURE WORK

Completion of the modeling efforts will require the measurement of residual stress by neutron diffraction be completed in order to validate the models. Stress free reference samples of ZrB$_2$ and SiC must be measured by HTXRD or neutron diffraction in order to complete the residual stress study. A more thorough study of residual stresses should be completed at the SMARTS facility at Los Alamos National Lab in New Mexico to further understand the residual stresses. These studies should also reveal the stress free temperature where the residual stresses begin to accumulate. This temperature should then be used as the initial temperature for the models. The values from the models using this temperature should then be compared to the measured values and the models adjusted accordingly.

To further improve the models, OOF2 should be used to import a mesh on a microstructure of the material measured in neutron diffraction. Using this mesh as well as the stress free temperature will provide a more exact model to compare the experimental results to and should improve accuracy of the model.

Validated models should be used to investigate novel SiC additions as well as determine new methods to limit residual stresses. The models may also be able to provide some insight into the relationship between residual stresses and crack propagation. Using OOF2 to import a mesh of a microstructure before and after a crack is produced, it should be possible to observe how the crack reacts to the various residual stresses in the part. More specifically, it will allow for visualization of impact of compressive stresses on the path of the crack (i.e. crack deflection).
The isotope effects of boron should also be more thoroughly studied. The fabrication of more $^{11}\text{B}$ materials, as well as materials made using $^{10}\text{B}$ could improve on the understanding the effect on thermophysical properties of ZrB$_2$-SiC by these isotopes. More thermal diffusivity samples of each material should be run to facilitate a better data set from which conclusions can be drawn. Thermal expansion and thermal conductivity of the $^{10}\text{B}$ materials should be determined and compared to the data for the natural boron and $^{11}\text{B}$ materials. Assuming $^{10}\text{B}$ improves thermal conductivity, a study should be conducted using combinations of $^{10}\text{B}$ and $^{11}\text{B}$ in specific amounts to observe the effects.

Heat capacity needs to be more accurately measured for $^{11}\text{B}$ to improve the thermal conductivity calculations. Samples should be prepared for ZrB$_2$, and ZrB$_2$-SiC, both made from the natural boron and the isotopes. These samples should then be analyzed at either Oak Ridge National Laboratory or sent to Netzsch for analysis. Only with complete heat capacity data can truly accurate thermal conductivity values be calculated.
APPENDIX A

FINITE ELEMENT MODELING
1. ABAQUS

1.1 PURPOSE/HISTORY

Computer aided modeling efforts were undertaken in order to help predict useful microstructures on the basis of strength, toughness, hardness, or any other important mechanical properties. Originally, the goal was simply to evaluate microstructures on the basis of strength, and to determine a way to maximize this property. Early efforts focused on creating a finite element model that could recreate a four-point bend test. The idea was to load a part in bending and run a crack through it to observe how far it would run under a given load. There was also some hope that certain toughening mechanisms, such as crack deflection, could be observed. However, the use of cracks in the models was never finished.

Another useful feature of the computer models was the ability to observe heat flow through a material. Models were created representing a fibrous monolith (FM) material (for Jim Zimmermann) to help understand the heat flow and the stresses that result due to the CTE mismatch between the cells and the cell boundaries (Fig. A.1). The models were able to recreate stresses on the same order as those predicted from his calculations, and helped explain the improved thermal shock resistance of the FM’s over conventional ZrB$_2$ composites.

Finally, the end goal was to model and understand the thermal residual stresses that develop after processing in a composite due to the CTE mismatch between the matrix and the dispersed phase. It was well known that residual stresses played some role in the strength of materials, but the exact nature and magnitudes of the stresses were
unexplored. Calculations based on the Eshelby model indicated the potential for several giga-pascals of residual thermal stress between the SiC and the ZrB$_2$. An effort was launched to investigate the affects of SiC particle size, shape, and volume percent on these stresses, with an end goal of hopefully predicting microstructures with the lowest possible residual stresses.

![2D Fibrous monolith model showing cooling of the part from the outside in through the cell boundaries. Blue represents cooler temperatures where red represents the hotter areas.](image)

**Fig. A.1:** 2D Fibrous monolith model showing cooling of the part from the outside in through the cell boundaries. Blue represents cooler temperatures where red represents the hotter areas.

### 1.2 PROCEDURE

The commercially available program, ABAQUS, was used to do the majority of the modeling. ABAQUS provided the ability to use the included CAD package to model any microstructure, and then used a powerful finite element solver to analyze that microstructure. Modeling with ABAQUS consists of several basic steps. First the
microstructure is simulated with the CAD software, sections are produced for each material, then boundary conditions are applied to the part, and finally the solver is run. Analysis of the results can also be done using the various tools that allow you to view the different variables (stress, strain, heat flux, etc), as well as plot them against each other.

1.3 MODEL DEVELOPMENT

Using the CAD tools, the first step was to produce a square matrix. ABAQUS will not allow the user to actually make a part 15µm in size, so typically it is better to make the part 15 units square and then convert all of the material properties accordingly (i.e. convert density from 6.19 g/cm$^3$ to 6.19e-15 kg/µm$^3$). To produce the square matrix, double click Parts under Model1 in the part tree. Select a 2D planar model, as well as a deformable, shell and set the approximate size to 30. The next step is to create the SiC particles. This was done by using the partition tool found under the Tools menu, and choosing the face tab then the sketch option. This gives the user the ability to sketch any desired shape out of the original matrix to become a dispersed particulate phase (i.e., SiC in a ZrB$_2$ matrix). Often it is a good idea to align the origin to the bottom left of the square by selecting sketcher options from the Edit menu. This will make creating the grid a bit easier. For size and shape effects, the first particle is drawn, and then given dimensional constraints to set the particle in the correct location close to the bottom left corner. Next, the grid option is selected and the correct number of particles and the proper spacing is provided. Upon completion there will be many different sections available for selection (Fig. A.2).
Material properties are added to the model by selecting the option from the part tree, inputting in all desired properties, and then assigning those properties to a section. For thermal-mechanical models the user must provide Young’s modulus, density, Poisson’s ratio, thermal conductivity, thermal expansion and specific heat. Sections must be created from these parts, so after selecting the create section tool, the matrix can be selected and titled accordingly. Similarly each of the SiC particles can be selected and placed into one section. At the end of the section creation a material will be assigned to that selection. Once the sections are created, expand the part tree by clicking the plus sign next to it, and double click section assignment. Here you can select the matrix, then assign it to the just created section, as well as do the same for the SiC particles.

Next boundary conditions should be applied. This can be anything from a pressure on one or more faces, to a heat flux across a part. These models are transient response models, meaning that they are time based. This allows the user to observe the
stresses at any time during cooling as well as to watch the heat flow out of the part. This is especially useful for FM’s and spiral shaped models where matrix material is wrapped up inside the SiC. Before applying boundary conditions an assembly must be created. This is done by expanding the assembly tree, double clicking the instance option, and for these models simply choosing the default configuration. Once this is accomplished steps can be defined by double clicking Steps. A step is a period of time during which some event or set of boundary conditions takes place. Each step type allows only certain boundary conditions, so it is important to choose accordingly. This model uses a coupled temp-displacement step type which allows for both heat transfer and mechanical stresses.

With everything in place the boundary conditions used for this model can be applied. The first step is to apply a field to the whole model. Making sure that the initial step is current, open the field option. Select the entire model, and input the desired starting temperature. Currently 1900°C is used, but this temperature will be the stress free temperature once it is determined by neutron diffraction. Next, apply the cooling film by opening the instance option, and choosing surface film condition. After selecting all of the external edges input the proper cooling rate and sink temperature. It is also possible to apply a different sink temperature to each side to investigate a situation where the piece being modeled is inside the part or maybe on an edge when some sides are cooled by air and others are in contact with the part. No other boundary conditions were used, because adding a displacement constraint would create a stress that is not actually indicative of the cooling process.

The final step is to mesh the part and define the element type (Fig. A.3). From the mesh creation section under the expanded part tree, the mesh option can be selected.
First the mesh must be seeded, which sets the distance between the nodes. The closer the nodes the more elements required which improves the results but takes longer to process. Next the element type must be selected. The models use the linear coupled temp-displacement quad elements. This element type will only work with quadrilateral elements, so when using a program such as OOF2 to create the mesh, always be mindful to keep only quadrilateral elements and not triangular ones. The final step is to click the button to create the mesh. Now the model is ready to be solved.

![ABAQUS model showing mesh with quadrilateral elements in place.](image)

To solve the model a job must first be created by opening the Jobs option. Once the job is created with the default settings it can be submitted to the solver and the solution obtained. A right click on the job title will show the results option, which is where the solution can be viewed. The first step is to click on the contour options button,
selecting the shape tab and setting the deformation scale factor to zero to eliminate the twist and other deformation visualizations. Select the contour plot icon and then click on Field Output under the results menu to view the different variables. Typically it is best to start with nodal temperature to make sure the part has cooled completely. Another variable of importance is the max in-plane stress which is what has been used to compare stresses to work in the past on SiC particle size effects.\textsuperscript{1,2} The pressure stress may also be of use as it should be related to the hydrostatic stresses which are often reported, however this option was not heavily explored during these initial studies. Some of the typical values that have been used in the models are presented in Table A.1.

1.4 SIZE EFFECT MODELS

To analyze size effect of SiC on residual stresses, models were created with varying sizes on SiC all on a similar grid. Patterns ranging from 2x2 up to 10x10 were created to evaluate this effect (Fig. A.4). The size of the particles was determined based on keeping a 30 vol\% (actually area percent) ratio of SiC to ZrB\textsubscript{2}. Every effort was made to keep the particles spaced equally apart and sufficiently far away from the sides of the part so to avoid major edge effects. Once the models were run, the maximum and minimum values of the stress were determined according to the maximum in-plane stresses. Using the Query values option available under tools, nodes in some of the maximum and minimum stress areas were picked to determine the actual maximum and minimum values. Early comparisons between the models and measured values\textsuperscript{1,2} were plotted and can be seen in the first paper of this thesis.
Table A.1: Some typical ABAQUS model values.

<table>
<thead>
<tr>
<th>Material Props</th>
<th>ZrB₂</th>
<th>SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/µm³)</td>
<td>6.27E-15</td>
<td>3.18E-15</td>
</tr>
<tr>
<td>Young’s Modulus (kg/µm·s²)</td>
<td>5.05E+05</td>
<td>4.30E+05</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>Thermal Conductivity (kg·µm/s³·K)</td>
<td>6.44E+07</td>
<td>1.10E+08</td>
</tr>
<tr>
<td>Thermal Expansion (ppm/K⁻¹)</td>
<td>6.80E-06</td>
<td>4.50E-06</td>
</tr>
<tr>
<td>Specific Heat (µm²/s²·K)</td>
<td>5.00E+12</td>
<td>6.70E+11</td>
</tr>
<tr>
<td>Section Thickness</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Increments</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Increment Step Size</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Field Temp</td>
<td>1900</td>
<td></td>
</tr>
<tr>
<td>Surface Film Coefficient</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Sink Temperature</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Seeding</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

Fig. A.4: Representative size effect models.
1.5 SHAPE EFFECT MODELS

Shape effects were evaluated using the same grid system developed for the size effect models. Round, square, hexagonal and peanut shapes were all modeled (Fig. A.5). The peanut shape was created after it was observed that the points on the hexagonal shapes that faced each other created an additive effect; meanwhile, the flat sides facing each other for the squares did not show this effect. The peanuts were created and modeled in such a manner that the convex sides of the peanuts faced a concave side. The results were a lower stress between the particles showing an excellent proof of concept. Once the models are verified by neutron diffraction then it would be of value to go back and investigate the models to better understand shape effects.

Fig. A.5: Shape effect model examples.
1.6 SPIRAL MODELS

Based on the results from the peanut shapes, there was a desire to investigate other novel particle shapes. Prior work had shown an ability to produce spiral shaped particles, so these shapes were modeled. Early modeling efforts showed that while the maximum tensile stresses were only a bit lower, the stress gradient created between the maximum and minimum stresses appeared to be substantially lower. The thinking was that a large difference in residual stresses between neighboring particles could induce microcracking and lower the strength of the material. As a result an effort was launched to create these microstructures.

1.7 PARTICLE SIZE COMPARISON AND PORE EFFECTS

Creation of actual parts with spiral SiC shapes in a ZrB$_2$ matrix did not yield the expected results. Strengths of the materials were substantially lower than expected so an investigation into the reason was undertaken. A model was created with a round particle of the equivalent scale to those spirals being created (~700µm) and a much smaller (2µm) round particle (Fig. A.6). By modeling the two different sized particles on the same model it was possible to observe that the much larger particle created a massive zone under high tensile stress. Even though the maximum stresses were not much higher, the volume of material affected was so large that the chance for a critical flaw to be inside this area was much greater. Addition of small voids, or pores, around the large particle indicated a massive spike in the tensile stress that would essentially guarantee the beginning of the failure of the part.
Fig. A.6: Model showing a very large particle compared to smaller particles and the effect of porosity. Notice that all the particles create similar stresses, however the affected zone around the largest particle, (a) is much greater than the other particles, (b and c). The pore, (d), creates the highest stress as indicated by the red/orange around the area.

1.8 RESULTS

Modeling efforts have proven to be a useful tool, but still require some refinement before being considered complete. Models can be created to understand complicated residual stresses and attempt to design around them. By limiting residual stresses in a part, the engineer should be able to improve the strength of the material. The true benefit of the models will be the ability to invent novel microstructures and investigate their potential before going through the lengthy and expensive process of actually processing them.
1.9 FUTURE WORK

The most important piece still missing from the models is validation of the results. For a given sample with known particles size, the stress free temperature must be determined by use of neutron diffraction. This temperature should be used as the initial temperature for the model, and then the results of the model should be compared to the actual measured residual stresses by that same neutron diffraction experiment. This will allow the adjustment of the model to better represent the experimental results. Once the model is considered accurate, then it could be universally applied to ZrB$_2$-SiC composites and improved upon to increase the functionality.

2. OOF2

2.1 PURPOSE

OOF2 (Object Oriented Finite Element Analysis) is a free finite element program that was developed at NIST. The program allows the user to import a micrograph and apply a mesh directly to that structure. The program allows for the analysis of actual microstructures that have been fabricated. Instead of running expensive or destructive tests on a sample, OOF2 can be used to run computer simulations on a part. The program can also be used to compare actual microstructures to the idealized ones modeled in ABAQUS, by meshing the micrograph in OOF2 and then importing it into ABAQUS. Once imported, the same boundary conditions can be applied to this mesh as used in the idealized case limited the variability in the results.
2.2 PROCEDURE

While the following details a rough procedure that has successfully been used to mesh a microstructure and then import it into ABAQUS, a very detailed and helpful set of tutorials are available under the help menu. It is highly recommended that each of the tutorials be followed prior to use of the program to better understand all of the capabilities of the program.

OOF2 is launched by opening a terminal window and typing “oof2”. If the Linux computer is used, “EXPORT DYLD_LYBRARY_PATH=/usr/bin/lib” must be entered before oof2 in order to set the proper path to open OOF2. From the main page, the center drop-down menu functions as the main gateway for the program. Select MICROSTRUCTURE from this menu, and add a new image from file. Here you can select an image for use in the mesh creation. Once the image, typically a microstructure, is loaded, the next step is to create pixel groups using the buttons available. Usually at this point it is a good idea to open the graphics window (CTRL + G), which will open another window and display the microstructure.

Before selecting pixels to add to the just created groups, often some adjustments must be made on the image. Selecting IMAGE from the main drop down menu, a wide variety of image enhancement tools will be available. The image should be enhanced such that different colors and sections have as much contrast as possible so that selection of these sections is easier. Once the image is sufficiently enhanced, go to the graphics window, and from the pull down menu select pixel selection. The selection tools are all detailed in the tutorials, but color or burn are the most useful tools. Color will select colors similar to the one the user clicks on, while burn selects pixels nearby that are
similar to the one selected. Both options can be modified using the sliders provided, which offer explanations to their function when the mouse is placed over them. Once all of the pixels associated with a particular material are selected, return to the microstructure tab in the main window and add these pixels to one of the groups. If there are only two materials, the invert button can be used to automatically select the other pixels, which should then be added to the other pixel group.

Materials can now be created from the MATERIALS pull down menu. Assuming the model is going to be imported into ABAQUS, there is no need to actually input any material properties, however, a material must be created and then assigned to the appropriate pixel group for each material in the microstructure using the tools provided.

Next the major function of OOF2 has to be executed. The creation of the skeleton on the microstructure represents what makes OOF2 such an impressive program (Fig. A.7). This skeleton is what the mesh will later be built off of in a later step. The program works with the user to create a system of elements that contain as close to 100% of a single pixel group in them as possible. This is referred to as the homogeneity index, and must exceed 0.98 to be considered a decent skeleton. To begin, select the SKELETON menu, and create a new skeleton using the default conditions. The homogeneity index displayed on the left of the window will probably be only a bit over 0.50, indicating that refinement of the skeleton is required. There are many tools available for this, which are documented in the tutorials. One very important detail when intending to import into ABAQUS is that for a coupled temp-displacement model, which is our standard model type, only quadrilateral elements can be used. This means no option that will split the quads into triangles can be used. The basic refinement tool is
called Refine. This tool randomly moves nodes as well as creates new nodes in an attempt to improve the homogeneity index. There are many sliders available that explain their function to aid in this task, but typically it is best to use a target of around 0.9, and an alpha value near 0.5. For an improved refinement, the SKELETON SELECTION menu can be opened and only elements with homogeneity below 90% can be selected. Then the refinements can be made only on these elements as opposed to the whole microstructure which can save time and create few elements in the end.

Fig. A.7: OOF2 skeleton creation. (a) Initial microstructure image, (b) final skeleton.

The last step is to open the MESH tab, and then create a new mesh with the default settings. This will place a mesh on top of the skeleton that has been created which can then be saved as and ABAQUS file using one of the pull down menus in the save window. This file must have the file extension type “.inp” added to the end of the
name for ABAQUS to recognize it. In ABAQUS, select import model from the file menu, and then add the file created from OOF2. Once in ABAQUS the material properties and boundary conditions can be set the same as any model created using only ABAQUS. This will allow the same conditions to be used for idealized models created using the CAD program, and for those created from an SEM micrograph of an actual microstructure.

2.3 RESULTS

OOF2 has successfully been used to import spiral shaped microstructures from SEM micrographs into ABAQUS (Fig. A.8). These models then had standard boundary conditions applied to them and the results were compared to other SiC particle shapes. This was done more for a proof of concept, and was not used as a major component in any research thus far.

2.4 FUTURE USES

OOF2 should be used to help validate the models along with neutron diffraction. An SEM image of the microstructure tested in neutron diffraction should be meshed using OOF2, and then run using ABAQUS. By using the newly determined stress free temperature as the starting temperature, it should be possible to more exactly replicate the residual stress values determined through the neutron diffraction measurement techniques.
The other significant future use for OOF2 will be the ability to compare meshed microstructures from actual parts to their idealized counterparts. This will not only help support the modeling effort, but could also potentially point to any effects within the microstructure that may be hindering the performance of the material. Such as, a sharp point defect that is causing an unusually high residual stress causing failure before expected.

Fig. A.8: OOF2 mesh imported into ABAQUS and solved. (a) Mesh as it appears in ABAQUS, (b) Highlighted area confirms sections imported properly, (c) Max in-plane stresses shown after solving (blue = compressive, red = tensile).
It may also be possible to use OOF2 to analyze before and after pictures of a part that has been fractured. For example a polished part could be mounted in epoxy, and an SEM image taken. Then using a hardness tester, induce a crack, and look at this crack using the SEM. By comparing the predicted stresses to the path the crack followed, an increased understanding of crack propagation and residual stresses could be obtained.

3. REFERENCES


APPENDIX B

NEUTRON DIFFRACTION
1. NEUTRON DIFFRACTION

1.1 INTRODUCTION

Neutron diffraction experiments were investigated as a method to physically measure the actual residual stresses that develop in ZrB$_2$-SiC ceramics. The idea to use neutron diffraction was presented to us by Dr. Dileep Singh during the 31$^{st}$ International Conference & Exposition on Advanced Ceramics & Composites meeting at Daytona Beach in 2007. The measurement of the residual stresses is necessary for the validation of the ABAQUS models. A proposal was submitted to Argonne National Lab (ANL) to run several samples of ZrB$_2$-SiC made using $^{11}$B in an attempt to determine the residual stresses.

1.2 PROCEDURE

Billets were made of ZrB$_2$, SiC, and ZrB$_2$-30vol% SiC replacing the standard boron with the $^{11}$B isotope to reduce the neutron absorption of the material to an acceptable level. Bars measuring 2x2x25mm were cut from each billet and taken to ANL to be run on the General Purpose Powder Diffractometer (GPPD). A powder sample of the ZrB$_2$-SiC was also taken to be used as a reference sample. For each run, four bars of a material were bound together with vanadium wire, and placed into the alumina holder which was then inserted into a molybdenum furnace. A rough vacuum was pulled down low enough that an ion pump could then be turned on and the chamber taken down to around 5·10$^{-4}$ Pa. A room temperature (~20$^\circ$C) measurement was taken for about an hour, and then the heating schedule was implemented. Between room temperature and
800°C measurements were taken every 100°C, pausing for 15 minutes to equilibrate and then holding for 30 minutes to take the diffraction measurement. From 800 to 1200°C measurements were taken for 1 hour every 50°C. Upon cooling, stops were made every 100°C down to 800°C and data was collected for 30 minutes. Similar heating schedules were used for all three materials. The powder sample was loaded into a vanadium can and measured for 2 hours at room temperature only.

1.3 RESULTS

Unfortunately it was not known that the powder data was needed at each temperature, so no stress free reference sample was measured. However, the data gathered for the solid bars was excellent. Due to the nature of the alumina sample holder on the data taken from Bank 4 (collection of sensors comprising $2\theta = 90^\circ$) could be used, which could limit some of the possible calculations, but should not affect residual stress calculations. EXPGUI was used to run Rietveld analysis on the data and the lattice parameters for each material were determined for every temperature measured. This data was used in thermal expansion calculations, and will be useful when eventually determining residual stresses and the stress free temperature.

1.4 FUTURE WORK

Stress free samples of ZrB$_2$ powder and SiC powder must be run at each temperature that neutron diffraction data was collected to complete the study and make possible the calculation of residual stresses. A proposal into the SMARTS facility at Los
Alamos National Laboratory will provide access to another set of neutron diffraction experiments under the supervision of experts who have performed similar experiments. More $^{11}$B powder may be required to produce larger samples if needed, as well as to produce more ZrB$_2$ powder for use as a stress free reference sample. The used of crushed ZrB$_2$-SiC composite specimens may not work as a stress free sample unless the particle size can be reduced to nearly 1µm size to completely separate the ZrB$_2$ and the SiC. Otherwise there will undoubtedly be some residual stresses in the powder, which will be evident in the diffraction patterns and add some error to the calculations.
VITA

Michael Phillip Teague was born November 24, 1981 in the desert oasis town of Albuquerque, NM. Michael graduated from the Albuquerque Academy in May 2000, and then moved to the bustling metropolis of Rolla, MO in early August to begin college as a Mechanical Engineering student at the University of Missouri-Rolla. After four days in Thomas Jefferson Hall, Michael moved out to pledge Beta Sigma Psi where, over his 9 semesters as an undergraduate student, he held an executive board office 7 times and helped rebuild the house from 9 members up to over 30. Michael was on the Student Union Board of Directors for one and half years as the Leisure and Recreation Director, during which time he helped facilitate the purchase of several thousand dollars worth of new canoes and trailers for OAR. Michael always had a desire to pursue a career in mechanical design, which led to 5 summer internships and a Co-Op at Sandia National Laboratories working with the satellite hardware design group. After graduating in May 2005 Cum Laude with a BS in Mechanical Engineering, Michael accepted an opportunity from Dr. Hilmas in the MS&E department to pursue his master’s degree.

Michael was hired to work on part of the current AFOSR contract and tasked with building a modeling program for the group. Although he began his master’s working mostly as a mechanical engineer on materials modeling tasks, Michael eventually found himself becoming more involved as a material engineer, processing materials and learning many of the basics of ceramic engineering. Working as the TA for the freshman level Ceramic Engineering 104 class, Michael learned basic ceramic engineering alongside the freshmen he was the TA for. During his time as a master’s student, Michael coached his city league softball team to a championship, as well brought softball and flag football championships to the Beta Sig fraternity, the first such accomplishments in more than 15 years. His research has led to two publications and 3 presentations and should lead to a third publication with the completion of the neutron diffraction studies. After completion of his master’s degree requirements and the receipt of his MS degree in August 2008, Michael will be moving to frigid Schenectady, NY to begin work as a mechanical engineer tasked with materials modeling for Knolls Atomic Power Laboratory, where he plans to enjoy the area’s two seasons, winter and July.