HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY ANALYSIS OF
THE INFLUENCE OF GRAIN BOUNDARY AND TRIPLE GRAIN JUNCTION
CRYSTALLINITY AND CHEMISTRY ON SILICON CARBIDE-BASED ARMOR
WITH SMALL ADDITIONS OF ALUMINUM, BORON, AND CARBON

By

SAMANTHA CRANE

A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2005
Copyright 2005

by

Samantha Crane
This document is dedicated to my parents for never letting me give up.
ACKNOWLEDGMENTS

I would like to acknowledge Ceramatec, Inc., for the funding of this project. I would also like to thank Dr. Darryl Butt for chairing my committee and for his continued guidance throughout my undergraduate and graduate studies. My committee members Drs. J. J. Mecholsky, Jr. and Amelia Dempere were invaluable resources on this project. In addition, I would like to thank Kerry Seibien of MAIC at the University of Florida and Dr. Helge Heinrich of MCF at the University of Central Florida for their help with performing the TEM and EFTEM studies presented in this thesis. Edgardo Pabit’s insight, help, and guidance were essential to the completion of my research. I would like to thank Dr. Erik Kuryliw and Soroya Benetiz for teaching me how to perform TEM sample preparation and how to polish. Finally, I would like to thank Dr. Butt’s research group for their help and support.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2 EFFECT OF SINTERING PARAMETERS ON MICROSTRUCTURAL DEVELOPMENT AND MECHANICAL PROPERTIES</td>
<td>5</td>
</tr>
<tr>
<td>Mechanical Behavior of Ceramic Armor Systems</td>
<td>5</td>
</tr>
<tr>
<td>Toughening Mechanisms</td>
<td>5</td>
</tr>
<tr>
<td>Crack bowing</td>
<td>6</td>
</tr>
<tr>
<td>Crack deflection</td>
<td>6</td>
</tr>
<tr>
<td>Crack bridging</td>
<td>7</td>
</tr>
<tr>
<td>Microcracking</td>
<td>8</td>
</tr>
<tr>
<td>Transformation toughening</td>
<td>10</td>
</tr>
<tr>
<td>Toughening Mechanisms in SiC</td>
<td>10</td>
</tr>
<tr>
<td>Structural Properties of Silicon Carbide</td>
<td>11</td>
</tr>
<tr>
<td>Sintering of Silicon Carbide</td>
<td>12</td>
</tr>
<tr>
<td>Solid State Sintered SiC</td>
<td>14</td>
</tr>
<tr>
<td>Liquid-Phase Sintered SiC</td>
<td>15</td>
</tr>
<tr>
<td>Liquid-phase sintering aides</td>
<td>15</td>
</tr>
<tr>
<td>Al-B-C additive system</td>
<td>17</td>
</tr>
<tr>
<td>Microstructural Features of Liquid-Phase Sintered SiC</td>
<td>19</td>
</tr>
<tr>
<td>Phase Transformation</td>
<td>21</td>
</tr>
<tr>
<td>Grain Boundary Films in Liquid-phase Sintered SiC</td>
<td>21</td>
</tr>
<tr>
<td>Triple Junction Phase Formation and Crystallization</td>
<td>21</td>
</tr>
<tr>
<td>3 MATERIALS AND METHODS</td>
<td>24</td>
</tr>
<tr>
<td>Materials Processing of ABC-SiC by Ceramatec Inc</td>
<td>24</td>
</tr>
<tr>
<td>Characterization</td>
<td>24</td>
</tr>
<tr>
<td>Toughness Testing by Ceramactec, Inc</td>
<td>24</td>
</tr>
</tbody>
</table>
Microhardness Testing by Ceramatec, Inc. .........................................................25
Reitveld Analysis by Ceramatec, Inc .................................................................25
Grain Morphology Characterization by Ceramatec, Inc .................................25
Transmission Electron Microscopy (TEM) .........................................................26
  Transmission electron microscopy sample preparation ...............................27
  High resolution lattice imaging ................................................................28
  Energy dispersive spectroscopy (EDS) ........................................................28
  Energy-filtered transmission electron microscopy (EFTEM) ......................29

4 RESULTS AND DISCUSSION .................................................................................31
  Transmission Electron Microscopy Characterization .........................................31
    Grain Boundary and Intergranular Film Characterization ................................31
    Triple Grain Junctions ..................................................................................34
  Compositional Studies .....................................................................................36
    0 wt. % Al .................................................................................................36
    0.5 wt. % Al .............................................................................................37
    1 wt. % Al ...............................................................................................42
    1.5 wt. % Al ............................................................................................44
    4 wt. % Al ...............................................................................................47
  Materials Characterization Performed at Ceramatec, Inc ...............................48
    Fracture Mode Determination by Ceramactec, Inc .......................................50
    Relationship Between Hardness and Toughness by Ceramactec, Inc ................54
    Grain Morphology Characterization by Ceramatec, Inc ..................................54
    XRD and Reitveld Analysis by Ceramatec, Inc ............................................54
  Correlation Between Microstructure and Mechanical Properties ..................55
    Toughness ..................................................................................................58
      Weak interfaces .......................................................................................58
      Residual stresses ....................................................................................60
      High aspect ratio grains .........................................................................68
      Large grains ............................................................................................69
    Hardness ....................................................................................................71
      Effect of grain size on hardness ...............................................................72
      Effect of aspect ratio on hardness ..........................................................73

5 SUMMARY AND CONCLUSIONS .........................................................................74
  Conclusions ....................................................................................................74
  Suggested Future Work ..................................................................................75

LIST OF REFERENCES ............................................................................................76

BIOGRAPHICAL SKETCH .......................................................................................81
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1. Ramsdell Notion of Common SiC Polytypes.</td>
<td>12</td>
</tr>
<tr>
<td>4-1. Grain Boundary Width and Intergranular Film Determination by HRTEM</td>
<td>34</td>
</tr>
<tr>
<td>4-2. Toughness and Hardness Measurements of SiC with 0-6 wt. % Al</td>
<td>58</td>
</tr>
<tr>
<td>4-3. Characterization of SiC with 0-6 wt. % Al</td>
<td>59</td>
</tr>
<tr>
<td>4-4. Rietveld Analysis for SiC Samples with 0-6 wt. % Al</td>
<td>63</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1.</td>
<td>Fracture toughness increase with particle size due to microcracking.</td>
</tr>
<tr>
<td>2-2.</td>
<td>Si-C tetrahedra, which form the basic structural unit of SiC polytypes.</td>
</tr>
<tr>
<td>2-3.</td>
<td>A close packed plane of spheres with the sphere centers denoted by A. Subsequent planes can be stacked in the sphere valleys denoted by B or C to form the different SiC structures.</td>
</tr>
<tr>
<td>2-4.</td>
<td>Schematic of the competing energy terms during densification.</td>
</tr>
<tr>
<td>3-1.</td>
<td>The above diagram illustrates electron-matter interactions in transmission electron microscopy.</td>
</tr>
<tr>
<td>4-1.</td>
<td>The grain boundaries in a) 0 wt. % Al, b) 0.5 wt. % Al, and c) 1 wt. % Al were completely crystalline and contained no intergranular film. In d) 1.5 wt. % Al and e) 4 wt. % Al the grain boundaries are amorphous and 1 nm wide. Please note that the scale marker in a), b), and c) is 2 nm. The scale marker in d) and e) is 5 nm.</td>
</tr>
<tr>
<td>4-2.</td>
<td>Triple grain junctions for ABC-SiC. a) 0 wt. % Al, b) 0.5 wt. % Al, c) 1 wt. % Al, d) 1.5 wt. % Al, and e) 4 wt. % Al. Please note that the scale marker is 20 nm in a) and b), 10 nm in c), 200 nm in d), and 100 nm in e).</td>
</tr>
<tr>
<td>4-3.</td>
<td>This is a series of micrographs and EDS spectra from a grain boundary in the 0 wt. % Al sample. There is no variation observed in composition between the grains and grain boundary.</td>
</tr>
<tr>
<td>4-4.</td>
<td>EFTEM elemental maps of a grain boundary in the 0 wt. % Al sample.</td>
</tr>
<tr>
<td>4-5.</td>
<td>The above figure is a micrograph of a three grain junction in the 0 wt. % Al sample and the corresponding EDS spectra. The EDS data shows no secondary phase present in the three grain junction, and no variation in composition between the three grain junction and surrounding grains.</td>
</tr>
<tr>
<td>4-6.</td>
<td>EFTEM elemental maps of a triple junction in the 0 wt. % Al sample. There is no change in composition between the three grains and the three-grain junction.</td>
</tr>
<tr>
<td>4-7.</td>
<td>The above STEM image and corresponding EDS spectra show the presence of carbon inclusions between SiC grains in the 0 wt. % Al samples.</td>
</tr>
</tbody>
</table>
4-8. EFTEM elemental maps of a C inclusion surrounding a pore in the 0 wt. % Al sample.

4-9. The above a) STEM image and b)-e) corresponding EDS spectra are taken from b), e) the grain boundary and c), and d) the surrounding grains.

4-10. EFTEM elemental maps of a grain boundary in the 0.5 wt. % Al sample.

4-11. The above STEM image and corresponding EDS spectra are taken from the triple junction and the surrounding grains in the 0.5 wt. % Al samples. The secondary phase is confined to the triple junction and does not extend into the grain boundaries. The scale marker is 100 nm.

4-12. EFTEM elemental maps of an Al-O rich inclusion in the 0.5 wt. % Al sample.

4-13. EELS spectra taken from a triple junction in the 0.5 wt. % Al sample shows does not show crystalline Al2O3.

4-14. A STEM image and corresponding EDS spectra showing metal and B-C rich inclusions. The scale bar is 200 nm.

4-15. A STEM image of two grains and a grain boundary from the 1 wt. % Al sample and the corresponding EDS spectra. The composition does not vary between the grains and grain boundary.

4-16. EFTEM elemental maps of a grain boundary and transgranular crack in the 1 wt. % Al sample. There is no variation in composition across the grain boundary or at the site of the crack.

4-17. A STEM image of a triple junction in 1 wt. % Al showing that aluminum and oxygen segregate on the triple point and that the composition changes as a function of depth into the triple junction. The scale marker is 100 nm.

4-18. EFTEM elemental maps of a triple junction in the 1 wt. % Al sample. Notice that the very center of the triple junction is Si and C free.

4-19. A STEM image and corresponding EDS spectra of grains and contaminations observed in the 1.0 wt. % Al sample.

4-20. A STEM image of two grains and a grain boundary from 1.5 wt. % Al ABC sample and the corresponding EDS spectra.

4-21. EFTEM elemental maps of a grain boundary in the 1.5 wt. % Al sample. Note the formation of an Al-O rich intergranular film. Scale marker is 20 nm.

4-22. A STEM image and EDS spectra of a triple junction in the sample containing 1.5 wt. % Al.
4-23. EFTEM elemental maps of a triple junction in the 1.5 wt. % Al sample. Notice that the entire triple junction is void of Si and C. .................................................................48

4-24. EELS spectra taken from the triple junction in the 1.5 wt. % Al sample shows that the triple junction is filled with Al₂O₃..................................................................................49

4-25. A STEM image and corresponding EDS spectra of two grains and a grain boundary in 1.5 wt. % Al sample. This site shows two different grains. The upper grain is a SiC grain and the lower grain is that of an Al-O rich grain. The presence of aluminum-rich grains were only observed for 1.5 wt. % Al and 4.0 wt. % Al....................................................................................................................49

4-26. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, two SiC grains, and a B-C rich inclusion in the 4 wt. % Al sample. ......50

4-27. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, a B-C rich inclusion, and an Al₄C inclusion in the 4 wt. % Al sample...51

4-28. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, two SiC grains, and an Al-O-C rich inclusion in the 4 wt. % Al sample. Note that the area of the grain boundary that is farthest from the inclusion contains Al, while the area closest to the inclusion is depleted in Al......51

4-29. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, a SiC grain, and a carbon inclusion imbedded in an Al-O-C rich inclusion in the 4 wt. % Al sample...........................................................................52

4-30. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, and two SiC grains in the 4 wt. % Al sample. Note the presence of Al at the grain boundary................................................................................................52

4-31. EFTEM elemental maps of a grain boundary between two SiC grains in the 4 wt. % Al sample. ........................................................................................................................53

4-32. EFTEM elemental maps of a multiple grain junction in the 4 wt. % Al sample. The circled grain is Al-B-C rich and may be Al₈B₄C₇. The area between the grains is Al-O rich. ..................................................................................................................................53

4-33. SEPB fracture surfaces for samples with 0-6 wt. % Al. There is a clear change in fracture mode between transgranular and intergranular between 1 and 15 wt. % Al. The scale marker is 10 µm. .........................................................................................................................55

4-34. Comparison of HV1 (left) and HK1 (right) for various SiC materials. A change in fracture mode is evident between 1 and 1.5 wt. % Al..........................56

4-34 continued. Comparison of HV1 (left) and HK1 (right) for various SiC materials. The onset of the transgranular fracture mode is accompanied by a high degree of
crack branching and crushing. A change toward mixed mode fracture occurs at 4 wt. % Al at which point the cracks are straight and there is no crushing. 

4-35. The above graphs plot Knoop hardness and SEPB toughness as a function of Al content. The change in hardness and toughness with changing Al content is inversely related. 

4-36. Change in aspect ratio and grain size with Al content. 

4-37. Polished and chemically or plasma-etched surfaces of SiC samples with 0- wt. % Al. 

4-38. X-ray diffraction patterns SiC with 0-6 wt. % Al. Note that starting powder was beta-3C and that in addition to SiC polytypes, Al8B4C7 phase is noted at high Al contents. 

4-39. Polytypes from Rietveld analysis for SiC-0.6 wt. % B-0.2 wt. % C samples with Al contents ranging from 0 to 6 wt. %. 

4-40. Plot of Stress vs. Temperature for a particle in an infinite matrix. 

4-41. Effect of residual stress fields around triple junctions on crack propagation. 

4-42. Intergranular cracking in the 1.5 wt. % sample. The figure on the left shows cracking through the intergranular film at the grain boundaries. The figure on the right shows a missing triple junction due to the crack deflecting around the triple junction, but within the amorphous secondary phase. Note that the image on the right is slightly out of focus, which makes the crack appear to be a broad region that is lighter in color. 

4-43. Plot of toughness vs. aspect ratio shows a negative slope and argues against crack bridging. The three data points at the bottom of the graph correspond to the samples that fail transgranularly. 

4-44. Plot of toughness vs. grain size. Toughness generally increases with increased grain size. 

4-45. Plot of the effect of grain size on hardness. The plot shows that hardness increases with grain size for the samples that fail via intergranular fracture.

4-46. The plot of hardness vs. aspect ratio shows that the hardness is not dependant on aspect ratio.
HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY ANALYSIS OF THE INFLUENCE OF GRAIN BOUNDARY AND TRIPLE GRAIN JUNCTION CRystallinity AND CHEMISTRY ON SILICON CARBIDE-BASED ARMOR WITH SMALL ADDITIONS OF ALUMINUM, BORON, AND CARBON

By
Samantha Crane
August 2005

Chair: Darryl Butt
Major Department: Materials Science and Engineering

Recent studies have shown that toughness, hardness, and fracture mode are a function of interface crystallinity and chemistry in silicon carbide-based armor systems. Therefore, a thorough investigation of the effects of varying additive concentration on the microstructure and chemistry of the intergranular phases including the grain-boundary films and triple-junction phases is essential in order to engineer a better ceramic-based armor. For this object four SiC-based materials were prepared and studied. The silicon carbide materials were created with the boron and carbon content held constant while varying the amount of aluminum available.
Ceramic armor systems have been in use against small caliber projectiles since the 1960s, however, the way in which combat is conducted has changed with the advance of defense related technology. For this reason, there is now greater emphasis on creating lower weight combat vehicles that need minimal combat preparation time and can endure attack by long rod penetrators (Gooch 2002).

The armor is designed to “defeat” the projectile at the interface by increasing its “dwell” time. To obtain long dwell times in ballistic tests, the armor material must have high hardness. In addition, an increase in ductility will result in improved resistance to penetration of the projectile if the hardness is maintained (Flinders et al. submitted). Advanced silicon carbide-based armor is amongst the United States Army’s top choices for ceramic armor systems.

Difficulty in obtaining fully dense compacts in silicon carbide due to the low self diffusion coefficient and the highly covalent nature of the Si-C bond (Huang et al. 1986) hindered the use of silicon carbide until Prochazka (Prochazka 1975) developed a technique in 1975 using boron and carbon additives for pressureless solid-state sintering. While Prochazka’s technique produced fully dense silicon carbide, its low fracture toughness, which is approximately 2.5 MPa-m$^{1/2}$ as measured by the single-edge precracked beam (SEPB) technique, limited its application (Flinders et al. submitted).

Since Prochazka’s pioneering work, a variety of additive systems including oxides, carbides, nitrides, and metals have been used with silicon carbide to promote liquid phase
sintering, which aids in lowering the full densification sintering temperature and
obtaining compacts close to the theoretical density (Biswas et al. 2001). Liquid phase
sintering, however, introduces intergranular phases at the grain-boundaries and triple-
junctions during sintering, which have a pronounced influence on the final properties
(Zhou et al. 2002). For example, strong intergranular bonding is desirable for creep
resistance and high temperature strength, while the activation of toughening mechanisms
such as crack deflection, crack bridging, and micro-cracking depend on “sufficiently
weak” intergranular bonding (Moberlychan and De Jonghe 1998). In addition, recent
studies have shown that toughness, hardness, and fracture mode are a function of grain
boundary and triple grain junction crystallinity and chemistry in silicon carbide-based
systems (Moberlychan and De Jonghe 1998). For the specific application of ceramic
armor, it is important to achieve both a high level of toughening and strength (Flinders et
al. submitted). Therefore, control of the microstructure and chemistry of the intergranular
phases is of particular interest when engineering ceramic armor systems.

Of particular interest is the aluminum, boron, and carbon system, which exhibits in-
situ toughening. The additives in this system aid in the cubic to hexagonal phase
transformation, which can be controlled to dictate the final microstructural morphology
(Moberlychan et al. 1998). In addition, the sintering aides diminish the number of flaws
that limit the strength and toughness of the final part (Zhang et al. 1998). While the
toughness of the final part usually increases due to a change in fracture mode from
transgranular to intergranular cracking, the hardness diminishes with increased additive
content. Thus, it is important to use a sufficiently small amount of additive in order to
maintain the high hardness, while still aiding in the sintering process and microstructural
development (Moberlychan and De Jonghe 1998).
There are several in-situ toughening mechanisms that can be employed in aluminum-boron-carbon silicon carbide (ABC-SiC); however, many of these mechanisms diminish the material’s hardness. Therefore, a thorough investigation of the effects of varying additive concentration on the microstructure and chemistry of the intergranular phases including the grain-boundary films and triple-junction phases is essential in order to engineer a ceramic-based armor with both high hardness and toughness. For this objective, four SiC-based materials were prepared and studied. The silicon carbide materials were created with the boron and carbon content held constant while the amount of aluminum was varied.

To address the effect of varying additive concentration on the intergranular microstructure and chemistry, the following tasks were performed: the measurement of the size of the grain-boundaries and triple-junctions, and the determination of the amount of crystallinity of the grain-boundaries and triple-junctions; and the quantification of the grain-boundary and triple-junction chemistries. To accomplish this task, high resolution transmission electron microscopy (HRTEM) in conjunction with the following techniques were performed: lattice imaging to determine grain boundary width and secondary phase crystallinity; and energy dispersive spectroscopy (EDS), and energy filtered transmission electron microscopy (EFTEM) to quantify chemical compositions.

The work presented in this thesis was done in cooperation with Ceramatec, Inc. of Salt Lake City, Utah, as part of an SBIR for the United States Army. Ceramatec, Inc. processed the ABC-SiC, performed toughness testing, microhardness testing, Reitveld analysis, X-ray diffraction, and grain morphology characterization. When the results of work performed at Ceramatec, Inc. are presented in this thesis, they will be identified as such in the section headings.
The thesis is organized as follows: a review of previous work on SiC-based ceramics with an emphasis on secondary phase formation in liquid-phase sintered SiC and the effects of SiC microstructure on mechanical properties will be given in Chapter 2. The experimental methods, including the analytical electron microscopy methods used in this study are introduced in Chapter 3. The results of the detailed investigation of the intergranular phases of ABC-SiC are presented in Chapter 4. Finally, in Chapter 5, conclusions from the results presented in Chapter 4 are drawn and a correlation is made between the microstructure and chemistry of intergranular phases and the mechanical behavior of the final part.
CHAPTER 2
EFFECT OF SINTERING PARAMETERS ON MICROSTRUCTURAL DEVELOPMENT AND MECHANICAL PROPERTIES

Mechanical Behavior of Ceramic Armor Systems

As discussed in the previous chapter, ceramic armor is designed to “defeat” the projectile at the interface by increasing its “dwell” time. To obtain long dwell times in ballistic tests, the armor material must have high hardness. In addition, an increase in ductility will result in improved resistance to penetration of the projectile if the hardness is maintained (Flinders et al. 2003). In this chapter, toughening mechanisms in ceramics and the necessary microstructural features for their activation are discussed. In addition, the effect of processing parameters such as type of sintering and sintering additives on the formation of specific microstructural features are discussed.

Toughening Mechanisms

Two classes of toughening mechanisms exist in ceramics. Intrinsic mechanisms, which include crack bowing and crack deflection, operate ahead of the crack tip and act as the material’s inherent defense against microstructural damage and cracking by increasing the material’s resistance to crack initiation. Extrinsic toughening mechanisms operate in the wake of the crack and reduce the local stress intensity at the crack tip. Extrinsic mechanisms, which include crack-bridging, microcrack toughening, and transformation toughening, are the main source of toughness in brittle materials. Extrinsic toughening mechanisms, which act in the crack wake, give rise to R-curve behavior, (Nalla et al. 2004). In a material exhibiting R-curve behavior, a greater applied load must be applied to continue the advance of the crack.
Crack bowing

Crack bowing occurs when the crack front interacts with tough particles or inclusions. The crack is initially pinned by the tough obstacle, but can pass it by bowing on the same plane. While the stress fields are quite different, crack bowing is conceptually similar to the interaction of a dislocation line with a precipitate. Crack bowing assumes that the obstacle is impenetrable; however, if the obstacle were to break before the bowing process is complete a cracked ligament would be left in the crack wake. If the crack passes without breaking the particle an uncracked ligament will be left in the crack wake and thus, crack bowing can be a precursor to crack-bridging (Green 1998).

Crack deflection

Crack deflection occurs when the crack is tilted or twisted out of the plane normal to the applied stress. The change in orientation reduces the crack extension force, which means that a larger applied stress is required for fracture and the toughness will therefore increase. This reduction is greater for twisting than tilting and has been shown to be dependant on the volume fraction and shape of the particle providing the obstruction with rod shaped particles providing the greatest increase in toughness. As the aspect ratio of the particles increases, the toughening increment increases due to the increase of twist angle with increased aspect ratio. In addition to the effect of geometry and the effect of the volume fraction of particles, crack deflection has been shown to also be the result of several factors: the local stress field at the obstacle, the presence of a low toughness interface, or the presence of a cleavage plane (Green 1998).

In multiple phase systems, such as one containing grains and intergranular films or triple junction phases, the difference in thermal expansion mismatch between the grains
and secondary phases can give rise to residual stresses. If the difference in thermal expansion between the grains and secondary phases is positive, a compressive radial stress is developed at the matrix-particle boundary and a tensile tangential stress is developed in the matrix. This will attract the crack to the particle. When the difference in thermal expansion is positive, the crack will be deflected between particles and a more tortuous crack path will be created, which will increase toughness (Hertzberg 1996). If one considers a material with an intergranular film in which the intergranular film is the matrix and the grains are the particles, this second case can be used to explain the origin of intergranular fracture.

With respect to intergranular films, the local compressive residual stresses around the grains cause diminishing stress intensity directly at the tip of the deflected crack and are a result of a difference in thermo-elastic properties between the intergranular film and grains (Sternitzke 1997). Crystallizing triple junctions can also cause residual stresses, the magnitude of which is dependent on the volume change upon crystallization (Pezzotti and Kleebe 1999).

**Crack bridging**

In the discussion of crack bowing it was mentioned that cracks can by-pass an obstacle and leave an intact ligament in the crack wake (Green 1998). For crack bridging to occur, the uncracked ligament, usually an elongated grain, must remain intact as the crack approaches and it must be energetically favorable for the crack to deflect along the ligament surface, rather than cutting through it. This can occur if interfacial bonding occurs due to the presence of a weak interface, which would reduce the stress intensity at the crack tip and allow the ligament to survive and bridge the crack (Nalla et al. 2004).
The uncracked ligaments span the crack wake and sustain part of the applied load that would otherwise be used to advance the crack. Thus, the crack bridges shield the crack tip from part of the applied load. This increases fracture toughness and gives rise to R-curve behavior (Green 1998 and Nalla et al. 2004).

Several testing methods can be employed to determine if crack bridging is the dominant toughening mechanism. First, the crack tip and immediate crack tip wake can be viewed directly with either scanning electron microscopy or transmission electron microscopy (Yuan et al. 2003). Second, a comparison of elastic compliance of the cracked specimen can be compared to the theoretical compliance of an ideal bridge- and microcrack-free crack of the same length. Since crack-bridging increases the modulus, a reduction in compliance would suggest the presence of crack-bridging (Nalla et al. 2004). Finally, when the ligaments have a plate-like geometry, the fracture toughness is given by

\[ K_{Ic}^2 = K_{Ic}^2 + 0.81E \tau \varepsilon_{L} \alpha_{L}^{1.67} d \]

where \( K_{Ic} \) is the fracture toughness measured by the SEBP technique, \( K_{Ic}^o \) is the toughness in the absence of crack bridging, \( E \) is Young’s modulus, \( \tau \) is the frictional stress between grains, \( \varepsilon_{L} \) is the bridging rupture strain, \( \alpha_{L} \) is the aspect ratio, and \( d \) is the mean grain size. A plot of \( K_{Ic}^2 \) as a function of \( \alpha_{L}^{1.67} d \) should yield a straight line if \( \tau \varepsilon_{L}^2 \) is a constant (Flinders et al. submitted).

**Microcracking**

Stress-induced microcracking can give rise to crack-tip shielding, which may increase a material’s toughness. During microcrack toughening a frontal process zone is developed in which the microcracks form. Microcrack formation, and subsequent opening, gives rise to a volumetric increase (Green 1998). The resulting dilation and reduction in modulus of the frontal process zone, if constrained by the surrounding rigid
material, will shield the crack tip and cause an increase in toughness (Nalla et al. 2004). In addition, microcracking can lead to crack branching. When crack branching occurs, a greater applied stress is required to drive the increased number of cracks and thus toughness will increase (Meyers and Kumarchawla 1999).

Microcracking occurs when residual stresses build-up due to the following phenomena: phase transformations, thermal expansion anisotropy in one phase materials, or thermo-elastic property mismatch in multiphase materials (Green 1998). Phase transformation can cause volumetric expansion and contraction. When this volumetric change occurs in a confined phase, residual stress can arise and lead to the formation of microcracks. Thermal expansion anisotropy arises when the crystal symmetry is less than cubic, such as hexagonal, rhombohedral, monoclinic, tetragonal, and triclinic. Expansion is different in each crystal direction. Thermal expansion anisotropy results in contraction of individual grains from neighboring grains at differing rates, depending on crystal orientation. This produces mechanical stresses at the interface, which can generate microcracks. Thermo-elastic property mismatch produces residual stresses in a similar manner as the two aforementioned mechanisms (Case et al. 2005). Areas of low toughness are particularly susceptible to microcracking: grain boundaries and intergranular films (Green 1998).

The degree of toughness increase due to microcracking is dependent on the grain size. As the particle size increases, the toughening increment will increase due to the creation of a tortuous crack path until the critical grain size is reached. At this point spontaneous microcracking will occur and the toughness will decrease since microcrack toughening is only effective in materials that experience microcracking upon crack
propagation. It should also be noted that there is also a critical particle size below which cracking will not occur (Green 1998).

![Fracture toughness increase with particle size due to microcracking](image)

Figure 2-1. Fracture toughness increase with particle size due to microcracking (Green 1998).

**Transformation toughening**

Transformation toughening occurs when a stress induced phase transformation of an unstable phase occurs in the process zone. The phase transformation is associated with a dissipation of energy and the development of compressive residual stresses that will oppose crack advance (Hertzberg 1996).

**Toughening Mechanisms in SiC**

Of the five toughening mechanisms discussed, crack deflection, crack bridging and microcracking are the most possible mechanisms active in SiC. The necessary conditions for these mechanisms are similar. Weak interfaces and a residual stress field are needed for the activation of all three mechanisms. In addition, crack deflection and crack bridging also rely on the particles, in this case grains, having a high aspect ratio, while
microcracking is dependent on grain size. All of these features can be manipulated by choosing the right processing conditions and additive systems. The remainder of this chapter will discuss the effect of sintering parameters on microstructural development.

**Structural Properties of Silicon Carbide**

Silicon carbide exists in several polytypes, of which the following are the most common: 3C, 2H, 4H, 6H, and 12R (Fischer et al. 1990). The polytypes consist of strong, primarily covalently bonded (88% covalent, 12% ionic) Si-C tetrahedra, which contain a Si-C bond length of 1.89 Å. The tetrahedra join at the corners to form the different SiC polytypes (Ye 2002).

![Si-C tetrahedra](image)

Figure 2-2. Si-C tetrahedra, which form the basic structural unit of SiC polytypes.

The structure of the polytypes can be simulated by stacking sheets of close packed spheres, each of which consists of both a layer of Si atoms and a layer of C atoms. The sequence in which these sheets are stacked distinguishes one polytype from another. In Figure 2-3, site A represents the position of the spheres in the first sheet. Subsequent sheets of spheres can either be stacked in the B or C sites, which represent the valleys between the spheres. Thus, the sheets can be denoted as A, B, or C-sheets, depending on the position of the spheres (Ye 2002).

The simplest stacking sequences are as follows: ...ABAB... and ...ABCABC..., which correspond to the hexagonal wurtzite and cubic zinc-blend structures, respectively.
The hexagonal and rhombohedral polytypes are collectively referred to as $\alpha$-SiC, whereas the cubic structure of SiC and is often referred to as $\beta$-SiC (Ye 2002).

![Diagram of close packed plane of spheres with sphere centers denoted by A. Subsequent planes can be stacked in the sphere valleys denoted by B or C to form the different SiC structures.]

In the Ramsdell notation, the number of sheets needed to define the stacking sequence is followed by a letter, which represents the crystal structure: C for cubic, H for hexagonal, and R for rhombohedral. Table 2-1 lists the common polytypes and their corresponding stacking sequences (Ramsdell 1947).

Table 2-1. Ramsdell Notion of Common SiC Polytypes.

<table>
<thead>
<tr>
<th>Ramsdell Notation</th>
<th>Type</th>
<th>Stacking Sequence (ABC Notation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C</td>
<td>$\beta$-SiC</td>
<td>ABC</td>
</tr>
<tr>
<td>2H</td>
<td>$\alpha$-SiC</td>
<td>AB</td>
</tr>
<tr>
<td>4H</td>
<td>$\alpha$-SiC</td>
<td>ABCB</td>
</tr>
<tr>
<td>6H</td>
<td>$\alpha$-SiC</td>
<td>ABCACB</td>
</tr>
<tr>
<td>15R</td>
<td>$\alpha$-SiC</td>
<td>ABCBACABACBCACB</td>
</tr>
</tbody>
</table>

The effects of different additive systems on polytype transformation and its relationship to mechanical properties will be discussed later in this chapter. Chapter 4 will discuss the specific effects of the Al, B, C additive systems used in this body of work to polytype transformation and its relationship to mechanical properties.

**Sintering of Silicon Carbide**

Sintering is the most common processing route for polycrystalline SiC; however, due to the highly covalent nature of the Si-C bond, it is difficult to produce final parts
with densities approaching the material’s theoretic density. Several factors contribute to
the limited thermodynamic driving force and sluggish kinetics: high grain boundary

The thermodynamic driving force for densification and mass transport is the
reduction of free energy in the system due to the formation of interfaces from free
surfaces. In the specific case of grain boundary formation, the grain boundary energy,
\( \gamma_{\text{GB}} \), must be less than twice the solid vapor energy, \( \gamma_{\text{SV}} \). For pore shrinkage, where a
three grain junction is formed, the ratio of the grain boundary energy to the solid-vapor
interfacial energy, \( \gamma_{\text{GB}} / \gamma_{\text{SV}} \), should be less than \( \sqrt{3} \) (Greskovich and Rosolowski 1976). In
a highly covalent material such as SiC, the grain boundary energy is so great that the
reduction of excess free energy is extremely small and densification is practically

![Figure 2-4. Schematic of the competing energy terms during densification.](image)

In addition to having an extremely low thermodynamic driving force for
densification, the kinetics of SiC densification are sluggish (Ye 2002). As previously
mentioned, the high degree of covalency in the Si-C bond limits densification. This
arises from the extremely low self diffusion coefficients of Si and C in SiC (~ 10\(^{-13}\) cm\(^2\)/s
for Si and ~ 10\(^{-11}\) cm\(^2\)/s for C), which limits mass transport and makes diffusion-
controlled solid-state sintering infeasible (Hong 1979). In addition, coarsening, not
densification, dominates during the sintering process due to silicon carbide’s relatively
high vapor pressure, which causes larger grains with larger radii of curvature to grow at
the expense of smaller grains with smaller radii of curvature. This leads to coarsening
without the elimination of pores (Prochazka 87).

Therefore, to produce final parts with densities approaching the material’s
theoretical density, the conditions contributing to the poor thermodynamics and kinetics
must be overcome. This has led to the use of sintering aides, which can lower the grain
boundary energy, increase the solid vapor interfacial energy, and increase the mass
transport. Depending on the additive system, the aforementioned behavior can be
achieved in the absence or presence of a liquid phase, which are referred to as solid-state
sintering and liquid-phase sintering, respectively (Ye 2002). It is also important to note
that the mechanical properties in ceramics are controlled by the flaw size and flaw size
distribution. Sintering aides are commonly used to achieve high density and thus
decrease the flaw size due to porosity (Zhang et al. 1998).

**Solid State Sintered SiC**

Prochazka was the first to develop pressureless sintering of SiC with small amounts
of B and C. He gave a thermodynamic explanation of the effect of additives on the
sintering of SiC. The Carbon removes the surface oxide by carbothermal reduction,
which increases the solid/vapor interfacial energy. The B segregates to the grain
boundaries and reduces the grain boundary interfacial energy (Prochazka 1975). As
discussed in the previous section, an increase in the solid-vapor interfacial energy and a
decrease in the grain boundary energy will favor pore shrinkage and grain boundary
formation.
Tanaka argued that the C also acted to decrease the grain boundary energy, since a certain amount of carbon was necessary, regardless of the oxide content of the starting powder (Tanaka 1984). In addition, B and C have the added effect of increasing self-diffusion in SiC (Birnie 1986).

While the combined effects of B and C allow for solid state sintering of SiC, the low fracture toughness, which is 2.5 MPa-m$^{1/2}$ as measured by the single-edge precracked beam (SEPB) technique, and exaggerated grain preclude the use of solid-state sintered SiC as ceramic armor (Flinders et al. submitted).

**Liquid-Phase Sintered SiC**

Liquid-phase sintering, which can be accomplished via pressureless sintering, gas-pressure sintering, hot-pressing, and hot-isostatic-pressing, is achieved when the melting temperatures of the additives are lower than the sintering temperature (Ye 2002). This condition allows for the formation of a liquid phase that will spread among the grains during sintering. Upon cooling, the liquid phase may persist as a secondary glassy or crystalline phase at the grain boundaries and triple grain junctions. Liquid-phase sintering results in more uniform densification and suppression of the exaggerated grain growth that may occur in solid state sintering. In addition, the secondary phases can alter the properties of the sintered ceramic (Kaneko et al. 2000).

**Liquid-phase sintering aides**

Several additive systems have been used in liquid-phase sintering of SiC. Aluminum additives have been used in several forms, such as Al-metal, Al$_2$O$_3$, Al$_4$C$_3$, and AlN (Kaneko et al. 2000), and in combination with several other additives, such as Y$_2$O$_3$, B, C, B$_4$C, and CaO (Kim et al. 1995, Gu et al. 1996, Zhou et al. 1999). Each additive
system has different effects on the microstructure and mechanical properties of the final sintered SiC (Ye 2002).

Al₂O₃ is frequently used in combination with Y₂O₃ to promote high aspect ratio α-SiC grains and a YAG (Y₃Al₅O₁₂) intergranular phase, which improve the fracture toughness and creep resistance. Chia and Lau suggested that the main toughening mechanism was microcracking between the YAG secondary phase and the SiC grains (Chia and Lau 1991). Nitrogen in the form of AlN is used either alone or in combination with Al₂O₃ and Y₂O₃ to retard the β→α transformation, suppress grain growth, and promote the formation of oxynitride glass, which have also been found to increase the fracture toughness (Kim and Mitomo1999). One example of AlN-containing SiC armor is SiC-N, which is manufactured by Cercom.

Inomata et al. (Inomata et al. 1980) showed that in the Al-B-C additive system a liquid phase was present at 1800°C near the composition of Al₈B₄C₇. This non-oxide system has recently received attention for its ability to produce a three-fold increase in the fracture toughness of SiC (Chen and Lau 2000). With respect to increased toughness, the Al-B-C system can achieve high toughness at lower processing temperature than the YAG system when a comparable amount of liquid phase is used (Flinders et al. 2003). However, for a given toughness SiC with YAG as a secondary phase is harder than SiC sintered with a comparable amount of Al-B-C additives (Flinders et al. 2003). The effects of B and C additives were discussed in the previous section. However, the combined effect of Al, B, and C differ greatly from those of B and C alone. This additive system promotes the β→α phase transformation, the 6H-SiC to 4H-SiC polytype transformation, the formation of elongated grains, the formation of intergranular films, and the formation of secondary phases at the triple-grain junctions (Cao et al. 1996).
Al-B-C additive system

The effects of B and C additive were discussed in the previous section, however the combined effect of Al, B, and C differ greatly from those of B and C alone. Researchers at the Lawrence Berkeley National Laboratory performed experiments on ABC-SiC in which they varied the amount of aluminum from 1-3wt%. The boron and carbon concentrations were held constant at 0.6wt% B and 2 wt% C. Similar to the work of Chia and Lau, the ABC-SiC exhibited R-curve behavior. They observed the formation of either crystalline or amorphous secondary phases in the SiC structure as large regions that wet amongst many matrix grains, triple point junctions, and grain boundaries. The Berkeley group observed the formation of an amorphous secondary phase at the grain boundaries, the crystallinity of which is dependent on the aluminum concentration with increasing crystallinity at higher wt% Al. According to the Berkeley group, the lowered work-of-adhesion afforded by the amorphous secondary phase that promotes toughening and intergranular cracking can be controlled by the second phase chemistry (Moberlychan and De Jonghe 1998).

In a different study at Lawrence Berkeley National Laboratory, two different experiments on ABC-SiC were performed. In the first set of experiments, aluminum foil was imbedded in ABC-SiC powder and hot pressed. This allowed for the formation of an aluminum gradient and the measurement of SiC properties as a function of wt% Al. In the second set of experiments, the wt% Al was varied from 3-7%. The boron and carbon concentrations were held constant at 0.6wt% B and 2 wt% C. In both sets of experiments the researchers observed a lowered densification temperature and an increased number of triple junctions at higher wt% Al (Zhang et al. 2003).
In the first set of experiments, they observed that the area density, aspect ratio, and size uniformity of the elongated grains varied as a function of aluminum content. The aspect ratio is particularly dependent on aluminum concentration. At low concentrations of approximately 1wt% Al, the aspect ratio is reduced to nearly unity, thus grains are equiaxed. In addition, the researchers observed a decrease in indentation toughness and a decreased tendency toward intergranular cracking as the wt% Al was decreased (Zhang et al. 2003).

The second set of experiments was run to better understand the effect of aluminum concentration on the properties of ABC-SiC. The variation in aluminum content from 3-7wt% Al altered the microstructure. As with the first set of experiments, the area density, aspect ratio, and size uniformity of the elongated grains varied as a function of aluminum content. A nearly linear increase in the aspect ratio is observed up to 6wt% Al while the length reaches a maximum at 5wt% Al. A bimodal grain distribution was observed at aluminum contents greater than 3wt%. In addition, the toughness degraded at concentrations greater than 6wt% Al (Zhang et al. 2003).

The increased aluminum content also had a profound effect on the crystallinity of the grain boundaries. As previously stated, the Berkeley group found that at aluminum concentrations lower than 3wt% the second phase was amorphous. Increasing the wt% Al lead to increased crystallinity of the grain boundaries. At 3wt% Al, 85% of the second phase films examined were amorphous and at 6wt% Al and above all of the second phase films examined were crystalline. It is also important to note that increasing the overall aluminum content raised the concentration of aluminum at the grain boundaries and in the grain. At aluminum concentrations greater than 5wt% the grains were saturated and metallic aluminum precipitated at the grain boundaries (Zhang et al. 2003).
According to the Berkeley experiments, increasing the boron content increases the number density of elongated grains, coarsens the grains, reduces the aspect ratio, promotes phase transformations, enhances grain boundary diffusion, and produces a driving force for mass transport. In addition, boron is more effective in promoting the \( \beta \rightarrow \alpha \) transformation (Zhang et al. 2003).

Increased carbon content promotes elongated grains, enhances phase transformation, enhances grain boundary diffusion, and produces a driving force for mass transport. It also increases the self-diffusion rate, as well as the grain boundary diffusion rate of SiC. In addition, the carbon increases apparent density up to 4wt% because of pore elimination and decreases apparent density after 4wt% because of appearance of carbon phase in materials. Furthermore, a decrease in grain growth was observed with increased carbon content. It is important to note that boron and carbon do not form intergranular films by themselves and in the absence of aluminum will incorporate into the SiC lattice (Zhang et al. 2003).

The grain morphology is controlled by the B/C ratio and when the B/C ratio favors elongated grain growth, the aluminum accelerates it and produces higher aspect ratios. When the Al/B and Al/C ratios are reduced, there are less liquid phases and the aluminum effects are diminished. When the Al/B and Al/C ratios are increased, boron and carbon are depleted from the lattice and dissolve into the liquid phases. In addition, at constant Al/B/C ratios, changing the total amount of additives will still change grain morphology and phase composition (Zhang et al. 2003).

**Microstructural Features of Liquid-Phase Sintered SiC**

As mentioned in the previous two sections, the sintering additives used and processing route can greatly affect the final microstructure of SiC materials. However,
there are several common microstructural features of liquid-phase sintered SiC: SiC grains, intergranular films at the grain boundaries, and secondary phases at the triple grain junctions (Moberlychan et al. 1996). However, cases have been reported where direct grain-to-grain interfaces are present (Kaneko et al. 1999). Figure 2-5 is a schematic of the aforementioned microstructural features.

Both $\alpha$-SiC and $\beta$-SiC starting powders may be used in liquid-phases sintering of SiC. Typically $\alpha$-SiC powders are used when a fine equiaxed microstructure is desired (Sigl and Kleebe 1993). However, when increased toughness is desired, $\beta$-SiC is generally used as a starting powder since the $\beta$-to-$\alpha$ phase transformation upon sintering will result in an interlocking microstructure of elongated plate-like grain, which has been shown to increase fracture toughness via crack-bridging and crack deflection (Gilbert et al. 1996). The phase transformation can be accelerated by seeding the $\beta$-SiC starting powder with $\alpha$-SiC (Baud and Theveno 2001), and retarded by incorporating N-containing sintering aides, such as AlN (Jun et al. 1997).

Figure 2-5. Schematic of the microstructural features of liquid-phase sintered SiC (Ye 2002).
Phase Transformation

As mentioned previously, the Al-B-C additive system promotes the $\beta \to \alpha$ phase transformation, the 6H-SiC to 4H-SiC polytype transformation, and the formation of elongated grains. The high aspect ratio grains offer reinforcement and increased toughness by promoting several toughening mechanisms.

Grain Boundary Films in Liquid-phase Sintered SiC

While the presence of intergranular films may appear to be a kinetic phenomenon, the existence of intergranular films at various experimental conditions suggests that these films may be in a state of thermodynamic equilibrium. Clarke devised a model to explain the existence of intergranular films based on a force balance between attractive Van der Waals forces across the grain boundaries and repulsive steric forces, capillary forces, and electric double layer forces in the film (Clarke 1987, Chen et al. 1993). The model predicted the presence of intergranular films on the order of 1-2 nm in several materials, which agrees with experimental data presented to date. While developing his model, Clarke considered the case of SiC without additives and concluded that SiC is the only material where the attractive forces are greater than the repulsive forces (Clarke 1987). Thus SiC without additives would not have a stable intergranular film.

Varying the width and composition of the intergranular film has a large effect on the mechanical properties of SiC. In Al-B-C-containing SiC, the intergranular film has been shown to increase the fracture toughness by a factor of three. Therefore, tailoring of the intergranular film is an important task.

Triple Junction Phase Formation and Crystallization

The Berkeley group observed that the reduction of large secondary phases resulted in the appearance of triple junctions. These regions are several nanometers wide and up
to 10 µm long. They form by heterogeneous nucleation on the basal plane of the SiC. Typically, only partial crystallization can occur and an amorphous region is observed between the crystalline secondary phase and the SiC grain (Moberlychan and De Jonghe 1998).

Full crystallization is hindered by several factors: the composition of the intergranular phase may shift into regions of the phase diagram in which crystallization capability is low; the volume change due to crystallization of the intergranular phase is constrained by the surrounding SiC grains, which causes internal stresses that create a thermodynamic barrier to complete crystallization; and there may be kinetic hindrance to crystallization (Bonnell et al. 1987, Raj 1981, Kessler et al. 1992).

The crystallization process greatly affects the composition distribution in the triple junction. The amorphous region between the crystalline secondary phase and SiC grains has a different composition from the crystalline secondary region. This is due to undesirable solute rejection to the side and ahead of the solidification front, which allows the secondary phases to grow free of SiC. Typically, the secondary phases at the triple junctions are a crystalline ternary or binary containing Al-O-B, Al-B-C, Al-C, or Al-O (Moberlychan and De Jonghe 1998).

In addition, the extent of triple junction crystallization can affect the mechanical properties of the final part. Kessler et al. (Kessler et al. 1992) found that the volume change due to crystallization is strongly dependant on the degree of crystallization with increased crystallization resulting in increased volume change. This volume change results in residual stresses whose magnitude is proportional to the volume change of the constrained phase, or triple junction. Pezzotti and Kleebe (Pezzotti and Kleebe 1999) found that a nearly 100% fraction of crystallized secondary phase at the triple junction
will create substantial tensile stresses due to volume contraction, which drives cracks
toward the triple junction and causes subsequent interface delamination. This
phenomenon can lead to crack branching and intergranular fracture.

Crack deflection will manifest itself as roughness in the final fracture surface.
When SiC fractures in an intergranular fashion, the fracture surface has a high degree of
surface roughness, which is associated with twist and tilt crack deflection (Moberlychan
et al. 1998).
CHAPTER 3
MATERIALS AND METHODS

Material processing, characterization, and electron microscopy methods used to investigate the microstructure and chemistry of the SiC-based materials are presented in this chapter.

Materials Processing of ABC-SiC by Ceramatec Inc.

β-SiC (Superior Graphite grade HSC-059) with surface area in the 15-17 m²/g range was mixed with Al, B, and C additives dispersed with a polyamine polyester polymer (Avecia Chemical grade Solsperse 24000) by adding one wt. % of the polymer, based on solids, to 400 grams of reagent grade toluene. The Al powder (Valimet grade H-3), which has an average size of 3 µm, was added in amounts of 0, 0.5, 1, 1.5, and 4 wt. %, whereas the boron (H. C. Starck, amorphous B grade S-432B) was kept constant at 0.6 wt. %. The carbon was introduced as 4 wt. % Apiezon grade W wax, assuming a 50 % yield after pyrolysis to give ~2 wt. % C. The slurries were deagglomerated for two hours with a paint shaker and then rolled overnight before drying. Powders were passed through a 44 µm screen before hot pressing at 28 MPa in stagnant Ar inside graphite dies at 2100 °C for 1 h.

Characterization

Toughness Testing by Ceramatec, Inc.

The hot pressed billets were ground in order to form 3 mm x 4 mm x 45 mm bars, which were subsequently indented with a 98 N Knoop indenter. The samples were then pre-cracked to initiate crack growth. The single edge pre-cracked beam (SEPB) tests
were performed with loads ranging from 4 kN to 18 kN using spans of 4, 5, or 6 mm. The original crack was marked by a dye (Magnaflux Zyglo ZL-60D), using vacuum infiltration and oven dried at 110°C overnight and cooled before testing. All crack planes were parallel to the hot pressing direction (Flinders et al. submitted).

**Microhardness Testing by Ceramatec, Inc.**

A Leco microhardness machine was used to perform Vickers and Knoop hardness measurements on polished SEPB bars under a 9.8 N load. The load was applied at 50 µm/s, with a 15 second dwell time (Flinders et al. submitted).

**Reitveld Analysis by Ceramatec, Inc.**

Rietveld analysis was used to determine SiC polytypes present in the densified samples with X-ray diffraction patterns collected from 30-80° 2-theta, with a step size of 0.02°/step and a counting time of 4 sec/step (Flinders et al. submitted).

**Grain Morphology Characterization by Ceramatec, Inc.**

Polished samples of liquid phase sintered SiC with Al content ranging from 0.5 to 6 t. % Al were plasma-etched by evacuating and back-filling with 400 millitorr of CF4-10% O₂ and etching for 20-40 minutes. The SiC sample with 0 wt. % Al was etched in molten KOH at 550°C for 10-15 seconds. Grain size was determined by the line-intercept method, where the multiplication constant ranged between 1.5 (equiaxed grains) and 2.0 (elongated, plate-shaped grains). Typically, 200-300 grains were measured for each composition in order to get a mean grain size. The aspect ratio of the five most acicular grains in each of three micrographs was used to estimate a comparative aspect ratio (Flinders et al. submitted).
Transmission Electron Microscopy (TEM)

Transmission electron microscopy, which uses a finely focused beam of electrons, is an important part of the experimental procedure used to investigate the microstructure and chemistry of the SiC-based materials. A wide variety of secondary signals from the specimen are produced when the electron beam interacts with the matter in the specimen. In addition to producing signals used for imaging, these secondary signals are also used to obtain chemical information (Williams and Carter 1996). Figure 3-1 illustrates some of the interactions between the electron beam and the sample.

![Diagram of electron interactions in TEM](image)

Figure 3-1. The above diagram illustrates electron-matter interactions in transmission electron microscopy (Williams and Carter 1996).

Electron interactions can be divided into two classes: elastic and inelastic-scattering events. While elastic and inelastic scattering give rise to many useful signals, only the
signals relevant to TEM and the associated characterization techniques will now be discussed. Elastic scattering events affect the trajectories of the beam electrons inside a specimen without altering the kinetic energy of the electrons. In TEM, elastically scattered electrons are the major source of contrast in images and also create the intensity distributions in diffraction patterns. Inelastic scattering events result in a transfer of energy from the beam electrons to the atoms of the specimen. Inelastic scattering events lead to the generation of characteristic X-rays, which are used in energy dispersive spectroscopy (EDS), and inelastically scattered electrons, which are used in electron energy loss spectrometry (EELS) (Williams and Carter 1996).

**Transmission electron microscopy sample preparation**

In order to perform the electron characterization techniques discussed later in the chapter, the samples must first be prepared for use in the TEM. Transmission electron microscopy specimens were prepared by the standard mechanical thinning method, which creates a self-supporting disk. A 3 x 4 mm rectangle with a thickness of 1 mm was cut from each bulk specimen (3 x 4 x 45 mm bars made for SEPB testing) with a low speed diamond saw. The samples were then mounted on an aluminum polishing stub with crystal-bond adhesive and wet polished to a 100 µm thickness and 3 µm finish. The samples were then cut into 3 mm diameter discs using an ultrasonic drill and then further thinned on a precision dimpling machine to 50 µm using a 3 µm diamond solution and a flattening tool. The center of the sample was subsequently thinned to 20 µm with a dimpling tool. Then four to five hours of Argon ion milling at 4 keV, 1µA and a beam angle of 12° was carried out until the sample was perforated.
High resolution lattice imaging

The high resolution lattice images presented in this thesis were generated on a JEOL JEM-2010F FEG with a point-to-point resolution of 1.9 Å. The images were obtained with the help of Kerry Seibien at the Major Analytical and Instrumentation Center at the University of Florida. High resolution lattice imaging, or phase-contrast imaging, requires the selection of several diffracted beams, in addition to the transmitted beam, to create the image. The collected beams interfere and cause the intensity of the beam to vary sinusoidally with different periodicities for different values of the diffraction vector. This in turn causes lattice fringes in an area of crystallinity. At high magnifications these fringes can be imaged and information on the spacing of the planes normal to the diffraction vector of the beams can be obtained (Williams and Carter 1996).

Lattice imaging can be used to investigate interfaces such as grain boundaries and three grain junctions by orienting the interface parallel to the electron beam and tilting the surrounding grains on-axis. The aforementioned experimental conditions will create lattice fringes in the surrounding grains. In the absence of a secondary phase, an abrupt interface of near atomic dimensions can be observed. If an amorphous region exists at the grain boundary, it will not exhibit lattice fringes and can be imaged directly. Thus, lattice imaging may be used to determine the existence of amorphous secondary phases at interfaces (Williams and Carter 1996).

Energy dispersive spectroscopy (EDS)

The EDS data presented in this thesis was generated on the JEOL 2010F equipped with an Oxford INCA 200 EDS system, which has a probe size of approximately 5 nm. Energy dispersive spectroscopy produces plots of the X-ray counts, or intensity, versus the X-ray energy. The plot consists of two types of signals: Bremsstrahlung X-rays, and
characteristic X-rays. Bremsstrahlung X-rays are the radiation which is emitted when electrons are decelerated due to interaction with the sample. It is characterized by a continuous distribution of radiation and gives no information on the chemical composition of the sample. On an EDS plot, Bremsstahlung X-rays make up the background peaks. The larger Gaussian peaks are the characteristic X-ray peaks. Characteristic X-rays occur when an incident electron ionizes an inner-shell electron, and an electron drops down from a higher energy level to fill the vacancy. The radiation energy produced is equal to the difference between the atomic energy levels. Since the difference in energy levels is unique to each element, characteristic X-rays give compositional data (Williams and Carter 1996).

Energy-filtered transmission electron microscopy (EFTEM)

The EFTEM performed in this thesis was done at the Materials Characterization Facility at the University of Central Florida with the help of Dr. Helge Heinrich on a Technai F30 equipped with a FEG and a GATAN GIF. Elemental maps can be formed using EFTEM by imaging with electrons that have lost energy corresponding to the inner-shell ionization edge of a particular element of interest (Hofer et al. 1997). For elemental mapping, the intensity of any part of the electron energy loss spectrum can be selected to form an electron spectroscopic image (ESI) (Williams and Carter 1996); however, it is necessary to remove the background contribution to the image intensity (Hofer et al. 1995). The three window technique was employed to create ESIs with the background contribution removed. This technique involves recording images at two energy-loss values before and one energy loss value after the ionization energy of the element under investigation, as seen in Figure 3-2 (Schaffer et al. 2003). Then an
extrapolated background image is calculated and subtracted from the ionization edge image, which gives an elemental map (Hofer et al. 1995).

Figure 3-2. Schematic of the three-window technique. Two pre-edge images are used to estimate the background and calculate an elemental map.
CHAPTER 4
RESULTS AND DISCUSSION

The discussion in chapter 2 focused on toughening mechanisms in ceramic materials and the microstructural features necessary for their activation. Per that discussion it was concluded that the most likely toughening mechanisms active in SiC depend on weak interfaces and the presence of a residual stress field. Tests performed at Ceramatec, Inc. showed a change in fracture mode from transgranular to intergranular between 1 and 1.5 wt. % Al. Therefore, this chapter will focus on characterizing the changes in microstructure of each of the five SiC materials described in chapter 3 and the effect of these changes on mechanical behavior.

Transmission Electron Microscopy Characterization

High resolution lattice imaging, energy dispersive spectroscopy, and energy filtered transmission electron microscopy data were taken for samples of SiC with Al wt. % content that varied from 0 wt. % Al to 4 wt. % Al, and a constant 0.6 wt. % B and 2 t.% C. The following sections include a detailed analysis of these samples based upon the crystallinity, thickness, and composition of the grain boundaries and triple grain junctions.

Grain Boundary and Intergranular Film Characterization

Based on the high resolution TEM data taken from the samples, shown in Figure 4-1, the thickness of the grain boundary and the intergranular film (IGF) varies between the samples with 0-1 wt. % Al, and the samples with 1.5 wt. % Al or greater. In the samples with 0-1 wt. % Al added, there is a direct transition from grain to grain, which results in a
negligible grain boundary thickness. The samples with 1.5 wt. % Al or greater contain
grain boundaries on the order of 1 nm. The crystallinity of the grain boundary, based on
the lattice image of the samples also varies. While the samples with 0-1 wt. % Al show a
completely crystalline grain boundary, the samples with greater than 1.5 and 4 wt. % Al
show an amorphous grain boundary. These observations are summarized in Table 4-1.

Konishita et al. found that the solubility limit of Al in SiC is 0.2 wt. % Al
(Konishita 1997). Hence, it would be expected that at Al contents greater than 0.2 w.%
Al, the Al would be expelled from the grain and form an intergranular film. Since this is
not the observed phenomenon, the presence, or lack, of the amorphous film can not be
explained based on the solubility limit alone. As Clarke explained in reference to
equilibrium intergranular film thickness, SiC in the absence of additives is one of the
only materials in which the attractive Van der Waals forces across the grain boundaries
are greater than the repulsive steric forces, capillary forces, and electric double layer
forces in the film (Clarke 1987). According to the equilibrium segregation theory of
McLean, the amount of solute present at the grain boundary is directly related to the
solute content in the grains and inversely related to temperature.

\[ C_D = A e^{Q/RT} \]

\( C_D \) is the solute atomic fraction at the grain boundary. \( A \) is a constant related to
vibrational entropy. \( Q \) is the free energy of segregation at the grain boundary, which is
related to the energy difference between an atom in the bulk and an atom at the grain
boundary. \( R \) is the gas constant and \( T \) is the absolute temperature (Konishita 1997).

Therefore, it is possible that there exists a critical level of additives necessary to
promote the formation of an intergranular film and it was not reached at the prescribed
processing temperature until 1.5 wt. % Al. This topic will be revisited in the discussion of the compositional studies performed on the five SiC materials.

Figure 4-1. The grain boundaries in a) 0 wt. % Al, b) 0.5 wt. % Al, and c) 1 wt. % Al were completely crystalline and contained no intergranular film. In d) 1.5 wt. % Al and e) 4 wt. % Al the grain boundaries are amorphous and 1 nm wide. Please note that the scale marker in a), b), and c) is 2 nm. The scale marker in d) and e) is 5 nm.
Table 4-1. Grain Boundary Width and Intergranular Film Determination by HRTEM

<table>
<thead>
<tr>
<th>Al Content (wt.%)</th>
<th>Grain Boundary Width</th>
<th>Grain Boundary Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>~0 nm</td>
<td>Crystalline</td>
</tr>
<tr>
<td>0.5</td>
<td>~0 nm</td>
<td>Crystalline</td>
</tr>
<tr>
<td>1.0</td>
<td>~0 nm</td>
<td>Crystalline</td>
</tr>
<tr>
<td>1.5</td>
<td>1 nm</td>
<td>Amorphous</td>
</tr>
<tr>
<td>4.0</td>
<td>1 nm</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>

**Triple Grain Junctions**

In general the sintering aides will attract impurities in the starting powder, react with the native oxide on the particle surface, and form a mass transport medium during densification (Falk 1997). In the specific case of Al-B-C additives, boron and carbon will not form a secondary phase without aluminum. This assertion has been proven experimentally by many researchers (Prochazka 1975 and Moberlychan and De Jonghe 1998).

Per the discussion in chapter 2, in SiC sintered without Al the carbon reacts with the native oxide to form SiO and CO. This reaction depletes the oxygen from the system (Stobierski and Guberat 2002). However in the presence of Al, O will be trapped in the system because of the highly negative free energy of formation and comparatively low vapor pressure of aluminum oxides. Thus, the O content will increase with increasing Al. The evidence of this behavior will be presented in later sections of this chapter. This phenomenon produces a greater volume and crystallinity of secondary phase for higher wt. % Al compositions, when the B and C compositions are held constant. Figure 4-2 illustrates the formation of triple junction phases once the solubility limit of Al in SiC has been reached (0.2 wt. % Al). The figure also illustrates that the volume of the triple junction phase increases with increasing aluminum content.
Figure 4-2. Triple grain junctions for ABC-SiC. a) 0 wt. % Al, b) 0.5 wt. % Al, c) 1 wt. % Al, d) 1.5 wt. % Al, and e) 4 wt. % Al. Please note that the scale marker is 20 nm in a) and b), 10 nm in c), 200 nm in d), and 100 nm in e).
Compositional Studies

Energy dispersive spectroscopy (EDS) was performed on the samples using the HRTEM in scanning transmission electron microscope (STEM) mode. EDS is a semi-quantitative chemical analysis method. There are several factors to take into consideration when performing EDS on TEM samples. First, the quality of the data is dependent upon the electron beam, or probe size with relation to the area of sample being studied. While the manufacturer lists the minimum probe size as 0.8 nm, the minimum attainable probe size in practice is closer to 3-5 nm. The grain boundaries in this set of samples are typically 1 nm wide. Thus, there may be signal coming from the surrounding grains as well. It should also be noted that the data is averaged through the bulk. Therefore, if there are overlapping grains, the grain boundary is not oriented parallel to the beam direction, or the grain boundary does not go all the way through the sample thickness characteristics X-rays will be generated from the grain as well and affect the chemical analysis. Therefore, it is more practical to use the difference in characteristic peaks present and in peak heights between the secondary phases and the grains to identify variations in composition than to try to use EDS as a quantitative chemical analysis technique.

In addition to EDS, which uses characteristic X-rays as the signal, EFTEM was also used to create elemental maps of the samples. Since the signal for EFTEM comes from the electron energy loss spectrum, EFTEM provides a method of verifying the presence of species in the samples.

0 wt. % Al

According to the literature, boron and carbon do not form intergranular films by themselves and in the absence of aluminum will incorporate into the SiC lattice (Zhang et
al. 2003). This can be seen in the EDS data in Figures 4-3 through Figure 4-6. However, several carbon inclusions were observed in this sample due to excess free carbon. This phenomenon can be seen in Figures 4-7 and 4-8.

As observed in Figures 4-3 through 4-6, there is very little variation in composition between the grain, the grain boundary, and the three grain junctions. The presence of a clean grain boundary combined with the grain boundary width and crystallinity data suggests the absence of an intergranular film. In addition, the triple grain junctions in this sample were usually clean except for the occasional carbon inclusion. An EDS spectra and EFTEM analysis of a triple junction in this sample shows no variation in composition between the grains and three grain junctions, which suggests the absence of a secondary phase at the triple junctions. The presence of secondary phases at the grain boundaries and triple grain junctions generate residual stresses that promote several toughening mechanisms and intergranular fracture. The absence of these secondary phases may explain the low toughness of solid state SiC.

0.5 wt. % Al

While this sample is above the solubility limit of Al in SiC, the grain boundaries are free of secondary phase and the composition does not change between the grains and
Figure 4-4. EFTEM elemental maps of a grain boundary in the 0 wt. % Al sample.

Figure 4-5. The above figure is a micrograph of a three grain junction in the 0 wt. % Al sample and the corresponding EDS spectra. The EDS data shows no secondary phase present in the three grain junction, and no variation in composition between the three grain junction and surrounding grains.
Figure 4-6. EFTEM elemental maps of a triple junction in the 0 wt. % Al sample. There is no change in composition between the three grains and the three-grain junction.

Figure 4-7. The above STEM image and corresponding EDS spectra show the presence of carbon inclusions between SiC grains in the 0 wt. % Al samples.

grain boundaries. This can be seen in Figures 4-9 and 4-10. This data in combination with the clean, narrow, crystalline grain boundary observed in the HRTEM images
Figure 4-8. EFTEM elemental maps of a C inclusion surrounding a pore in the 0 wt. % Al sample.

testifies to the assertion that no intergranular film exist at the grain boundaries. Unlike the 0 wt. % Al sample, the 0.5 wt. % Al sample shows a small O peak at the grain boundary. This may be due to the diminished effectiveness of the C additive at removing the native oxide in the presence of Al.

Since the solubility limit of Al in SiC has been reached in this sample, rejection of Al from the grains and the formation of a region of secondary phase are expected. While this was not observed at the grain boundaries, it was observed in the triple junctions as an Al-O rich phase. EELS spectrum taken from these regions did not show the characteristic peaks for Al or O in Al₂O₃ (see Figure 4-13); however, the spectrum did show the peaks of elemental Al and O. This would suggest that the region is amorphous. The triple junctions may retain the second phase since the energy to create a film free grain boundary is less than that to create a clean triple junction. In addition, since the
Figure 4-9. The above a) STEM image and b)-e) corresponding EDS spectra are taken from b), e) the grain boundary and c), and d) the surrounding grains.

Figure 4-10. EFTEM elemental maps of a grain boundary in the 0.5 wt. % Al sample.

triple junctions start out as pores, which are larger in volume, the liquid may be pushed into the pores as the SiC-SiC grain boundaries form first.

In addition to the triple junction phase, transition metal inclusions and B-C rich inclusions, which are larger than the triple junctions, were observed. These can be seen in Figure 4-14.
Figure 4-11. The above STEM image and corresponding EDS spectra are taken from the triple junction and the surrounding grains in the 0.5 wt. % Al samples. The secondary phase is confined to the triple junction and does not extend into the grain boundaries. The scale marker is 100 nm.

Figure 4-12. EFTEM elemental maps of an Al-O rich inclusion in the 0.5 wt. % Al sample.

1 wt. % Al

Although the change from transgranular to intergranular fraction occurs between 1 and 1.5 wt. % Al, there is still very little variation in composition between typical grains and grain boundaries in this sample as shown in Figures 4-15 and 4-16. However, the
Figure 4-13. EELS spectra taken from a triple junction in the 0.5 wt. % Al sample shows does not show crystalline Al$_2$O$_3$.

Figure 4-14. A STEM image and corresponding EDS spectra showing metal and B-C rich inclusions. The scale bar is 200 nm.

Overall counts of O in the sample are greater than those of the 0.5 wt. % sample with the majority of the increase in the triple junctions. This lends credence to the assertion that the Al is retaining the O in the system.

The nature of the triple grain junction of this sample differs from that of the 0.5 wt. % Al sample as shown in Figures 4-17 and 4-18. While the increase in volume of secondary phase is insignificant, the change in composition is great. The secondary
phase in the 0.5 wt. % Al sample was found to be amorphous; however, the 1 wt. % Al sample contains crystalline Al₂O₃ in the center of the triple junction and an amorphous phase separating the triple junction phase from the grains. In addition, the concentration of aluminum and oxygen increases with the distance into the triple junction. This is in agreement with the Berkeley group’s assertion that the crystallization process greatly affects the composition distribution in the triple junction and that the amorphous region between the crystalline secondary phase and SiC grains has a different composition from the crystalline secondary region (Moberlychan and De Jonghe 1998).

In addition to the secondary phases observed at the triple junctions, grains of transition metals were also observed. These grains, which are shown in Figure 4-19, are the result of transition metals present in the starting powder.

![STEM image of two grains and a grain boundary from the 1 wt. % Al sample and the corresponding EDS spectra. The composition does not vary between the grains and grain boundary.](image)

**Figure 4-15.** A STEM image of two grains and a grain boundary from the 1 wt. % Al sample and the corresponding EDS spectra. The composition does not vary between the grains and grain boundary.

### 1.5 wt. % Al

The change in fracture mode from transgranular to intergranular fracture is evident at 1.5 wt. % Al. This sample differs from those at lower wt. % Al, which fracture transgranularly, in that there is now an intergranular film that is rich in Al and O present
Figure 4-16. EFTEM elemental maps of a grain boundary and transgranular crack in the 1 wt. % Al sample. There is no variation in composition across the grain boundary or at the site of the crack.

Figure 4-17. A STEM image of a triple junction in 1 wt. % Al showing that aluminum and oxygen segregate on the triple point and that the composition changes as a function of depth into the triple junction. The scale marker is 100 nm.

at the grain boundaries (Figures 4-20 and 4-21), and the triple junction is filled with Al\textsubscript{2}O\textsubscript{3} (Figures 4-22 through 4-24). In addition, there is an increase in O at the triple
Figure 4-18. EFTEM elemental maps of a triple junction in the 1 wt. % Al sample. Notice that the very center of the triple junction is Si and C free.

Figure 4-19. A STEM image and corresponding EDS spectra of grains and contaminations observed in the 1.0 wt. % Al sample.

junctons with respect to the lower wt. % Al samples. Moreover, the appearance of Al-O rich grains is observed in this sample (Figure 4-25).
Figure 4-20. A STEM image of two grains and a grain boundary from 1.5 wt. % Al ABC sample and the corresponding EDS spectra.

Figure 4-21. EFTEM elemental maps of a grain boundary in the 1.5 wt. % Al sample. Note the formation of an Al-O rich intergranular film. Scale marker is 20 nm.

4 wt. % Al

The 4 wt. % Al containing sample also exhibits high concentrations of Al and O at the grain boundaries (see Figures 4-26 and 4-27). The triple junctions are high in aluminum, and oxygen. In addition, this sample had aluminum-rich grains that may be $\text{Al}_3\text{C}$, carbon precipitates, and a B-C rich grains that may be $\text{B}_4\text{C}$. In addition, the XRD
performed by Ceramatec showed that a crystalline phase of Al$_8$B$_4$C$_7$ at 3 wt. % Al. This phase was observed as an Al-B-C rich grain in the EFTEM images.

**Materials Characterization Performed at Ceramatec, Inc.**

This section will detail the material characterization performed at Ceramatec, Inc. Determination of fracture mode, grain morphology, and phase assemblage will be discussed.

Figure 4-22. A STEM image and EDS spectra of a triple junction in the sample containing 1.5 wt. % Al.

Figure 4-23. EFTEM elemental maps of a triple junction in the 1.5 wt. % Al sample. Notice that the entire triple junction is void of Si and C.
Figure 4-24. EELS spectra taken from the triple junction in the 1.5 wt. % Al sample shows that the triple junction is filled with Al<sub>2</sub>O<sub>3</sub>.

Figure 4-25. A STEM image and corresponding EDS spectra of two grains and a grain boundary in 1.5 wt. % Al sample. This site shows two different grains. The upper grain is a SiC grain and the lower grain is that of an Al-O rich grain. The presence of aluminum-rich grains were only observed for 1.5 wt. % Al and 4.0 wt. % Al.
Figure 4-26. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, two SiC grains, and a B-C rich inclusion in the 4 wt. % Al sample.

Fracture Mode Determination by Ceramactec, Inc.

The fracture mode was determined by inspecting the fracture surface of samples after SEPB testing. Figure 4-33 shows the fracture surfaces. From this data it is apparent that there is a change in fracture mode from transgranular to intergranular between 1 and 1.5 wt. % Al. The samples develop some degree of mixed mode fracture above 3 wt. % Al. While SEPB measurements give more accurate values of toughness, often indent surfaces are more instructive as to the fracture mode. Thus, the change to mixed mode can be seen more clearly in the Vickers hardness indents in Figure 4-34.
Figure 4-27. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, a B-C rich inclusion, and an Al₄C inclusion in the 4 wt. % Al sample.

Figure 4-28. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, two SiC grains, and an Al-O-C rich inclusion in the 4 wt. % Al sample. Note that the area of the grain boundary that is farthest from the inclusion contains Al, while the area closest to the inclusion is depleted in Al.
Al-O-C Rich Grain

Figure 4-29. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, a SiC grain, and a carbon inclusion imbedded in an Al-O-C rich inclusion in the 4 wt. % Al sample.

Grain Boundary

Figure 4-30. The above STEM image and corresponding EDS spectra are of a SiC-SiC grain boundary, and two SiC grains in the 4 wt. % Al sample. Note the presence of Al at the grain boundary.
Figure 4-31. EFTEM elemental maps of a grain boundary between two SiC grains in the 4 wt. % Al sample.

Figure 4-32. EFTEM elemental maps of a multiple grain junction in the 4 wt. % Al sample. The circled grain is Al-B-C rich and may be Al₈B₄C₇. The area between the grains is Al-O rich.
**Relationship Between Hardness and Toughness by Ceramactec, Inc.**

The hardness of the SiC samples initially diminishes as Al is added; however, once the fracture mode changes to intergranular the hardness increases again and reaches a maximum at 4 wt. % Al. The toughness remains constant until the fracture mode changes to intergranular. From this point, the toughness increases dramatically and reaches a maximum at 2 wt. % Al. This relationship can be seen in Table 4-2 and Figure 4-35.

**Grain Morphology Characterization by Ceramatec, Inc.**

Several possible toughening mechanisms in SiC are dependant on the size and aspect ratio of the grains. The data on the size and aspect ratio of the grains is presented in Table 4-3. Figure 4-36 illustrates how aspect ratio and grain size change as a function of Al content. In general, the grain size increases as the aspect ratio increases. Figure 4-37 presents the SEM micrographs upon which the grain morphology calculations were performed.

**XRD and Reitveld Analysis by Ceramatec, Inc.**

Per the discussion in chapter 2, the transformation from $\beta$-SiC to $\alpha$-SiC and the formation of secondary phases can affect the toughness. When SiC transforms from a cubic to hexagonal structure, the grains grow anisotropically into a three dimensional structure of interlocking elongated grains. The formation of this network of interlocking grains has been shown to offer some degree of hardness in other studies. In addition, the formation of secondary phases has been known to produce residual stresses, which are needed to initiate several toughening mechanisms in ceramics. It is therefore important to understand the phase assemblage in the SiC samples under study.

Figure 4-38 is the XRD data collected from the samples containing 0-6 wt. % Al. The formation of the secondary phase Al$_5$B$_4$C$_7$ begins at 3 wt. % Al. It is important to
Figure 4-33. SEPB fracture surfaces for samples with 0-6 wt. % Al. There is a clear change in fracture mode between transgranular and intergranular between 1 and 15 wt. % Al. The scale marker is 10 µm (Flinders et al. submitted).

note that Al₂O₃, Al₄C, and B₄C do not appear in the XRD spectra. This would suggest that the volume fraction of these species is much less than that of Al₈B₄C₇.

Figure 4-39 and Table 4-4 show the results of the Reitveld analysis. Unlike the Berkeley group who processed at 1900°C, all of the β-SiC has transformed to α-SiC.
Figure 4-34. Comparison of HV1 (left) and HK1 (right) for various SiC materials. A change in fracture mode is evident between 1 and 1.5 wt. % Al (Flinders et al. submitted).
Figure 4-34 continued. Comparison of HV1 (left) and HK1 (right) for various SiC materials. The onset of the transgranular fracture mode is accompanied by a high degree of crack branching and crushing. A change toward mixed mode fracture occurs at 4 wt. % Al at which point the cracks are straight and there is no crushing (Flinders et al. submitted).
However, this data does agree with the Berkeley group assertion that the 4H content increases up to 3 wt. % Al and then decreases thereafter.

**Correlation Between Microstructure and Mechanical Properties**

**Toughness**

Per the discussion in chapter 2, the viable toughening mechanisms in SiC - crack deflection, crack bridging, and microcracking - depend on at least one of the following: weak interfaces, residual stresses, high aspect ratio grains, and large grains. This section will analyze the observed effect that these properties have on SiC sintered with Al-B-C additives and suggest a possible toughening mechanism.

**Weak interfaces**

The high resolution lattice imaging and compositional analysis presented earlier in this chapter support the formation of a weak intergranular film between 1 and 1.5 wt. % Al. This film was primarily composed of an amorphous film that contained Al and O. Konoshita et al. concluded that the segregation of Al and O atoms to grain boundaries will weaken the grain boundary strength and therefore provide an energetically favorable crack path (Konoshita et al. 1997).

**Table 4-2. Toughness and Hardness Measurements of SiC with 0-6 wt. % Al.**

<table>
<thead>
<tr>
<th>Al (g/cc)</th>
<th>Density (g/cc)</th>
<th>Fracture Mode</th>
<th>Toughness (MPa-m_1/2)</th>
<th>HK1 Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.17±0.01</td>
<td>T</td>
<td>2.6±0.2</td>
<td>20.4±0.4</td>
</tr>
<tr>
<td>0.5</td>
<td>3.17±0.01</td>
<td>T</td>
<td>2.6±0.1</td>
<td>19.4±0.2</td>
</tr>
<tr>
<td>1.0</td>
<td>3.17±0.01</td>
<td>T</td>
<td>2.7±0.1</td>
<td>19.2±0.3</td>
</tr>
<tr>
<td>1.5</td>
<td>3.13±0.01</td>
<td>I</td>
<td>6.1±0.3</td>
<td>13.7±0.2</td>
</tr>
<tr>
<td>2.0</td>
<td>3.13±0.01</td>
<td>I</td>
<td>6.7±0.4</td>
<td>14.3±0.3</td>
</tr>
<tr>
<td>3.0</td>
<td>3.14±0.01</td>
<td>I</td>
<td>6.2±0.4</td>
<td>16.6±0.7</td>
</tr>
<tr>
<td>4.0</td>
<td>3.12±0.01</td>
<td>I</td>
<td>6.1±0.2</td>
<td>16.9±0.8</td>
</tr>
<tr>
<td>6.0</td>
<td>3.07±0.01</td>
<td>I</td>
<td>5.6±0.3</td>
<td>15.0±0.6</td>
</tr>
</tbody>
</table>

T = Transgranular Fracture
I = Intergranular Fracture
Figure 4-35. The above graphs plot Knoop hardness and SEPB toughness as a function of Al content. The change in hardness and toughness with changing Al content is inversely related (Flinders et al. submitted).

Table 4-3. Characterization of SiC with 0-6 wt. % Al (Flinders et al. submitted)

<table>
<thead>
<tr>
<th>x</th>
<th>Density (g/cc)</th>
<th>Grain Size (µm)</th>
<th>Aspect Ratio</th>
<th>Fracture Mode</th>
<th>Toughness (MPa-m(^{1/2}))</th>
<th>HK1 Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.17±0.01</td>
<td>4.7±0.4</td>
<td>5.4±1.1</td>
<td>T</td>
<td>2.6±0.2</td>
<td>20.4±0.4</td>
</tr>
<tr>
<td>0.5</td>
<td>3.17±0.01</td>
<td>4.6±0.2</td>
<td>5.9±1.3</td>
<td>T</td>
<td>2.6±0.1</td>
<td>19.4±0.2</td>
</tr>
<tr>
<td>1.0</td>
<td>3.17±0.01</td>
<td>4.1±0.5</td>
<td>5.4±0.9</td>
<td>T</td>
<td>2.7±0.1</td>
<td>19.2±0.3</td>
</tr>
<tr>
<td>1.5</td>
<td>3.13±0.01</td>
<td>5.2±0.4</td>
<td>3.9±0.6</td>
<td>I</td>
<td>6.1±0.3</td>
<td>13.7±0.2</td>
</tr>
<tr>
<td>2.0</td>
<td>3.13±0.01</td>
<td>5.8±0.5</td>
<td>5.0±1.3</td>
<td>I</td>
<td>6.7±0.4</td>
<td>14.3±0.3</td>
</tr>
<tr>
<td>3.0</td>
<td>3.14±0.01</td>
<td>11.9±1.2</td>
<td>4.5±1.0</td>
<td>I</td>
<td>6.2±0.4</td>
<td>16.6±0.7</td>
</tr>
<tr>
<td>4.0</td>
<td>3.12±0.01</td>
<td>5.3±0.5</td>
<td>5.1±1.0</td>
<td>I</td>
<td>6.1±0.2</td>
<td>16.9±0.8</td>
</tr>
<tr>
<td>6.0</td>
<td>3.07±0.01</td>
<td>7.1±0.6</td>
<td>8.7±2.7</td>
<td>I</td>
<td>5.6±0.3</td>
<td>15.0±0.6</td>
</tr>
</tbody>
</table>
Figure 4-36. Change in aspect ratio and grain size with Al content.

The effect of the weak intergranular film on toughness is apparent. Upon formation of the intergranular film at 1.5 wt. % Al, the toughness more than doubled. In addition, the formation of the intergranular film was accompanied by a change in fracture mode from transgranular to intergranular. It is therefore apparent that the intergranular film plays a large role in increasing the toughness due to a change in fracture mode. However, since all three of the previously mentioned toughening mechanisms could be affected by this intergranular film, or at least weak interfaces, no conclusion can be drawn with respect to the dominant toughening mechanism.

**Residual stresses**

The analysis of residual stresses due to thermal expansion anisotropy in single phase systems and thermo-elastic property mismatch in multiphase systems is important
Figure 4-37. Polished and chemically or plasma-etched surfaces of SiC samples with 0-wt. % Al (Flinders et al. submitted).
Figure 4-38. X-ray diffraction patterns SiC with 0-6 wt. % Al. Note that starting powder was beta-3C and that in addition to SiC polytypes, Al$_8$B$_4$C$_7$ phase is noted at high Al contents (Flinders et al. submitted).

Figure 4-39. Polytypes from Rietveld analysis for SiC-0.6 wt. % B-0.2 wt. % C samples with Al contents ranging from 0 to 6 wt. %.
Table 4-4. Reitveld Analysis for SiC Samples with 0-6 wt. % Al (Flinders et al. submitted).

<table>
<thead>
<tr>
<th>Al Content (wt. %)</th>
<th>Phase Assemblage (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3C</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
</tr>
</tbody>
</table>

in determining crack behavior. As mentioned in chapter 2, in multiple phase systems such as one containing grains and intergranular films or triple junction phases, the difference in thermal expansion mismatch between the grains and secondary phases can give rise to residual stresses. If the difference in thermal expansion between the grains and secondary phases is negative ($\alpha_m < \alpha_p$), a compressive radial stress is developed at the matrix-particle boundary and a tensile circumferential stress is developed in the matrix. The particle will be in tension and the crack will be attracted to the particle.

When the difference in thermal expansion is positive ($\alpha_m > \alpha_p$), the crack will be deflected between particles and a more tortuous crack path will be created, which will increase toughness (Hertzberg 1996). If one considers a material with an intergranular film in which the intergranular film is the matrix and the grains are the particles, this second case can be used to explain the origin of intergranular fracture.

With respect to intergranular films a local compressive tangential residual stress around the grains can cause diminishing stress intensity directly at the tip of the deflected
crack and are a result of a difference in thermo-elastic properties between the intergranular film and grains (Sternitzke 1997).

Crystallizing triple junctions can also cause residual stresses, the magnitude of which is dependent on the volume change upon crystallization (Pezzotti and Kleebe 1999). The extent of triple junction crystallization can affect the mechanical properties of the final part. Kessler et al. found that the volume change due to crystallization is strongly dependant on the degree of crystallization with increased crystallization resulting in increased volume change. This volume change results in residual stresses whose magnitude is proportional to the volume change of the constrained phase, or triple junction (Kessler et al. 1992). Pezzotti and Kleebe found that a nearly 100% fraction of crystallized secondary phase at the triple junction will create substantial tangential tensile stresses at the interface between the grains and triple junction due to volume contraction, which drives cracks toward the triple junction and causes subsequent interface delamination. This phenomenon can lead to crack splitting and intergranular fracture (Pezzotti and Kleebe 1999).

It is therefore necessary to determine the local residual stresses between the grains and grain boundaries, and between the grain and triple junctions. For the sake of simplicity, the residual stresses with respect to the grain boundaries will be calculated with the assumption that the grains are fibers in an infinite matrix and are bonded to the grain boundaries. This is obviously a simplification considering the fact that the matrix, or intergranular film, is narrower than the particle, but serves as an approximation and means of relative comparison. Superposition of stress fields would be expected, however, they are ignored in this calculation. The grain boundary film is an amorphous glass containing Al and O, and is most likely an aluminosilicate glass with a low silica
volume fraction. The properties of an aluminosilicate with 64.4% Al2O3 and 36.6% SiO2 were used for the amorphous intergranular film. Thus, the residual stress due to a fiber in an infinite matrix can be calculated as follows (Green 1998):

Fiber:

\[ \sigma_{rr} = \sigma_{\theta\theta} = -P \]

Matrix:

\[ \sigma_{rr} = \frac{Pa^2(r^2 - b^2)}{r^2(b^2 - a^2)} \]

\[ \sigma_{\theta\theta} = \frac{-Pa^2(r^2 + b^2)}{r^2(b^2 - a^2)} \]

Where \( a = \) fiber radius, \( b = \) the radius of the fiber plus the radius of the matrix

\[ P = \frac{E_f E_m(\alpha_m - \alpha_f)(T_0 - T_A)(1 + \nu_f)}{(1 + \nu_f)E_m(1 - 2\nu_f) + E_f(1 + \nu_m)} \]

\[ = \frac{430GPa70GPa(9.7 \text{ µm/m°C-4.5 µm/m°C})(1373K-298K)(1+0.17)}{(1+0.17)(70GPa)(1-.34) + 430GPa(1+0.22)} \]

\[ = 340MPa \]

Thus, the stresses in the fiber are compressive and the stresses in the matrix are tensile in the radial direction. This stress state will cause matrix cracking. This residual stress state can therefore explain the transition to intergranular fracture when an intergranular film is present.

It is also important to understand the effect of the triple junction phases on residual stress. For the sake of simplicity, the effect of superposition of stresses will be ignored, and the triple junction phase is assumed to be a spherical particle in an infinite matrix. The properties of alumina will be used for the triple junction and those of SiC will be used for the matrix. The stress state will be calculated as a function of temperature. The residual stress due to a particle in an infinite matrix can be calculated as follows (Green 1998):
Particle:

\[ \sigma_{rr} = \sigma_{\theta\theta} = -P \]

Matrix:

\[ \sigma_{rr} = -2\sigma_{\theta\theta} = -\frac{r^3 P}{r^3} \]

\[
P = \frac{2E_mE_p(\alpha_m - \alpha_p)(T_0 - T_A)}{2E_m(1 - 2\nu_p) + E_p(1 + \nu_m)} \]
\[
= \frac{2(430GPa)(370GPa)(4.5 \, \mu m/m^\circ C - 8.2 \, \mu m/m^\circ C)(T_0 - 298K)}{2(430GPa)(1 - 2*0.22) + 370GPa(1 + 0.17)} \\
= -2.72 \times 10^6 \, Pa(T_0 - 298K)
\]

T\textsubscript{0} may be one of several temperatures: the processing temperature, the melting point of alumina, the melting point of mulite, or 2/3 of the homologous temperature.

Therefore, the stress, P, is plotted vs. temperature to determine the sign of P, which allows for the determination of the residual stress fields in the secondary phases at the triple junctions and in the surrounding SiC grains.

Figure 4-40. Plot of Stress vs. Temperature for a particle in an infinite matrix.
From the graph, the calculated load can be between -3 GPa using 2/3 of the homologous temperature and -6 GPa using the processing temperature. The entirety of this range is negative, thus the stresses in the particle are tensile and the stresses in the matrix are tensile in the radial direction and compressive in the circumferential direction. As the crack is attracted to regions of tension, this stress state will cause the crack to be driven toward the triple junction and cause delamination.

The combined effect of tensile stresses in the grain boundary phase and the triple junction phase will cause the crack to propagate within the intergranular film and around the triple junctions. This behavior was observed in the 1.5 wt. % Al sample and is shown in Figure 4-42.

Figure 4-41. Effect of residual stress fields around triple junctions on crack propagation (Pezzotti and Kleebe 1999).
Residual stresses contribute to all three toughening mechanisms discussed earlier in the section. Therefore, it would be difficult to conclude a specific toughening mechanism at this point. However, a probable origin of the intergranular cracking has now been proposed.

**High aspect ratio grains**

Both crack deflection and crack bridging depend on the aspect ratio of the grains (Green 1998). If either of these mechanisms were active, an increase in toughness with aspect ratio would be expected. In the case of crack deflection, the SiC grains are taken to be the particles and thus the volume fraction of high aspect ratio grains is close to unity. Faber and Evans found that after the volume fraction reaches 0.2 no additional increase in toughening will be observed with increased volume fraction of elongated grains (Green 1998). In addition, the crack wake on the indented samples does not show
the deflection of the crack and therefore, it is unlikely that crack deflection is the main toughening mechanism in the samples.

If crack bridging were to occur, the toughness would increase as a function of aspect ratio according to the following equation (Flinders et al. submitted):

\[ K_{Ic}^2 = K_{Ic}^o + 0.81E \tau \epsilon^2 L^2 \alpha L^{1.67} d, \]

However, when the square route of toughness is plotted against aspect ratio raised to the 1.67, Figure 4-43, the slope is negative. In addition, no crack ligaments are observed in the crack wake in the hardness indents. Thus, the evidence points away from crack bridging.

**Large grains**

Microcracking occurs when residual stresses build-up due to the following: phase transformations, thermal expansion anisotropy in one phase materials, or thermo-elastic property mismatch in multiphase materials (Green 1998). The previous section on residual stresses showed that residual stresses existed at the interfaces between the intergranular film and SiC grains, and the triple junctions and SiC grains. These stresses were also shown to cause cracking at the interface and debonding of the triple junctions, thus satisfying one of the conditions necessary for microcracking.

The degree of toughness increase due to microcracking is dependent on the grain size. As the particle size increases, the toughening increment should increase due to the creation of a tortuous crack path until the critical grain size is reached. Baud and Theveno found that the assertion that the toughness increases with grain size, or more precisely the square route of grain size, holds true for liquid-phase sintered SiC (Baud and Theveno 2001). However, the composition of the starting powers was all the same and only grain size varied in the materials that Baud and Theveno investigated. For the
case of the SiC sintered with Al-B-C additives under investigation, not only does the grain size change, but the types and volume fraction of secondary phases change. This would in turn affect the magnitude of the residual stresses developed and therefore the degree of toughening gained by microcracking. Therefore, there may be a synergistic effect between the grain size and the volume fraction of secondary phases, which would result in the plot of toughness vs. grain size showing no correlation between the two. Therefore, the possibility that microcracking is the dominant toughening mechanism should not be dismissed.

Indeed, an inspection of the Vickers indents reveals a high degree of crushing and crack branching in the 1.5 wt. % sample. The 4 wt. % Al sample experiences a much lower degree of crack branching and crushing than the 1.5 wt. % sample. This may be due to the formation of additional secondary phases in this sample such as $\text{Al}_8\text{B}_4\text{C}_7$, $\text{Al}_4\text{C}$,

![Toughness vs. Aspect Ratio](image)

Figure 4-43. Plot of toughness vs. aspect ratio shows a negative slope and argues against crack bridging. The three data points at the bottom of the graph correspond to the samples that fail transgranularly.
Figure 4-44. Plot of toughness vs. grain size. Toughness generally increases with increased grain size.

B₄C, and an Al-O-C rich phase. Not only are more species present, but they are present in much greater volume fraction than the secondary phases in the 1.5 wt. % Al sample. As shown in the calculation performed in the residual stresses section, the secondary phases surrounded by the intergranular film will create compressive stresses in the secondary phase, which will deflect the crack. If these phases are present in high enough concentration, it could explain the change in fracture mode from intergranular to mixed mode at this composition, and the drop in toughness.

**Hardness**

The hardness initially drops when small amounts of aluminum are added with the largest drop in toughness occurring when the fracture mode changes to intergranular fracture. From this point, the hardness begins to increase again, reaching a maximum at 4 wt. % Al, and then decreases again. The large drop in hardness upon the formation of an intergranular film is due to the increased ability of the SiC grains to move under the
indentation load, which results in lower hardness (Flinders et al. 2003). The increase in hardness up to 4 wt. % may be explained in a similar fashion to the drop in hardness. The increased number of secondary phases that exist in a state of compression would resist grain movement under the indentation load. By building-up compressive stresses in the material, a greater applied load is needed to deform the material.

**Effect of grain size on hardness**

While the grain size had little effect on toughness, it does affect the hardness. Often a Hall-Petch type relationship is applied to correlate the hardness with the grain size; however, this model is not as useful for ceramic as it is for metals. The relationship was originally designed to explain an increase in strength due to dislocation pile-up at

![Hardness vs Grain Size](image_url)

Figure 4-45. Plot of the effect of grain size on hardness. The plot shows that hardness increases with grain size for the samples that fail via intergranular fracture.
grain boundaries, since the number of grain boundaries increases with decreasing grain size. Yet, the hardness does scale inversely with grain size. This effect is more likely due to the reduction of the inherent size of the flaws when the grain size is reduced than to an increase in dislocation piles.

**Effect of aspect ratio on hardness**

By plotting hardness vs. the aspect ratio, it observed that the aspect ratio has no effect on the hardness. This behavior can be seen in Figure 4-46.

![Hardness vs. Aspect Ratio](image)

Figure 4-46. The plot of hardness vs. aspect ration shows that the hardness is not dependant on aspect ratio.
CHAPTER 5
SUMMARY AND CONCLUSIONS

Conclusions

With the use of high resolution lattice imaging, energy dispersive spectroscopy, and energy filtered transmission electron microscopy, it was determined that an amorphous intergranular film forms between 1 and 1.5 wt. % Al. The film is composed primarily of an Al-O rich phase and contains an equilibrium film thickness of approximately 1 nm. The residual tensile stresses in this film allow for cracking through the film, promote the change in fracture mode from transgranular to intergranular fracture, and increase the toughness values by a factor of two.

The addition of aluminum to the samples promoted the formation of secondary phases at the triple junctions. These secondary phases were Al-O rich and the oxygen content and crystallinity increased as the Al content was increased, with the formation of alumina occurring at 1.5 wt% Al. Additional secondary phases were formed as discrete grains and inclusions at Al contents greater than 1.5 wt. % Al. These phases may include: Al₄C, an Al-O-C phase, Al₈B₄C₇, and B₄C. The crystallization of the secondary phases generated a compressive stress field in the particles that caused the crack to deflect through the amorphous phase around the crystalline triple junctions in the 1.5 wt. % Al sample, which has a lower volume fraction of secondary phase. However, as the volume fraction of secondary phases increased, as in the 4 wt. % Al sample, the amount of residual compressive stress in the samples increased and caused a simultaneous increase in hardness and decrease in toughness.
**Suggested Future Work**

While some conclusions were made to possible toughening mechanisms in SiC sintered with Al-B-C additives, additional investigation into the toughening mechanisms is needed. In-situ cracking studies performed in a scanning electron microscope in secondary electron mode could be used to monitor the advance of the crack and image the crack tip and crack wake. This study would produce potential identification of the toughening mechanism.

In addition, a comparison of the elastic compliance of the cracked specimen can be compared to the theoretical compliance of an ideal bridge- and microcrack-free crack of the same length. Since crack-bridging increases the modulus, a reduction in compliance would suggest the presence of crack-bridging. Conversely, a decrease in the compliance would suggest microcracking (Nalla et al. 2004).
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Samantha Crane moved from her childhood home in Roslyn Heights, NY, to Weston, FL, at the age of 15. She graduated high school from The University School of Nova Southeastern University in 1999. In the summer of 1999 she enrolled in the Honors College at the University of Florida. She graduated cum laude from the University of Florida with her Bachelor of Science in materials science and engineering in May 2003 and will receive her Master of Science in materials science and engineering in August 2005. Samantha has a particular interest in nuclear materials, which began with her senior research project on burnable poison rod assemblies. She has pursued this interest by participating in two summer internships with the United States Nuclear Regulatory Commission (NRC) in Rockville, MD. Samantha will be returning to the NRC for full-time employment in the fall of 2005.