EFFECT OF SINTERING TIME AND COMPOSITION OF SINTERING AIDS ON THE CORE-RIM MICROSTRUCTURE AND MATERIAL PROPERTIES OF SPARK PLASMA SINTERED SILICON CARBIDE

by

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A thesis submitted to the

Graduate School-New Brunswick
Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the Degree of

Master of Science

Graduate Program in Materials Science and Engineering

Written under the direction of

Professor Richard A. Haber

And approved by

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New Brunswick, New Jersey

May 2013
Silicon carbide is an industrial ceramic used for many applications. Due to its complicated crystal structure, many different types exist and can be made to have a “core-rim” microstructure in individual grains. In this work, SiC samples were processed via a co-precipitation and spark plasma sintered to examine the core-rim microstructure by altering the sintering time when spark plasma sintered, the additive amounts, and the polytype composition. Samples were characterized via density, hardness, FESEM, XRD, and Raman analysis depending on the type of samples. The density and hardness of samples showed that the samples for the dwell time studied were densified but the ones of varying polytype were not. The hardness generally increased with longer sintering dwell times, whereas the density measurements were too similar to discern any appreciable difference between samples. The extent of the core-rim structure as seen from FESEM images had a large variability, but preliminary results hint at less core-rim
features with longer dwell times. The XRD results were typical of the materials present in the sample and showed a SiO\textsubscript{2} phase.
Acknowledgements

It’s been one and a half years, but there are already so many people I would like to thank for making this journey possible. First of all, I’d like to thank Dr. Klein & the admissions committee for accepting me into the program. I wouldn’t have had this chance if it weren’t for you. I’d like to thank Dr. Haber for bringing me on board, getting me excited the first semester, and providing direction for the research. Even if you didn’t know the answer, you always knew the right person to direct me to. Many thanks to Michelle, for reserving SEM time, helping out with orders, report reminds, etc. amidst all the other necessary work you do. And thanks to all the MSE professors & staff: Dr. Mathewson for teaching 3 of the courses on the qualifier exams and being among the best teachers in MSE, Dr. Cosandey for teaching & providing hands on experience with the TEM, Dr. Mann for a very clear course in mechanical properties of materials, Claudia for helping out with all the administrative work, and Dr. Klein for teaching kinetics, arranging the seminars, & continuing to run the graduate program.

I also want to thank the researchers & post-docs in the group who’ve helped me out. I’d like to thank Steve Miller, the man who really understood the SEM inside & out, for always having good advice and the awesome SEM training. And of course Sukanya for continuing the SEM training & helping out with the SEM. I definitely cannot forget to thank Vlad, one of the most intelligent researchers, who is always willing to help explain the real science behind what we’re doing and is a true master of Raman.

And of course, I’d like to thank all the Haber group members & classmates. I’d like to thank the old Steve B. for showing me some of the instruments my first week,
explaining how they work, and always being such a cool helpful guy. Also many thanks to Dan who spent the time teaching me about B₄C, how to use the XRD unit, and even helped with some XRD problems it had after his graduation. Both of you are have been very helpful, & your expertise shows despite the short time I met you guys. Even though he was before my time, I would also like to thank Steve Mercurio for the extensive work on co-precitation that really helped guide most of this work, and Bob Bianchi for continuing it. I’d like to thank Doug for being such a nice guy all the time, and showing me the polisher & hardness tester. Fatih, I’d like to thank for being the first Haber grad student I met & always providing good advice whether it’s about classes to take or help making decisions. Vince, Nick, & Minh I’d like to thank for also helping me out around the lab, showing me where stuff is, and always boosting the group’s morale. And thanks to Kanak, Tyler, & Metin for joining Haber group as well my undergrad, Matt Sperling, for doing a lot of the tedious work and helping out a lot with the manual labor.

Lastly, I would like to thank my friends and family: everyone who supported me through all of this. Thanks to my brothers, my parents, & Grandma. And I’m deeply grateful to have such supportive friends: Wei, Andrew, Malachy, Connie, Boris, Nirav, Steve T., Brendan G., Brendan C., Joe Leo, Samer, Rob, Allan, Vicky, Saskia, Dan K., Ori, Mike S., Mikey P., and I’m sure there are tons I missed, but each of you had a positive impact these past couple years in some shape or form. And thank you very much to Joan, who despite only meeting a few months ago, has been very supportive of my decisions, and always knowing how to uplift my mood.
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Chapter 1: Introduction

1.1 Background on SiC & Crystal Structure

Silicon Carbide (SiC) has been widely used in industry for a variety of applications. The range of its applications spans from abrasives, refractories, wear resistant bearings, semiconductors, electronic devices, and even in armor ceramics due to its strong covalent bonding between lightweight atoms [1, 2].

SiC is commercially produced by a carbothermic reduction of a silicon oxide in contact with a source of carbon, otherwise known as the Acheson process [3]. The resulting product is comminuted to produce sub-micron sized particles for ceramic processing, such as sintering. A variety of grades (and therefore crystal structures) of SiC can be produced depending on the extent of reacted starting materials.

The vast range of applications for Silicon Carbide is partly due to its bonding & crystal structure. The crystal structure can be visualized more easily as an array of tetrahedral molecules such as Si at the center & C at the edges of the tetrahedron (or vice versa equivalently). These tetrahedra are joined at the corners in one plane, in this example by the C atoms. The next plane of tetrahedra can then be arranged in either a parallel fashion where the Si atoms lies directly above the gaps between C atoms in the first plane or an anti-parallel fashion where the Si atoms directly above
the C atoms in the first plane (See Figure 1) [4].

![Figure 1. Parallel vs Anti-Parallel stacking structure of SiC [4]](image)

This structure can result in an infinite number of combinations of different stacking layers, and to distinguish the layers Ramsdell notation will be predominantly used. Ramsdell notation designates the crystal structure as $nL$ where $n$ is the number of layers before the pattern repeats itself and $L$ is the crystal symmetry with $L = H$ for hexagonal, $L = R$ for rhombohedral, and $L = C$ for cubic symmetry. The most common of these polytypes is 2H, 4H, 6H, 15R, and 3C (also known as $\beta$-SiC).

It is also possible to visualize the stacking sequence in a ‘ABC’ scheme. A, B, and C each indicate one of the 3 possible stacking orientations described above. For example, 2H SiC would have a stacking sequence ABABAB… and so on. A visual
depiction of the stacking sequences for some of the more common polytypes is shown in Figure 2.

![Image of SiC polytypes](image)

**Figure 2. Stacking sequence of common SiC polytypes. [5]**

### 1.2 Stacking Faults & Core-rim structure

While it is easy to describe SiC’s crystal structure as polytypes, it is also important to note that multiple polytypes often exist in SiC. One part of SiC’s stacking sequence might exist as 2H but then get interrupted and continue in a 4H stacking sequence before going back to 2H or shifting to yet another polytype. These shifts are known as stacking faults and they are very important because
they offer a way to alter SiC’s properties from within the grains as opposed to intergranular & grain boundary engineering.

There’s an energy associated with creating these stacking faults, which may provide not only some fundamental insight into how to improve properties such as the materials strength, toughness, density, etc., but also possible mechanisms of fracture behavior. There has been theoretical work on calculating these energies [5] in Silicon Carbide in good agreement with available experimental data [6, 7]. The motivation for this work is to begin exploring potential pathways of utilizing stacking faults as a mechanism of absorbing the impact energy, minimizing crack propagation, and creating tougher materials.

One possible method of modifying these stacking faults could be via a “core-rim” microstructure that has been observed in AlN-doped SiC ceramics, which is likely due to diffusion of AlN into the SiC grains or a solution re-precipitation mechanism [2, 8]. H. Gu et al. used a hot-pressed AlN-SiC system and observed grains with an outer rim surrounding the grain’s core with analytical electron microscopy [8]. They found that it is possible to shift 6H-SiC into 2H SiC by adjusting the amount of AlN in their samples but too much AlN results in AlN grains.

1.3 Co-precipitation of SiC

Coprecipitation is a novel method of introducing sintering aids into SiC powder as a reactive coating, resulting in improved sintering and mixedness of
sintering aids [2]. During co-precipitation, an insoluble phase nucleates out of a supersaturated solution onto the site of interest. This process can be used to get a wide variety of particle sizes, shapes, and other properties. Because the insoluble phase precipitates out very rapidly, it can be used to add fine nanoscale particles to the powder resulting in improved mixedness & reactivity [9-12].

The co-precipitation process involves a precursor salt dissolving into a polar solvent. After the precursor dissociates into its ions, they become attracted to the oppositely charged surface of interest. Then the remaining ions are still attracted to their oppositely charged counterparts, but because their counterparts are already attached to the surface, the attraction isn’t as strong. This is known as a double layer formation as shown in Figure 3. This weaker attraction and solvation process results in a higher chance of ions repelling each other causing a well-mixed distribution of components.

![Figure 3. Formation of electrical double layer during co-precipitation process. Surface is shown at left & solvated ions are shown as circles. [2]](image)

When an additional solvated ion pair is introduced, there’s the possibility of the solvated ions reacting to form an insoluble product. For example:
$\text{Al(NO}_3\text{)}_3 (\text{aq}) + 3 \text{Na(OH)} (\text{aq}) \rightarrow \text{Al(OH)}_3 (\text{s}) + 3 \text{Na(NO}_3\text{)} (\text{aq})$

In some cases, the reaction is dependent on pH, temperature, saturation, rate of addition and/or other side-reactions. Adjusting all these variables can be used to modify features of the final product such as particle size, purity, agglomeration, etc. [10 - 12].

Bellosi et al. coprecipitated SiC with Y and Al additives and found improved mechanical and sintering behavior [13, 14]. They found that coprecipitation increased the densification rate and lowered the final grain size compared to ultrasonication. Furthermore, the amount of secondary phase was shown to decrease by using co-precipitation. The strength of the materials was not as high as expected likely due to processing but work has been done to address these issues by focusing on a more homogenous mixture of sintering aids [2].

1.4 Sintering

Sintering is required to densify SiC powders into a solid dense ceramic object. It works by dramatically increasing atomic diffusion across powder particles by increasing the temperature and/or pressure. The main driving force for this compaction is a decrease in the surface free energy. It is typically carried out below the melting point of the dominant component and can be accelerated through the formation of a liquid phase to fill up pores [15]. A typical sintering process involves an initial, intermediate, and final stage. During the initial stage, the particles shape
does not change significantly but ‘necks’ between particles begin growing. These necks grow from atomic diffuse at the points where powder particles come into contact with each other (See Figure 4). During this stage, there is also some shrinkage of the powder particles.

Figure 4. Neck formation between individual particles. The smaller blue spheres illustrate atomic diffusion & larger blue spheres are powder particles. [16]

After the initial phase, the pores begin to shrink and the shape of particles change shape to form a grain-like structure. The grain boundaries can move and rearrange to squeeze out pores and move them to three grain junctions. And rather than atoms diffusion from the surface, there is now a bulk or lattice diffusion occurring from deeper portions of the grains [16].

Then, in the final stage of sintering, pores are ideally isolated at three-grain junctions. The grains grow in this stage and it occurs at a much slower rate than the initial and intermediate stages. Gases can get trapped in the pores limiting the final density, unless the process is used in conjunction with a vacuum system to remove gases [2,16].

1.5 Liquid Phase Sintering
One method devised to improve densification and microstructure control is through the use of liquid phase sintering [17, 18]. Even with advanced methods like spark plasma sintering, the desirable densities & microstructure are not achieved, so liquid phase sintering is an attractive method.

Liquid phase sintering consists of introducing additives and appropriate sintering cycles to form a liquid phase that enhances material transport. It causes capillary forces to arise, resulting in faster sintering and provides an additional medium for atomic transport. Liquid phase sintering has typical stages it goes through but the only requirement is that a liquid forms during the sintering process [10].

The three stages of liquid phase sintering are rearrangement, solution re-precipitation, and solid state sintering. These stages are shown in Figure 1.5:
The most beneficial aspect of liquid phase sintering is due to the solubility of the components in the system. This is typically the solubility of the solid into the liquid phase, although the reverse is also possible. When the liquid is formed & particles redistribute themselves, this is known as the rearrangement phase. The liquid fills up any open pores and increases capillary pressures that start squeezing the particles closer to each other. [10, 2]

The second stage, solution precipitation, is when the smaller bits of solid particles dissolve in the liquid phase. This causes a concentration gradient, allowing the solid particles to move through the liquid phase and deposit themselves into open crevices. This also results in more rounded, uniform grains, thus increasing the

Figure 1.5 The stages of sintering [15]
densification [17, 19]. This precipitation process can also result in a core-rim development in the final microstructure, which is a large focus of the current work [8, 2].

The final stage of liquid phase sintering is solid state sintering, which is the same as the later stages of solid state sintering. The pores shrink up, move to three grain junctions, and some grain growth occurs. This stage is much slower than the earlier stages & can exacerbate grain growth if not properly controlled.

1.6 Spark Plasma Sintering

One of the latest developments in the sintering field is a technique called spark plasma sintering. Spark plasma sintering is a technique that uses a large electrical current that passes through the sample via a conductive die. This results in faster and more efficient heating.

The actual mechanism is still not entirely understood and it’s unclear whether an actual plasma is generated. One of the more popular theories is that the pulsing current generates extremely high temperatures at the contacts between particles, creating a small local plasma. As this plasma discharges, it travels along intergrain pathways resulting in local temperatures in excess of thousands of degrees. This immense local heating is thought to lead to vaporization of impurities & surface material, and forming transient liquid phases. This efficient heating process leads to lower temperature and quicker sintering cycles than conventional methods [20, 21].
Others have studied spark plasma sintering of SiC, which sheds light on some of the optimal sintering cycles. Xu et al. spark plasma sintered SiC and noticed that it did not sinter well below 1600 °C, but they did observe rapid neck formation after sintering it at 1850 °C [22]. It is possible to sinter SiC without additives to greater than 92% dense [21], but the use of additives can result in even higher relative densities. Hojo was able to spark plasma sinter nano-SiC with the help of AlN and Y$_2$O$_3$ sintering aids. They were able to achieve very fine grained, dense microstructures via this method because the sintering aids hindered abnormal grain growth during sintering [23]. These additives were adopted by Mercurio et al. and verified that they resulted in fine grained, dense microstructures[2], which is why the additives were used in the current work.

Chapter 2: Experimental

2.1 Method of Attack

The scope of this work is to investigate the effects of the core-rim microstructure on material properties in spark plasma sintered SiC with AlN and Y$_2$O$_3$ additives because this knowledge could potentially be used to engineer intragranular energy absorption mechanisms due to stacking faults. In order to study
this core-rim structure, however, only two specific pathways were undertaken as stepping stones toward these goals.

The first path involved SiC powders of varying polytype compositions from a chunk of SiC, produced by carbothermic reaction. This was done because the SiC closest to the electrode would have purer SiC near the electrode, and therefore a different polytype composition than the parts further away.

These powders were co-precipitated, and then spark plasma sintered to create the samples. In order to characterize them, density & hardness was measured to verify the sinterability. Raman analysis was also performed to analyze the amounts of each polytypes present in the sintered samples.

The second pathway was to use SiC powder that was already known to sinter well and vary the amount of sintering additives, as well as the dwell time of the highest temperature in the sintering cycle. This allows us to see if any polytype transitions are occurring during the sintering cycle and/or AlN diffusing into the SiC grains.

These powders were also co-precipitated and spark plasma sintered, but for dwell times of 5, 10 and 15 minutes. The characterization consisted of density & hardness to verify they successfully densified, scanning electron microscopy to examine grain sizes & the extent of core-rim features, and x-ray diffraction to analyze the polytypes and other phases present.
2.2 Sample Powders

The samples produced by carbothermic reaction were made from a piece of SiC acquired from Washington Mills (Niagra Falls, NY). The samples were retrieved every 2”, starting from the electrode edge as depicted in Figure 2.1. The SiC was broken down with Fritsch Pulverisette® jaw crusher into a finer powder, around 1-10mm. Attrition milling was then used to further reduce particle size to ~10 micrometers in size. The last step to reduce the particle size was jet milling, which was achieved using Sturgevant Qualification Micronizer®. The particle size analyzer instrument used was a Mastersizer® unit by Malvern Instruments. The nomenclature used for these samples was “WM” followed by the numbered location the SiC was initially retrieved from as indicated in Figure 2.1.
Figure 2.1 Silicon carbide piece from a carbothermic reactor. The samples were collected from different zones as indicated by consecutive numbers in the direction of increasing distance from the electrode edge.

The samples for the dwell time study were made from H.C. Starck UF-25 silicon carbide powder (H.C. Starck GmbH, Goslar, Germany). This powder is a fine grained powder produced by the Acheson process. The manufacturer reported it consists primarily of the 6H polytype and has an average grain size of 0.45 microns. The nomenclature for these samples is indicated in Table 2.1.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>N3P-5</th>
<th>N3P-10</th>
<th>N3P-15</th>
<th>N4P-5</th>
<th>N4P-10</th>
<th>N4P-15</th>
<th>N1P-5</th>
<th>N1P-10</th>
<th>N1P-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.% of additives</td>
<td>3%</td>
<td>3%</td>
<td>3%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>10%</td>
<td>10%</td>
<td>10%</td>
</tr>
</tbody>
</table>
2.3 Co-precipitation

Both powders were processed using the same co-precipitation procedure. The coprecipitation procedure used has been proven to facilitate SiC densification during sintering [2]. Aluminum nitride and yttrium nitrate hexahydrate were used as co-precipitation agents. The amount of SiC, AlN, and Y(NO$_3$)$_3$ · 6H$_2$O was calculated to get a resulting composition of 5 wt.% AlN and Y$_2$O$_3$ additives, with a molar ratio of AlN : Y$_2$O$_3$ of 3 : 2. The calculated amount of SiC powder and AlN was measured out and placed into a 250 mL Nalgene bottle. Isopropanol was then added until a paint-like viscosity resulted. This slurry was then ball milled in the Nalgene bottle for 2 hours with 3/16” SiC milling media. After milling, the slurry was sieved, pan-dried, and the powder was put in a 100 °C oven overnight.

In order to start the co-precipitation, the powder was added to a beaker with isopropanol and mixed by propeller for roughly 1 hour before starting the co-precipitation. The Y(NO$_3$)$_3$ · 6H$_2$O was dissolved in isopropanol and added to one buret, while another buret was filled with ammonia hydroxide. A pH meter was submerged in the stirring solution to ensure the pH remained around 9.5 throughout the coprecipitation. This was found to be the optimal pH required for co-precipitation to occur [2]. In order to bring the pH to 9.5, Ammonia hydroxide...

| Dwell time (minutes) | 5 | 10 | 15 | 5 | 10 | 15 | 5 | 10 | 15 |
from the buret was added to the AlN & SiC solution. The yttrium solution was slowly added, and the pH of the solution was adjusted with ammonia hydroxide as needed. After all of the yttrium solution was added, it continued to mix for 2 hours, while maintaining a pH around 9.5.

Following this titration, the solution was allowed to settle and the organic layer was sucked off to remove most of the nitrates and organics. The slurry was washed with isopropanol, allowed to settle again and the organic layer was removed one more time before pan drying the powder and crushing with a mortar and pestle.

The powder was then further dried using a CM, Inc. tube furnace under an Argon gas atmosphere. The purpose of the tube furnace was to remove any residual organics from the coprecipitation process, and results in better sinterability [2]. The cycle used was as follows: furnace was ramped up to 500 °C at a rate of 180 °C per hour, dwelled at 500 °C for 1 hour, then cooled down to room temperature at a rate of 240 °C per hour.

2.4 Spark Plasma Sintering

After obtaining the dried co-precipitated powders, the samples were densified using a 10 ton SPS unit (Model 10-4, Thermal Technologies, Santa Rosa, CA). The powders were loaded into a graphite die by surrounding the inside of a 20 mm inner diameter die with a small sheet of graphite foil. A punch was added to the bottom of the die, & small circular sheets of graphite foil placed inside the die, on top of the punch. Then around 4-5 grams of SiC powder was
added, followed by another circular disk of graphite foil and the top punch. The purpose of adding the graphite foil is to prevent reaction & bonding with the graphite dies/punches. The die assembly was insulated with graphite felt with a small hole cut in it for the pyrometer.

The SPS unit used consisted of a movable hydraulic ram and a stationary ram at the bottom of the chamber. A graphite spacer was placed on top of the stationary ram, followed by a smaller spacer and then the die unit. The pyrometer was lined up accurately by rotating the die and/or adjusting the punches if needed. After alignment, symmetrical spacers were then placed on top of the die and the upper hydraulic ram was lowered into place. The pyrometer alignment was checked again to ensure the ram did not shift the die and realigned if necessary.

After loading the samples, the chamber was evacuated with a roughing pump to $10^{-2}$ Torr. A turbo pump was then turned on to achieve a vacuum of $10^{-4}$ to $10^{-5}$ Torr. At this point, the power system was activated.

The sintering cycle was programmed with a Eurotherm controller and software on a connected laptop. The cycles were as follows: The first segment ramped to 600 °C at 200 °C/min and to a hydraulic ramp pressure of 10 MPa at 6.6 MPa/min. The second segment dwelled at 600 °C and 10 MPa for 10 seconds. The third segment ramped to 1400 °C at 200 °C/min and to 50 MPa at 10 MPa/min. The fourth segment dwelled at 1400 °C and 50 MPa for 1 minute. The remaining of the cycle retained a hydraulic pressure of 50 MPa. The fifth segment ramped to 1900 °C at 200 °C/min and the final segment dwelled at 1900
°C for either 5, 10, 15, or 25 minutes depending on the sample. After dwelling at 1900 °C, the voltage was removed immediately to allow rapid cooling and the pressure was relieved to 5MPa. This final dwell time was the dwell time of interest for this study. This sintering cycle was inspired by previous work done on similar samples [2].

In order to remove the graphite foil, an Econoline sandblaster with #150 grit aluminum oxide blast media was used. The samples were sandblasted until no visible graphite remained.

2.5 Density

Density was measured by the Archimedes displacement method reference. Samples were cleaned off with acetone & allowed to dry. Five to ten measurements of dry and suspended weights were taken for each sample. Suspended weights were taken by suspending the sample in deionized water.

The theoretical densities were calculated using the weight percents of SiC, Y₂O₃, and AlN as expected from the initial calculations. This calculation assumes a complete reaction of nitrate precursors and ignores any effects from volatilization during the sintering process and any amounts of Silica (SiO₂) present in the powder.
2.6 Grinding, Cutting, Polishing

The samples were surface ground on a Dedtru surface grinder prior to polishing. The samples were then cut into small pieces (roughly 5 x 5 x 7 mm) using Leco VC-50 diamond blade saw. The surface ground side was placed face down into a Simplimet 1000 (Buehler, Lake Bluff, IL) and mounted into epoxy (Epomet F, Buehler, Lake Bluff, IL). The samples were then placed into a Buehler Ecomet 3000 autopolisher and polished on 125, 45, and 15 micron diamond embedded polishing pads. Polishing continued using 8, 6, 1, and 0.25 diamond slurries.

2.7 Hardness

Hardness measurements were made using a Knoop diamond indenter on a Leco hardness tester, model M-400-G-3. Hardness values were calculated using the length of the longer diagonal in microns. The value was then entered into the following equation to calculate the Knoop hardness:

\[ HK = \frac{P}{C_p L^2} \]

Where \( P \) is the load in kg, \( C_p \) is a shape correction factor, and \( L \) is the length in mm. The value of \( C_p \) is 0.070279 for standard Knoop indenters. Indents were made at loads of 1 and 2 kg, with 10 indents for each load.

2.8 Plasma Etching and SEM

Plasma etching was used to elucidate the grain boundaries for SEM characterization of the polished samples. A plasma etching system (SPI Plasma
Prep II, West Chester, PA) with a CF$_4$O$_2$:O$_2$ mixture (Air Liquide America Specialty Gases), ratio of 92 wt. % O$_2$ and 8wt. % O$_2$, was used to etch samples. The samples were etched for 60 to 80 minutes, depending on the sample.

Scanning electron microscopy was performed on the samples using a Zeiss Sigma FESEM (Carl Zeiss AG, Germany). Images were taken at a voltage of 2.5 to 3.0 eV, depending on where the minimal amount of charging was observed for the specific sample. Working distances were taken around 6 – 8.5 mm for the samples and the main imaging method used was to first focus using the SE2 lens, and then switching to the In-lens condition. The core-rim features of the grains are invisible if using the SE2 lens so all pictures for analysis were taken using the in-lens condition.

### 2.9 Grain Size Measurements, Extent of core-rim

Grain size measurements were calculated using a linear intercepts method with Lince Linear Intercept 2.4.2 β (© TU Darmstadt, FB Materialwissenschaft, FG NAW, Germany). Using Lince, a minimum of 6-7 lines originating & ending on a grain boundary were drawn across the images. The intersections of the line with grain boundaries and second phases were marked. From this information, the lengths of the secondary phases were subtracted out and average grain sizes were calculated from the lengths of the line segments.

The extent of the core-rim structure was measured in two ways. The first was simply counting the number of grains & total grains, in order to see what percentage of grains exhibited some type of core-rim structure. However, this
method may not be accurate due to different orientations of crystallographic planes among the grains. Therefore, the extent of the core-rim was also measured by looking at grains with a clear core-rim structure and measuring the ratio of the core area to rim area.

To measure the ratio of core to rim content in grains, ImageJ 1.45s (Wayne Rasband, National Institute of Health, USA) was utilized. For the grains showing core-rim features (10–30 grains per sample), ImageJ’s ‘polygonal sections’ tool was used to carefully outline the shape of the grain and its corresponding core. The areas were used to obtain a value for the percentage of core & rim within each grain.

2.10 X-Ray diffraction & Polytype composition

In order to gain insight into which polytypes are present and how they affect the development of the core-rim microstructure, X-ray diffraction was performed on the sintered & polished samples. The X-ray diffractometer used was a Phillips PANalytical X’Pert system. The samples were loaded into a bulk sample holder using sticky tack. Precautions were taken to ensure the sample was flat and parallel to top of the sample holder to avoid displacement errors.

All scans were run at a voltage of 40 kV and current of 45 mA. A quick preliminary scan on each sample was performed to determine the dwell time & step size that would give a sufficient intensity for quantitative analysis of the phases. Compositional analysis of the samples was performed using Jade software.
2.11 Raman

Raman spectroscopy was performed on the powders with varying grades of SiC (& hence varying amount of polytypes). A Renishaw InVia® unit equipped with a 633 nm wavelength laser and a 1200/mm diffraction grating was used. The laser beam was focused to a 4 micrometer area on the sample surface by using an x20 objective lens. The spectra were taken at both high and a reduced laser power to verify that there were not any foreign artifacts due to heating the sample. Spectra were also taken from 10 random points on each sample to obtain statistically significant results.

Chapter 3: Analysis and Results

3.1 Density & Hardness

3.1.1 Samples with Varying dwell times & Sintering additives

Density was calculated via Archimedes method as in the equation below:

\[
\text{Density} = \frac{\text{Dry Weight of sample}}{\text{Dry Weight–Submerged Weight}}
\]
A summary of the results is shown graphically in Figure 3.1 and Table 3.1 shows the actual values.

**Figure 3.1** Density of the SiC with varying amounts of additive composition and sintering dwell time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N1P</th>
<th>N4P</th>
<th>N3P</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min</td>
<td>3.291</td>
<td>3.256</td>
<td>3.213</td>
</tr>
<tr>
<td>10 min</td>
<td>3.287</td>
<td>3.243</td>
<td>3.222</td>
</tr>
<tr>
<td>15 min</td>
<td>3.270</td>
<td>3.137</td>
<td>3.219</td>
</tr>
</tbody>
</table>

**Table 3.1** Densities (g / mL) of Spark plasma SiC for 5, 10, and 15 minutes dwell time and 10, 5, and 3 wt. % additives (N1P, N4P, N3P respectively).
The densities generally decrease with longer dwell times, except for N3P, which does not seem to varying significantly, possibly because the small amount of additives was too little to see any differences in density measurements, which could be due to grains eventually engulfing other grains, creating an inhomogeneous grain structure and therefore resulting in lower densities.

The samples with more additives also generally have higher densities, which verify that the co-precipitation procedure enhances densification. The only exception is N4P- 15 minutes, which had a drastically smaller density. Thus far repeated trials yielded similar results, but it is possible that the powder being used was faulty and should be remade from scratch to verify whether this value is correct.

Knoop hardness values of the samples are displayed in Figure 3.2 with the varying additive compositions and dwell times:
Figure 3.2  Hardness values of Spark Plasma Sintered SiC with varying dwell times, and compositions.

The sample with 10 wt. % additives (N1P) shows a clear trend of hardness increasing with dwell time, which is counterintuitive since the density decreased with dwell time. However, the density changes were very small and close to each other, meaning the differences in density are more likely to not be statistically significant, depending on the accuracy of the method used. The 5 wt. % (N4) and 3 wt. % sample (N3P) hardness decreases in the 10 minute sample but more samples should be done to verify whether there’s simply a lot of variation in the methodology or if the hardness actually goes through a minimum around 10 minutes. Most likely the variation is due to the various sources of variation adding up in the processing procedures, such as the ball milling, co-precipitation process, sintering, sandblasting, the localized region chosen for hardness testing, etc. Overall, the hardness values appear to increase with longer dwell times. If the small amount of additives in N3P accounts for insignificant differences for different dwell time, then this would explain why we don’t see a clear hardness increase for this sample.

3.1.2 Samples with varying polytype composition

The density and hardness values of the samples with varying polytype compositions are presented graphically in Figure 3.3 and the actual values are presented in Table 3.2:
Figure 3.3 Density and Hardness values of SiC samples with varying polytype compositions.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Density (g/cc)</th>
<th>Relative density (%(\rho_{th}))</th>
<th>Knoop hardness (kgf/mm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>2</td>
<td>3.10</td>
<td>94.4</td>
<td>1045 ± 80</td>
</tr>
<tr>
<td>3</td>
<td>2.06</td>
<td>93.1</td>
<td>1059 ± 79</td>
</tr>
<tr>
<td>4</td>
<td>3.12</td>
<td>95.7</td>
<td>1067 ± 120</td>
</tr>
<tr>
<td>5</td>
<td>3.14</td>
<td>95.7</td>
<td>1267 ± 127</td>
</tr>
<tr>
<td>6</td>
<td>3.31</td>
<td>1.01</td>
<td>1591 ± 47</td>
</tr>
<tr>
<td>7</td>
<td>3.16</td>
<td>96.4</td>
<td>1247 ± 65</td>
</tr>
</tbody>
</table>
Table 3.2  Density and Hardness of samples from powders with varying polytype compositions.

<table>
<thead>
<tr>
<th></th>
<th>Density</th>
<th>Hardness</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>9</td>
<td>3.21</td>
<td>97.8</td>
<td>1401 ± 36</td>
</tr>
<tr>
<td>10</td>
<td>3.10</td>
<td>94.5</td>
<td>1003 ± 83</td>
</tr>
<tr>
<td>11</td>
<td>3.17</td>
<td>94.5</td>
<td>1273 ± 44</td>
</tr>
</tbody>
</table>

The theoretical density of the samples produced using the co-precipitation procedure was assumed to be 3.28 g/cc. However this value does not take into account glass formation, assumes a complete coprecipitation reaction, ignores volatilization effects, nor takes into account free carbon or silicon that might be present in the starting powders (as will be discussed in the Raman analysis). As follows from the data shown in Table 3.2, the density of the majority of the sintered samples is significantly lower than the theoretical density, indicating that the co-precipitation procedure was unable to fully densify these samples. To evaluate the mechanical properties of the sintered samples, Knoop hardness measurements at 1 kgf were carried out, and the results are also reported in Table 3.2. This data and optical images (not shown) suggest that the hardness of the samples was determined primarily by the degree of densification for a particular specimen. The correlation between density and Knoop hardness (lower density → lower hardness) of the samples sintered using the co-precipitation procedure is also evident on examination of the data shown in Fig.3.3.
3.2 SEM analysis

FESEM images of the samples are shown in Figures 3.4. Results from the grain size analysis & extent of the core-rim are presented in Table 3.3, and Figures 3.5 to 3.7. FESEM images of the samples with varying polytypes were not taken since they were not fully densified.
Figure 3.4 In-lens FESEM images of the samples with varying dwell times and compositions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain Size (microns)</th>
<th>Percent of core (%)</th>
<th>Grains exhibiting core-rim features (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3P-5</td>
<td>0.589±0.09</td>
<td>31.7±7.5</td>
<td>26.4±2.8</td>
</tr>
<tr>
<td>N3P-10</td>
<td>0.684±0.17</td>
<td>24.8±10.6</td>
<td>11.5±3.93</td>
</tr>
<tr>
<td>N3P-15</td>
<td>0.649±0.29</td>
<td>32.6±7.8</td>
<td>11.5±4.01</td>
</tr>
<tr>
<td>N4P-5</td>
<td>0.801±0.19</td>
<td>18.0±5.8</td>
<td>15.2±3.81</td>
</tr>
<tr>
<td>N4P-10</td>
<td>0.621±0.15</td>
<td>39.5±9.2</td>
<td>24.4±4.75</td>
</tr>
<tr>
<td>N4P-15</td>
<td>2.914±0.46</td>
<td>12.5±35.8</td>
<td>4.4*</td>
</tr>
<tr>
<td>N1P-5</td>
<td>47.474±11.53</td>
<td>31.7±9.7</td>
<td>30*</td>
</tr>
<tr>
<td>N1P-10</td>
<td>56.626±16.77</td>
<td>10.9±27.1</td>
<td>1.1*</td>
</tr>
<tr>
<td>N1P-15</td>
<td>72.952±44.18</td>
<td>17.7±2.3</td>
<td>16.9*</td>
</tr>
</tbody>
</table>
Table 3.3 Summary of Grain Sizes, percentage of core area within an average grain, and the percent of grains that showed a clear core rim structure. *Values without error limits were not calculated due to insufficient information.

Figure 3.5 Grain sizes of samples with carrying dwell times & composition. Variance of N1P omitted since the large variation would fail to show any significant trends.
Figure 3.6 Percent of the core area within the average grain that exhibits a core-rim structure.
Figure 3.7 Percent of grains that exhibited a clear core-rim structure in the FESEM images.

The grain size analysis (Figure 3.5) shows that N3P has no significant change in grain size as consistent with the density results, corroborating the idea that there is too little additive to see any significant changes with dwell time from diffusional processes of the additives. N1P is not shown in Figure 3.5 because the error bars were so large that we cannot confidently say the samples were any different from each other. The one point worth mentioning is that the N4P-15 minute sample shows a much larger grain size. This is reasonable because as the sintering time increases, the chance of grains engulfing other grains becomes more likely. Again, further replication is needed to reduce the variation among samples. If the variation is still large, then the processing techniques
should be refined so that they are consistently replicable and independent of the person following them.

There are no definitive trends with how the dwell time affected the extent of core-rim. A 95% confidence interval was used for estimates of the error, and there is insufficient data to show that there is any significant difference between different sintering dwell times. The only exception is that the N3P-5 minute sample shows a greater percentage of grains with a core-rim structure than the 10 & 15 minute samples. Since the 10 & 15 minute samples are very similar, this might be an indication of a diffusion process settling down somewhere between 5 and 10 minutes. This reduction in the % of grains exhibiting core-rim could be because of minor grain growth, but none was observed in the SEM images. This is also merely based on the difference between N3P-5 min, and N3P-10 min. Therefore, it is crucial to replicate the values to ascertain the validity of whether diffusional processes are ceasing and maintaining some sort of equilibrium.

The percent of core within the core-rim grains varies too much to provide any appreciable difference among samples. One possibility is that there is much longer range variation throughout the sample than representative in the SEM picture chosen for analysis. Therefore, some insight may be gained from averaging over multiple representative FESEM images throughout the sample. While not expected, there is also the chance that the dwell times chosen are so close that there is not any difference between samples and longer increments may be necessary.
3.3 X-Ray Diffraction and Polytype Composition

X-Ray diffraction (XRD) was used to get a very rough estimate of the predominant polytypes and phases present in the samples. XRD patterns of the nine samples, with varying dwell times are shown in Figures 3.8 to 3.16:
Figure 3.8 XRD pattern and dominant phases for N3P samples with 5 minute dwell time.
Figure 3.9 XRD pattern and dominant phases for N3P samples with 10 minute dwell time.
Figure 3.10 XRD pattern and dominant phases for N3P samples with 15 minute dwell time.
Figure 3.11 XRD pattern and dominant phases for N4P samples with 5 minute dwell time.
Figure 3.12 XRD pattern and dominant phases for N4P samples with 10 minute dwell time.
Figure 3.13 XRD pattern and dominant phases for N4P samples with 15 minute dwell time.
Figure 3.14 XRD pattern and dominant phases for N1P samples with 5 minute dwell time.
Figure 3.15 XRD pattern and dominant phases for N1P samples with 10 minute dwell time.
Figure 3.16 XRD pattern and dominant phases for N1P samples with 15 minute dwell time.

The XRD patterns show that the majority of the phases were the 6H phase of SiC, and in most samples, the 4H phase was found, but in relatively smaller amounts. The transition between 6H and 4H does not seem to have any distinct trends, due to the having such small amounts of 4H and the limitations of the XRD unit used on these samples.
As expected, the AlN additive was found in the XRD pattern in small amounts, compared to the SiC. This verifies that the additives are indeed in the samples. The amount of $Y_2O_3$ was not detected because the mount was too little. There was also a quartz phase identified, which is likely a native oxidized layer from the starting powder. One method to remove this SiO$_2$ layer would be to wash it with HF and quantify the amount through precise oxygen analysis during the sintering cycle. However, these techniques were not available at the time of the study. Doing so may not dramatically improve mechanical properties, but would still be likely to improve the final sample after sintering.

### 3.4 Raman Analysis of varying polytype samples

Raman analysis of SiC polytypes was based on the methodology developed by L. Patrick et al. [24-27]. In the Raman spectra of SiC, the bands at 200 cm$^{-1}$, 610 cm$^{-1}$, and 837 cm$^{-1}$ are unique to the 4H polytype, the bands at 147 cm$^{-1}$, 238 cm$^{-1}$, 506 cm$^{-1}$, and 886 cm$^{-1}$ are unique to the 6H polytype, the bands at 170 cm$^{-1}$, 255 cm$^{-1}$, 334 cm$^{-1}$, 573 cm$^{-1}$, and 858 cm$^{-1}$ are unique to the 15R polytype, the bands at 132 cm$^{-1}$, 219 cm$^{-1}$, 453 cm$^{-1}$, 592 cm$^{-1}$, and 908 cm$^{-1}$ are unique to the 21R polytype, and the bands at 84 cm$^{-1}$, 305 cm$^{-1}$, 433 cm$^{-1}$, 537 cm$^{-1}$, 598 cm$^{-1}$, 875 cm$^{-1}$, and 958 cm$^{-1}$ are unique to the 33R polytype. At the same time, the bands in the range of 238-264 cm$^{-1}$, 766-791 cm$^{-1}$, and the bands at 977 cm$^{-1}$ may belong to any of 3C, 2H, 4H, 6H, 15R, 21R, or 33R polytypes.
and therefore only allow identification of silicon carbide without providing exact information on its polytype structure.

In addition to various SiC polytypes, free silicon (a single narrow band at 520 cm\(^{-1}\) [28]) and graphitic carbon (the \(D\) band at \(~1330\) cm\(^{-1}\) and the \(G\) band at \(~1580\) cm\(^{-1}\) [29]) were identified in selected samples by Raman spectroscopy. A summary of the results is shown in Figure 3.17.

**Figure 3.17.** Distribution of selected SiC polytypes and graphitic carbon in SiC samples sintered using a coprecipitation procedure. Analysis is based on the number of observation of Raman bands pertaining to a particular SiC polytype/graphitic carbon.
The results indicate more relative 6H SiC closer to the electrode, and roughly more free carbon and 4H SiC further away from the electrode. The results indicate that the polytype compositions are indeed different among samples and therefore applicable to the present study if successfully densified. For samples 2, 6, 8, 12, and 16 inches from the electrode, there is an increase in density. And because the samples further from the electrode have more 4H & 15R SiC, the highest densities tend to have more 4H and/or 15R SiC present.

Chapter 4: Conclusions

SiC samples were made via a co-precipitation process and spark plasma sintering to examine the core-rim microstructure by altering the sintering time, additive amounts, and polytype composition.

For the samples where the dwell time was varied, the density appeared to decrease with longer dwell times, but this decrease was very small and likely insignificant due to the fact that hardness values increased with longer dwell times more significantly. One exception was with the 3 wt. % sample, which did not show any significant differences in density nor other properties measured. This is likely because having such a small amount of additives resulting in failing to detect any small differences, which was also observed in the FESEM analysis. The FESEM analysis showed a lot of variation in the results, but indicated that the number of grains with a core rim feature decreased as the dwell time
increased. However, this is based on only the 3 wt. % sample from 5 min to 10 min. The XRD results clearly showed that the dominant phase in the samples was 6H SiC, but also consisted of 4H SiC, AlN, and SiO$_2$.

For the samples with varying polytypes, there was trouble in fully densifying the powders so most tests were not carried out. Their low densities correlated with poor hardness values, and the Raman analysis indicated free carbon in some samples. The purer samples, closer to the electrode used during production, had a higher content of 6H-SiC and generally had more 4H-SiC, 15R-SiC, and free carbon further away from the electrode.

**Chapter 5: Future Work**

For future work, identical powders should be replicated from scratch, the characterization tests repeated and averaged multiple times in order to ensure statistical validity of results. If a large variation still exists between identical powders, further work into creating a more robust processing method should be carried out. Also, adding more samples with wider spaced sintering dwell times would also help see any clear trends in characterizing the extent of core-rim microstructure.

A high resolution Transmission Electron Microscope (TEM) would also be greatly helpful in characterizing the polytypes present in samples. The TEM would shed light
onto possible variations in the crystal structure and how it changes with different sintering dwell times, amount of additives, and polytype composition.

And lastly, to quantify eliminate the SiO$_2$, washing the starting powders with HF would be helpful. Depending on how successful this method is, monitoring the oxygen content during sintering may also help so the amount of oxygen can be quantified and factored into the theoretical density calculations.
References

7. M. H. Hong, A. V. Samant, P. Pirouz. Stacking fault energy of 6H-SiC and 4H-SiC single crystals, Philosophical Magazine A, 2000 Vol. 80, Iss. 4


