QUANTIFYING AMORPHOUS CONTENT
OF COMMERCIALY AVAILABLE SILICON CARBIDE FIBERS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Ian Mark Wolford ENTITLED Quantifying Amorphous Content of Commercially Available Silicon Carbide Fibers BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Materials Science and Engineering.

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SiC/SiC ceramic matrix composites (CMCs) with potential applications at ≥2700°F (1482°C) are of significant interest to the Air Force. The high temperature performance of SiC fibers used within these composites is greatly affected by the presence of amorphous SiOC and free carbon in the fibers. Therefore quantification of this non-SiC material in commercially available SiC fibers is extremely important. In this work Hi Nicalon, Hi-Nicalon Type-S, Tyranno-SA3, Cef-NITE, and Sylramic SiC fibers were studied. Changes in mass, grain size, and amorphous content were measured as a function of processing temperature and time. The amorphous material in each fiber was quantified using the Spike-In method in conjunction with Rietveld refinement. Trends in amorphous content were observed, as well as trends in grain size and crystallized fraction. Transmission electron microscopy (TEM) was used to confirm changes in fiber microstructure.
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1 Introduction

1.1 Motivation

Silicon carbide (SiC) is recognized as an important structural ceramic due to its special combination of properties; exceptional oxidation resistance, retention of tensile strength at high temperatures, creep resistance, wear resistance, plus high thermal conductivity and thermal shock resistance. [1] AFRL’s Aerospace Systems Directorate has outlined next generation turbine engine performance goals that require an operating temperature where hot-section component temperatures will reach in excess of 1482°C (2700°F). Ceramics make an ideal choice for high temperature application due to their refractory properties, but suffer from brittle fracture when used in monolithic form. Adding a ceramic fiber to a bulk matrix material improves fracture performance by forming a composite, particularly when the interface between fiber and matrix is weak. Ceramic composites composed of SiC fiber and SiC matrix are a prime candidate for these temperatures, but efforts so far have been limited by SiC fiber creep performance. The current generation of commercially available fibers do not meet requirements for use in the desired temperature application range. As a result, there is an interest in enhancing the performance of commercially available fibers using various heat treatments and developing more rapid and improved characterization techniques.
Improved high temperature SiCf/SiC composite performance depends on microstructural features that affect creep. DiCarlo has outlined the properties that should lead to better fibers; stating that a higher performing fiber should be thermally stable, contain a stoichiometric one-to-one carbon-to-silicon ratio, have an average grain size near 400 nm to maximize creep resistance while retaining acceptable strength, and exhibit high crystallinity and therefore very low amorphous content. [2] While commercially produced silicon carbide fibers claim to be thermally stable, highly crystalline, nearly stoichiometric, and fine-grained; verification of these properties is prudent, particularly from a quality assurance perspective. Characterization methods that allow for quick and accurate quantification of these properties is therefore desirable from a manufacturing perspective to verify batch to batch consistency.

In order to understand changes in SiC fiber microstructure and composition, earlier research has used elemental analysis [3-5], transmission electron microscopy (TEM) imaging [6], and X-ray diffraction (XRD). [7, 8] Characterization methods such as energy dispersive X-ray spectroscopy (EDS), wavelength dispersive X-ray spectroscopy (WDS), and X-ray photoelectron spectroscopy (XPS) are generally used for elemental analysis. The change in oxygen content in SiC fiber, as measured by EDS, WDS and XPS, has been used as a surrogate for the change in amorphous SiO$_x$Cy content. There are several flaws to elemental analysis using this assumption. CO$_{(g)}$ and SiO$_{(g)}$ both volatilize preferentially from this phase during heat treatment, although at differing rates [9]. Figure 1 [10] shows a phase diagram of the thermodynamically stable solid phases present in the Si-O-C system: SiC, SiO$_2$, Si, and C; as well as the gaseous phases: O, CO, CO$_2$ and SiO. This diagram also includes the SiO$_x$Cy glassy phase known
to form during formation and processing of preceramic-polymer derived SiC. The three color arrows indicate changes in composition based on high temperature volatilization of; CO\(_{(g)}\), shown in red; SiO\(_{(g)}\), shown in blue; and the gray arrow shows where the loss of CO\(_{(g)}\) equals the loss of SiO\(_{(g)}\). This graphically illustrates that oxygen depletion from this SiO\(_x\)C\(_y\) phase does not necessarily leave behind stoichiometric SiC. Assigning oxygen loss as a proxy for amorphous content does not account for the presence of amorphous free carbon or other potential amorphous materials. Given the surface sensitive nature of XPS, a native oxide layer would tend to yield an overestimation of amorphous content using this method. [11] According to Key et al, “TEM can confirm the presence of an amorphous phase; but, it may not interrogate a statistically significant portion of the sample or reliably allow quantification due to through thickness overlap of amorphous and crystalline material.” [12] Conventional powder XRD analysis has been used for grain size analysis [7, 8] but using this approach is problematic for observing amorphous
content in silicon carbide fiber XRD patterns. The structure of the amorphous content in SiC fibers does not generate an identifiable peak. Intensity generated by the amorphous content in SiC fibers only has a small contribution to the overall intensity in the XRD pattern and is therefore difficult to separate from the background [12].

The goal of this study is to characterize the amorphous content and grain size of commercially available silicon carbide fibers in both their as-received (factory produced) condition and after experiencing heat treatments between 1400-2000°C. The quantification of this amorphous content will occur in two stages: validation of the XRD-pattern based Spike-In technique with Rietveld refinement, using a powder system analogous to SiC fiber; followed by the application of the Spike-In approach to SiC fibers. [13, 14] Using the Scherrer equation and Williamson-Hall plots, XRD patterns will then be used to calculate grain size for as-received fibers as well as heat treated fibers. [7, 8] Since previous work has used electron microscopy to verify the presence of amorphous material in SiC fibers, SEM & TEM imaging will be used to qualitatively confirm the results of the XRD analysis. [15] Additionally, assuming the amorphous material is primarily a combination of SiOx Cy and free carbon, a decrease in amorphous content and a corresponding increase in crystallinity should be accompanied by a mass loss among the heat treated fibers. [9]

1.2 Silicon Carbide

Stoichiometric silicon carbide consists of one silicon and one carbon per unit compound. The nucleation and crystallization of SiC during processing is not straightforward and SiC is known to occur in over 100 known polytypes. [16] This variety arises from the low energy differences between polytypes, as discussed by Käckell, “The
differences in the cohesive energies of different polytypes are smaller than the thermal energies at reasonable crystal-growth conditions. Hence, nonequilibrium effects related to the details of the growth and effects of the vibrating lattice are expected to be of major importance.” [17] These polytypes occur in three major crystal systems; cubic (C), hexagonal (H), and rhombohedral (R). The two most common forms of bulk SiC are cubic (3C) β-SiC and hexagonal (6H) α-SiC, as shown in the sketch in Figure 2, but SiC is also known to occur as 2H, 4H, 8H, 10H, 15R, 39H, 39R and higher stacking varieties. The cubic β-SiC exhibits the zinc-blende structure with sp3 hybridized tetrahedrons occurring in the same pattern as diamond crystal structure. This tetrahedron structure can also be seen in each type of hexagonal SiC. [1] The difference between a + and – hexagonal stacking layer (Figure 2) is denoted by a 180° rotation of that layer’s tetrahedrons about the z-axis. Changes in the stacking sequence of these tetrahedrons give rise to the other hexagonal polytypes; 2H, 4H etc. Using the nomenclature of Figure 2, 2H and 4H would be simplifications of 6H; 2H would be A+, A- stacking; 4H would be A+, B+, A-, B- stacking. Higher order hexagonal polytypes would continue a similar pattern. To explain of the large number of known polytypes, N. W. Jepps of Cambridge
University makes the following assertion, “The possibility for polytypism arises through variants in the stacking of these layers with endless permutations of stacking sequences theoretically possible.” [18]

The 3C and 6H SiC polytypes are of primary concern in this study, but it is important to understand the complexity of the silicon carbide system, particularly when characterizing heat treated SiC. The thermodynamically stable phase is temperature dependent; (3C) $\beta$-SiC is stable up to $\sim$1700°C where (6H) $\alpha$-SiC becomes the stable phase. SiC crystals that begin as $\beta$-SiC will begin taking on stacking characteristics that resemble $\alpha$-SiC at or above 1700°C. The high temperature manifestation of these polytype permutations is intragranular short-range stacking faults which perturb long range order for certain crystallographic directions. This will be challenging for X-ray diffraction analysis, as discussed in later sections.

2 XRD Based Amorphous Quantification

2.1 Introduction

Quantification of amorphous content can be divided into two categories, direct and indirect. Both use X-ray diffraction to quantify amorphous content. The direct method relies on the ability to accurately assess contribution of both the crystalline and amorphous phases to the diffraction pattern. The indirect method only uses the crystalline phases, however, it requires a specific amount of a known crystalline standard to be added. Both rely on phase quantification, whether by Reference-Intensity-Ratio (RIR) or Rietveld, and obtaining the required confidence in assessment is the issue.
2.1.1 Amorphous and Crystalline Phases

The formulae for calculating a phase’s intensity in an X-ray diffraction pattern require a description of the structure. The incident beam is composed of copper generated X-rays (for the devices used in this work) and the diffracted X-ray beam is composed of the sum of the X-rays coherently scattered by the sample material. The position of peaks in a diffraction pattern is fairly straightforward and is a function of incident wavelength, d-spacing in a crystal lattice, and inclination angle as described by the Bragg equation, below in equation 1. [19] The geometry for this coherent scattering is illustrated in Figure 3, where electron clouds responsible for scattering are shown in green and photon vectors are shown in orange.

\[ n\lambda = 2ds\sin(\theta) \]  \[1\]

Figure 3 – Bragg’s Law showing constructive interference of photons
Figure credit: Rice University.

However, peak intensity is not as straightforward as peak position. Peak intensity depends on many variables, but more importantly for amorphous content calculation, it is directly proportional to the square of the structure factor, or \( F(hkl)^2 \), shown in equation 2.
\[ I_{hk\ell} = \left( \frac{1}{32\pi^2} \right) \left( \frac{e^4}{m^2} \frac{\hbar}{4\pi} \right)^2 \left( \frac{1}{v^2} \right) \left| F(hk\ell) \right|^2 p \left( \frac{1 + \cos^2(\theta)}{\sin^2(\theta) \cos(\theta)} \right) \left( e^{-2M} \right) \]  \quad [2]

The structure factor “F” depends directly on the scattering factor “f”, which is defined as the efficiency of scattering; \((|\text{wave}/\text{atom}|)/(|\text{wave}/\text{electron}|)\). Mathematically in forward scattering, this is simply atomic number \(Z\), but will decrease with \(\sin(\theta)/\lambda\). \(F^2 = f^2\) for the single element, simple cubic case. But as crystal structure increases in complexity so does the structure factor. Shown here is the structure factor for zinc-blende cubic 3C silicon carbide, where there is a separate scattering factor for each atom type. \([19]\)

\[ F^2 = 16(f_{\text{Si}} \pm f_{\text{C}})^2 \]  \quad [3]

Any deviation from zinc-blende would create a more complex structure factor. When considering an amorphous structure with no long range order, as in SiO\(_x\)C\(_y\), the structure factor cannot be defined. The compositional gradient of the amorphous phases further complicates the problem; where this variation in composition, specifically SiO\(_x\)C\(_y\), covers an area (rather than a point) in the ternary diagram in Figure 1. This glassy phase has a disordered structure, particularly when intimately mixed with excess carbon and nanosized silicon carbide, as shown in Figure 4. This disordered structure will affect scattering and diffraction which in turn will affect the background and peak intensities. \([20]\)

Structural definition files (cif or .pdf) for input into software for phase fraction refinement are required for direct quantification of each amorphous phase. Lutterotti was able to define amorphous silica in a way that allowed for direct quantification \([21]\) but with only a single amorphous phase present. The structural description of phases present in a sample is critically important to quantification using the Spike-In technique, described below, but phase description files of the complex structures in SiC fiber.
amorphous phases are either not available, not accurate, or too complex to attempt to define in the scope of this work for the phases being studied. This is due to difficulty in correctly describing the amorphous phases (free carbon, SiOxCy, amorphous SiC, etc.), since structure files cannot be used to quantify the amorphous content as a discrete phase, an alternative method must be used. There are two methods available for this task, direct and indirect detection. The direct method relies on the ability to see the intensity contribution to a diffraction pattern generated by an amorphous phase. [21] The indirect method relies on the addition of an external standard and calculates the amorphous fraction by difference. Quantification of amorphous content using the direct method can be difficult for several reasons. Broad amorphous peaks can be difficult to observe, particularly if the amount of amorphous fraction is small, which is true in SiC fibers. In materials where more than one amorphous peak occurs, broad peaks can result in increasing peak overlap. Therefore, it is often difficult to clearly discern low, broad
amorphous peaks and their associated tails from the pattern’s background intensity. So it is not practical to measure amorphous material directly as a constituent of a larger crystalline phase to the accuracy required for this study, ideally to an accuracy of +/-1%. In this study, an indirect technique, where the sample is spiked with a known amount of an external standard, was used to quantify amorphous content. [22]

2.1.2 Phase quantification methods

2.1.2.1 Spike-In

The Spike-In technique is a tool for quantifying the amorphous fraction of a given powder sample by comparing the crystalline phase fractions present. There are several steps to the process, beginning with combining a known mass of Spike-In powder to a known mass of sample powder. An X-ray diffractometer is then used to collect a diffraction pattern. The resulting pattern is used to quantify the crystalline phases present. Knowing the initial masses of the starting powders, the amount of amorphous content present can be calculated as shown in the following equations (Eqn. 4-8). These equations were used to assess a model powder system designed as a proof of concept of the Spike-In technique for use with SiC fibers. The crystalline phases were the alumina (Al₂O₃) spike-in agent and the silicon carbide (SiC) component of the sample. The goal is to compare the mass fractions of sample and alumina to the XRD based crystalline phase fractions to calculate the amorphous fraction. [12, 14, 22]

Equation 4 shows the simple relation between total sample weight and constituent alumina powder and SiC experimental powder weights, where the experimental powder is known to contain amorphous content. The Spike-In powder (Al₂O₃) was assumed here
to be purely crystalline. To account for the presence of amorphous material, the experimental powder (SiC + Amorphous) is not assumed to be purely crystalline.

\[
100 \text{wt\%} = \text{Al}_2\text{O}_3{}^{\text{mass}} \text{wt\%} + (\text{SiC}_{\text{Crystaline}} + \text{Amorphous})^{\text{mass}} \text{wt\%} \tag{4}
\]

The only crystalline signal seen by XRD in the experimental powder is from the SiC, labelled SiC\(_{\text{XRD}}\) below. To allow for the possibility that the SiC is either 100\% or 0\% crystalline, a correction ratio on the SiC\(_{\text{XRD}}\) term is necessary, which compares known weight fraction of alumina to the experimental (XRD based) alumina phase fraction.

Equation 5 has been solved for the unknown, amorphous content (wt\%).

\[
(\text{Amorph.}) \text{wt\%} = 100 \text{wt\%} - \left(\frac{\text{Al}_2\text{O}_3{}^{\text{mass}} \text{wt\%}}{\text{Al}_2\text{O}_3{}^{\text{XRD}} \text{wt\%}} \right) \frac{(\text{SiC}_{\text{XRD}} \text{wt\%})}{100 \text{wt\%} - \text{wt\%(Amorph.)}} \tag{5}
\]

If amorphous content is present in the sample, the integrated intensity of the SiC peaks will be reduced, compared to a purely crystalline SiC sample. This reduced intensity of the SiC phase will change the reported relative phase fractions in a spiked sample, such that the SiC\(_{\text{XRD}}\) term decreases relative to an increased Al\(_2\)O\(_3\)\(_{\text{XRD}}\) term. This causes a reduction in the Al\(_2\)O\(_3\)\(_{\text{mass}}\)/Al\(_2\)O\(_3\)\(_{\text{XRD}}\) ratio, which will in turn create a positive value for the amorphous content term. In this binary system, containing only two crystalline phases, the crystalline phase fractions will be consistent with equation 6:

\[
100 \text{ wt\%}_{\text{XRD}} = \text{SiC}_{\text{XRD}} \text{ wt\%} + \text{Al}_2\text{O}_3{}_{\text{XRD}} \text{ wt\%} \rightarrow \text{SiC}_{\text{XRD}} = 1 - \text{Al}_2\text{O}_3{}_{\text{XRD}} \tag{6}
\]

The relation in equation 6 can be substituted into equation 5, yielding equation 7:

\[
(\text{Amorph.}) \text{wt\%} = 100 \text{wt\%} - \left(\frac{\text{Al}_2\text{O}_3{}^{\text{mass}} \text{wt\%}}{\text{Al}_2\text{O}_3{}^{\text{XRD}} \text{wt\%}} \right) \frac{(\text{SiC}_{\text{XRD}} \text{wt\%})}{100 \text{wt\%} - (\text{Al}_2\text{O}_3{}_{\text{XRD}} \text{wt\%})} \tag{7}
\]

Equation 7 can then be simplified to equation 8:

\[
(\text{Amorph.}) \text{wt\%} = 100 \text{wt\%} - \frac{(\text{Al}_2\text{O}_3{}^{\text{mass}} \text{wt\%})}{\text{Al}_2\text{O}_3{}^{\text{XRD}} \text{wt\%}} \tag{8}
\]
Accurately calculating the crystalline phase fractions becomes extremely important for determining amorphous content. Two methods of acquiring crystalline phase fractions from XRD diffraction patterns were considered; Reference-Intensity-Ratio (RIR) [19] and Rietveld refinement [23].

2.1.2.2 RIR

The RIR method relates the XRD peak intensity \( I_i \) for the highest peak of a random polycrystalline sample material to the highest peak for a random polycrystalline sample of alumina (corundum). The constant \( K \) relates the ratio of the weight concentrations \( X_i \) of sample and corundum to the intensity ratio as shown in equation 9.

\[
\frac{I_{\text{sample}}}{I_{\text{corundum}}} = K \frac{X_s}{X_c} \tag{9}
\]

In the current Powder Diffraction File crystallography database (PDF-4, 2015), there are experimental values of \( K \) for thousands of sample materials. These database values are based on a 50/50 (wt\%) mixture ratio of sample material to corundum, thereby forcing \( X_s/X_c \) to 1, leading to equation 10:

\[
\frac{I_{\text{sample}}}{I_{\text{corundum}}} = \frac{I_s}{I_c} = K \tag{10}
\]

Using experimental peak areas and these \( K \) values, software tools can interface to the PDF database and generate phase fractions of mixtures as in equation 11.

\[
\frac{I_{\text{Phase 1}}}{I_{\text{Phase 2}}} = \frac{(I/I_c)_{\text{Phase 1}}}{(I/I_c)_{\text{Phase 2}}} \times \frac{X_{\text{Phase 1}}}{X_{\text{Phase 2}}} \tag{11}
\]

Given the broad availability of these database values, this PDF-based RIR method appears to be a quick and easy way to obtain phase fraction data from a powder mixture.
However, there are several potential sources of inaccuracy using the RIR method: using only the most intense peaks which may be low angle and more subject to z-displacement effects [24]; various levels of quality to PDF values; peak overlap; asymmetric broadening due to faulting; complicated background subtraction; using the XRD peak heights rather than integrated intensity, where grain size broadening affects peak heights. The quickest form of RIR, which relies on peak heights and database K-values, must be disregarded to minimize these inaccuracies. Progressively more complex adaptations of the RIR method incrementally add functionality to the peak comparison model, but only approach the fidelity of the second method considered for this study, the Rietveld refinement.

2.1.2.3 Rietveld

In principle, Rietveld refinement determines phase fractions in a manner analogous to the RIR method, in that it compares the relative intensity from two phases to calculate phase fractions. However, Rietveld also accounts for multiple peaks, overall peak shape, broadening effects, background and instrumental effects. More broadly, the Rietveld refinement method analyzes the entire integrated intensity, or area under an XRD pattern, providing a more robust assessment of intensity. The Rietveld refinement process uses crystal phase models and an instrument model to calculate a simulated XRD pattern. Rietveld software mathematically iterates and refines a variety of selected material parameters until a fit to the XRD experimental data pattern is made, as shown in Figure 5. The parameters that are refined during the Rietveld refinement process are directly correlated to features on the experimental XRD pattern; crystal lattice parameters
give rise to peak position; atomic parameters give rise to peak intensity; and size and strain components give rise to peak width and broadening. [19]

Figure 5 – Rietveld Refinement

Given that the Rietveld method accounts for the entire XRD pattern area, the overall precision and accuracy is higher than the RIR methods described above. There are some drawbacks to the technique. Rietveld is best used for highly crystalline samples; if the amorphous content is too high, and crystalline content too low, there will only be a small signal generated from Bragg diffraction. This lack of crystalline signal will cause signal to noise ratio problems in the analysis and lead to large errors. Furthermore, the lack of RIR database values for the materials under investigation make Rietveld refinement the obvious choice.
2.2 Experimental

2.2.1 Spike-In Validation Powders

Before applying the Spike-In with Rietveld technique to SiC fibers, a validation study was performed to assess the accuracy and precision of the technique. Since the goal of this study is to quantify amorphous content in SiC fibers, powders for the Spike-In validation study were chosen to closely approximate the primary constituent phases of SiC fibers. A model system was developed comprised of commercially available silicon carbide and glass powders plus an alumina Spike-In agent. The silicon carbide powder chosen to represent the fiber crystalline material was an Advanced Chemical $\alpha$-SiC powder, <1µm Avg. particle size, 99.9% purity, Lot: X0041093-3. The glass powder chosen to represent the fiber amorphous material was a finely ground Corning type 118 WAG/E, infrared reflective, highly amorphous SiO$_2$ containing a small amount of potassium. To find the limits of the Spike-In technique, $\alpha$-SiC powder was chosen over $\beta$-SiC. Even though fibers are $\beta$-SiC, and $\beta$-SiC powder would more closely resemble the experimental system, the greater number of peaks in $\alpha$-SiC allowed better fits during Rietveld refinement (see MAUD description below).

The Spike-In agent powder is an important part of each experimental sample. It must be highly reliable from scan to scan; as discussed above, any variation in values of the Spike-In powder creates variation in the amorphous content values. It must also have a similar linear absorption coefficient to the material being probed. Additionally, it should not exhibit preferred orientation. Any preferred orientation of particles in the powder packing pile during sample preparation will result in one or more dominant peaks
appearing in subsequent XRD patterns of that powder. These dominant peaks skew results during Rietveld analysis that can be accounted for with more complicated models, but should be avoided if possible.

Several Spike-In agents were tested. Silicon powder was tested, produced by Alfa Aesar (1-5µm particle size, 99.9% purity, Lot: J15Y028), but after characterization by XRD and SEM it was concluded that this powder suffered from preferred orientation. Two alumina powders were tested, Sigma Aldrich (99.5%, <10µm Avg., Lot: MKBH8890V) and NIST 676a (Alumina Powder for Quantitative X-ray Diffraction). The Aldrich powder produced also suffered from preferred orientation. The best and most accurate results were produced using the NIST alumina as the Spike-In agent. This powder, from NIST was designed to be a quantitative phase analysis standard, such experiments as those described in this work. The NIST 676a certification document states that the alumina is phase pure; with sub-micrometer, equi-axial particles; and alumina crystalline content listed as: 99.02 % ± 1.11 %. [25] The NIST alumina was confirmed by SEM to be <1µm equiaxed particle size.

2.2.1.1 XRD Setup and Alumina Selection

An XRD scan was performed on both the Sigma-Aldrich and NIST alumina powders to assess their feasibility as Spike-In agents. X-ray diffraction measurements were performed on a Bruker D2 Phaser with a Lynxeye position sensitive 1-dimensional detector with a Cu source and a nickel filter. There are several settings of interest when programming an X-ray diffractometer; scan step width, scan time per step, and total scan range. The scan step was optimized for maximum resolution. Accelerating voltage and current were set to 40kV and 44mA. Step size of 0.01° had a similar signal to noise ratio
and peak fidelity to 0.02°, but 0.05° had poor peak fidelity so step size 0.02° was selected for all Bruker scans for optimal resolution. Scan time per step was optimized to provide low signal to noise ratio between the peaks and the background. The 2θ scan range was set to 10°-100° (2θ) in order to capture all of the large primary peaks and several smaller high angle peaks. The Bruker uses Bragg-Brentano geometry which is a constant volume process that yields accurate counts at any angle and as such is ideal for this research. [19]

The comparison of the two alumina scans is shown in Figure 6, where several cues are visible confirming preferred orientation. The pattern for the Sigma Aldrich alumina has relative peak intensities that are inconsistent with the calculated pattern for a random polycrystalline powder sample. The NIST alumina pattern is generally more consistent with the simulated polycrystalline alumina pattern than the Sigma-Aldrich alumina. This is most evident in the error line below the overlapping experimental and calculated lines. The error plot for each alumina type is generated by comparing the experimental pattern to the Rietveld calculated pattern. The Sigma Aldrich alumina has considerably larger error peaks than the NIST. Even though the NIST alumina errors are in the same place and direction as the Aldrich their magnitudes are much smaller. This is evidenced in the weighted residual (Rw), where Rw for NIST was 10.1 and Rw for Sigma-Aldrich was 22.5. The patterns were fit using software called MAUD, or Materials Analysis Using Diffraction. [26] The MAUD characterization method used in this work is described at the end of this section.
2.2.1.2 SEM Powder Characterization

Visual powder characterization studies were performed on a FEI Quanta Scanning Electron Microscope (SEM), at 10kV and spot size 4. Initial preferred orientation observed in the XRD patterns for Alfa Aesar silicon and Aldrich alumina powders was confirmed using Everhardt-Thornley detector imaging. Platelet shapes and lamellar preferential piling were observed for both silicon and alumina powders. Figure 7 shows the preferred orientation of the Sigma Aldrich alumina powder as well as the largely

Figure 6 – XRD patterns comparing preferred orientation in Sigma Aldrich alumina (A) vs. NIST alumina (B) with errors
equiaxed particles of NIST alumina and Advanced Chemical SiC. Energy Dispersive Spectroscopy (EDS) was performed on each powder confirming the presence of silicon and carbon in the SiC powder; aluminum and oxygen in the alumina; silicon, oxygen, and potassium in the glass powder, and Si in the silicon powder.

![SEM images of powders for model system](image)

**Figure 7 – SEM images of powders for model system**

### 2.2.1.3 Powder Humidity

Alumina exposed to air has both chemisorbed and adsorbed water on its surface. Although humidity contribution to the mass of NIST 676a powder was minimized by storing in inert Argon and also by minimizing the time from dry storage environment to mass measurement in an open lab environment, it was desirable to account for possible unwanted contribution to the amorphous weight fraction due to water on the surface of the alumina. So an experiment was designed to evaluate this contribution. One nearly empty bottle of NIST powder was placed on a counter in regular lab air to humidify in ambient conditions and second nearly empty bottle of NIST powder was placed in the BRAUN MB10 argon environment glovebox to passively dry the powder, both with lids removed. The interior liners of the bottle lids were used to cover the openings to prevent contamination but still allow atmospheric interaction. After one week stabilizing in their
respective environments, the two powders were characterized in a TA Instruments Q600 Thermo-Gravimetric Analyzer (TGA). Experimental conditions were set to ramp speed of 5°C/minute up to 600°C, where the temperature was held for 10 hours. The profiles of the two powders are similar from time 0 to 120 minutes, as shown in Figure 8. This suggests that primarily adsorbed water was being removed at approximately the same rate for both up to 600°C, where 0.45wt% is lost in the first 2 hours. A difference in the profile emerges at 120 minutes showing a difference in removal of chemisorbed water, where the dry powder clearly loses less mass during the 600°C hold time. The final difference in the dry versus humidified NIST alumina powder adsorption was found to be 0.35wt% after heating.

![NIST 676a - Weight Change vs. Time](image)

**Figure 8 – Drying profile for NIST 676a Alumina up to 600°C**

Mass loss for both the dry and humid NIST powders were within the amorphous fraction range listed in the certification document from NIST for the 676a alumina standard, where the amorphous can be as high as 2.09wt%. [25] It is worth noting that
additional humidity pickup after mass measurement was irrelevant to the weight fraction equations since it would not contribute to either SiC or Al₂O₃ crystalline component.

Silica glass powder and silicon carbide, which has a native passively oxidized SiO₂ surface, both have minimal adsorbed water. Given that X-ray penetration is on the order of ~200µm for these two materials, as shown by Lambert’s Law, equation 12 below, the effect of adsorbed water in an XRD pattern should be the same for both glass powder and the oxide surface of SiC powder (or for SiC fiber). [28] The amount of water is surface area dependent, but should be roughly the same for glass and SiC powder.

2.2.1.4 SiC Powder Phase Determination

The SiC powder used for this study was labelled as α-SiC. However, the name α-SiC can refer to any of the hexagonal forms, so the powder was scanned and compared to simulated patterns 2H, 4H, 6H, and 3C patterns for SiC to determine the appropriate .cif file to use during Rietveld analysis, shown in Figure 9. Comparing the black pattern line to normalized simulated patterns, shown in color, it is clear that the α-SiC powder is not 3C as there are not enough peaks to account for all of the peaks in the α-SiC pattern. It is also clearly not 2H or 4H which have either too many peaks, not enough peaks, displaced peaks, or incorrect intensities. The black SiC powder pattern most closely resembles the 6H α-SiC pattern, in red, which is the expected phase. Looking closely at the 6H pattern, the presence of small peaks in the black SiC powder pattern, near 33.7° and 34.7° (2θ), that coincide with 4H peaks and are not accounted for by the 6H pattern are likely the result of faulting.
2.2.2 Samples and Processing

Two experiments were devised to test the operating range of the Spike-In technique, tabulated in Table 1. Multiple mixtures comprised of varying amounts of alumina and silicon carbide powders to a fixed fraction of glass were prepared. The goal for experimental Set 1 was to determine the optimum mixture of Spike-In agent to sample. In the case of an expensive sample or an expensive Spike-In agent, it would be beneficial to minimize one or the other component. The second experiment, as defined by Set 2, was based on the outcome of the first experiment. The Set 2 experiment was designed to find the minimum amount, or detection limit, of amorphous content in a crystalline sample. As discussed below, a homogenous mixture is desirable from a linear absorption coefficient perspective, which would suggest a 50/50 mixture would yield high accuracy. The signal from each constituent phase should also be maximum at a 50/50 ratio in a mostly crystalline sample. So the ratio of alumina to SiC was set to a

![Figure 9 – Confirmation of phase for commercial SiC powder](image-url)
fixed 50/50 ratio and glass was varied according to estimated ranges of amorphous content in silicon carbide fiber.

**Table 1 – Model spiked samples expressed in parts by mass**

<table>
<thead>
<tr>
<th></th>
<th>NIST 676a α-Al₂O₃</th>
<th>α-SiC</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Set 1</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>1</td>
<td>1</td>
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<td></td>
<td>5</td>
<td>5</td>
<td>1</td>
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<td>7</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td><strong>Set 2</strong></td>
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<tr>
<td></td>
<td>5</td>
<td>5</td>
<td>0</td>
</tr>
</tbody>
</table>

Mixing of powder samples was performed using a boron carbide (B₄C) mortar and pestle. Samples were ground and stirred for 15 minutes using 1mL isopropanol to wet the powders for thorough mixing. The potential contamination from boron carbide was expected to be extremely small, since it has hardness greater than both alumina and silicon carbide and as such should abrade very little from the mortar during mixing. On the knoop hardness scale (kg/mm²) this can be shown as: alumina (2100) < silicon carbide (2480) < boron carbide (2750) < diamond (7000). [29, 30] Since B₄C peaks were not observable in any XRD pattern, its presence did not contribute to the observed crystalline phase fractions. Because any additional mass from B₄C contamination would have been introduced after massing, it would not have affected the Spike-In analysis.

After mixing and drying, the samples were stored in air in glass vials. All powders masses were measured with a Mettler AE240 200g mass balance, accurate to ten thousandths of a gram. NIST alumina powder was stored in an MBRAUN MB10 Compact glovebox to minimize humidity absorption between experiments. The devices
used to hold the powder mixtures for scanning in the X-ray diffractometer were offcut-silicon zero-background holders with 5mm (dia.) x 1 mm deep wells. Four samples of each of the spiked-in compositions were loaded into the sample wells, pressed and scanned. Like the possible contribution of B$_4$C contamination, any contribution from a native oxide layer on the zero-background holders would not appear as a part of the crystalline phases being analyzed and as such would not affect the Spike-In analysis.

2.2.2.1 X-ray Sampling Depth

There are two questions that must be addressed with regard to penetration depth. First, does the X-ray penetration depth adequately generate consistent and representative sampling through multiple Spike-In powder particles and fiber diameters? Second, does the beam penetrate through a 1mm sample depth of a well-mixed homogeneous sample and generate signal from the sample holder? A mathematical understanding of the sampling depth is important to ensure the representative sampling of the spiked samples. This is true for both the ~1μm SiC powder and the relatively large 15μm fiber diameters in the fiber characterization work later in this study. In the interest of statistical sampling, a sufficient number particles of each type should be captured in a scan for an accurate representation of the total sample. This mathematical understanding is also necessary to ensure that a given crystalline sample-holder is not being detected, particularly for the case of the least dense powder mixture.

The penetration depth of X-rays depends on several factors; the X-ray source intensity, photon energy, incident angle, the constituent phases and their composition. Here Lambert’s Law [31] is used to address the distance X that an X-ray photon beam can penetrate a sample.
\[ I(E) = I_0(E)e^{-[\rho \mu(E)X]} \]  

[12]

I is transmitted beam intensity, Io is incident intensity, E is X-ray energy, \( \rho \) is density, \( \mu \) is mass absorption coefficient and X is the thickness of the material. I, Io and \( \mu \) are functions of energy. However, they are not functions of energy in the case of a monoenergetic beam, or monochromatic beam, such as the Cu source used in this study. So the prior equation can be simplified as:

\[ I = I_0e^{-[\rho \mu X]} \]  

[13]

This is shown by Shull [31] to be a summation of all the transmitted intensities of all of the constituent members of the sample being probed, in this case the three powder particles, or later in this study, alumina and ground SiC fiber powders. This summation can be simplified to show an average X-ray penetration depth across a sample, given similar powder sizes, shown in equation 13.

\[ I = I_0e^{-[\rho_{SiO_2} \mu_{SiO_2}X_1 + \rho_{Al_2O_3} \mu_{Al_2O_3}X_2 + \rho_{SiC} \mu_{SiC}X_3]} \]  

[14]

Assuming \( X_1 = X_2 = X_3 \) gives an average X-ray penetration depth for a homogeneous mixed powder sample. Solving for X (in cm) leaves:

\[ X = \frac{-\ln(I/I_0)}{\rho_{SiO_2} \mu_{SiO_2} + \rho_{Al_2O_3} \mu_{Al_2O_3} + \rho_{SiC} \mu_{SiC}} \]  

[15]

This version of the equation represents a 1:1:1 mixture of the three materials. However, two versions of this formula must be solved; the least opaque and the most opaque. The opacity is primarily a function of the sample composition and the linear absorption coefficients present. The following equation shows the glass contribution removed.

\[ X = \frac{-\ln(I/I_0)}{\rho_{Al_2O_3} \mu_{Al_2O_3} + \rho_{SiC} \mu_{SiC}} \]  

[16]
Figure 10 shows $I/I_0$ as a function of penetration depth $X$. Using the prior two equations, it is evident for both sample types that the X-ray photons can only transit 1mm of either powder mixture. The intensity from a depth of 1000μm was calculated to be 0.00001%. For a reflection geometry, the sample depth would be limited to less than 500μm, accounting for the path length into and out of the material. Looking at the cumulative plots in Figure 10, the bulk of the XRD pattern will be generated within the top 300-400μm of the sample. An assumption is made here that the entry into and out of the material consists of two photons, even though they constructively interfere and only one “count” is measured by the X-ray detector. [19] This transmitted intensity argument does not assume some fraction of incident beam becoming coherent diffraction, it does assume that the XRD pattern signal intensity will be proportional to the path length into and back out of a sample. In other words, if a given photon would not have escaped through the thickness by transmission, then neither would a coherently scattered photon.
The values in Figure 10 also assume the simplest geometric case with penetration angle of 90° to the surface of the sample. When scanning a powder sample in a diffractometer this is never actually the case. With a scan range progressing from 5° to 140° (2θ) the maximum inclination angle with the sample surface is 70°, so the perpendicular depth for observed diffracted intensity would be even smaller. Throughout a Bragg-Brentano scan, a constant sampling volume is maintained. Considering the average vertical penetration depth, at 50% of the cumulative transmitted intensity, the total transmission path X will be 60µm and X/2 will be 30µm for the highest opacity mixture. The transmission path X will be 90µm and X/2 will be 45µm for the least opaque samples. This is shown in Figure 11, where the two plot lines represent the average penetration depth as a function of 2θ, where half of the scattered X-rays will come from above that depth and half from below at a given angle. The orientation of penetration depth is clearly angle dependent, where at the lowest angles of the scan the

![Transmission vs. I/Io (1-way)](image)

**Figure 10 – Sample penetration curve based on SiC, SiO₂, & Al₂O₃**
average sampling depth is just a few microns near the sample surface and at high angles
the average sampling depth is between 25-50µm. Even if a packing fraction of 50% is
used to increase the values to a range of 50-100µm, this depth profile suggests that
effectively zero signal will be generated from any sample-holder underneath a given
powder sample for all sample depths used in this study, where all sample depths are at
least 1000µm.

![Average X-ray Depth vs. 2θ](image)

**Figure 11 – Differences in average X-ray penetration depth showing
differences in depth depending on composition**

With regard to powder particle sampling, the first peak for alumina is over 25°
(2θ) and the first SiC peak is over 33° (2θ). For a submicron alumina powder this is
sufficient to sample multiple particles of alumina powder, as well as a submicron SiC
powder particle. Even for a large 15µm fiber, assuming radial symmetry for each, a
representative pattern could be collected by sampling the top half of a fiber. At 33° (2θ)
the average sampling depth is roughly half of a fiber diameter. This suggests that a whole
or ground fiber would be well sampled. This is also experimentally shown in the fiber characterization section below during the fiber grinding test.

2.2.3 Phase Quantification by Rietveld Analysis

X-ray diffraction patterns consist of many parts that must be accounted for during phase fraction analysis. The two top-level constituents are the background and peaks. The background can be further subdivided into signal originating from a sample, the sample holder as well as the air, where unwanted scattering occurs from each. The individual peak positions, intensities and profiles must be correctly analyzed to obtain the phase fractions in a mixture, which then allows for the quantification of any amorphous material present. There are a variety of software tools that can perform Rietveld analysis and generate phase fraction values with good accountability for the background and phase analysis. MAUD was chosen as the analysis software for this study due to its ability to handle a separate file for use as a background, in addition to polynomial background fitting functions common in other Rietveld software suites. This allows the fit of the background to be obtained more consistently, reducing variability in the fraction of the background that could be incorrectly associated with peak intensity.

MAUD requires four major inputs to perform Rietveld analysis; a crystallographic model, an instrument model, a background model, and the experimental data file. It uses these inputs to generate and then iteratively minimize the difference between a calculated theoretical fit and the experimental file. The necessary Crystallographic Information File (CIF) models, for alumina (corundum) and 6H alpha silicon carbide, were sourced from the Crystallography Open Database (COD) [32]. The X-ray diffractometer instrument model was generated using a tutorial from the creators of the MAUD software. [33] Each
background file used was generated from an empty zero-background holder that was particular to each sample-holder’s well diameter. The data files used correspond to the samples defined in Table 1.

Once the CIF, instrument, and background models are loaded, one experimental file is loaded. Parameters are then set to either refine or stay fixed. Initial values such as cell parameters from the CIF file, for each setting in the initial model must be close to their experimental value so the fitting algorithms will stay within realistic bounds. Poorly prepared initial conditions can lead to very poor fits and unrealistic results. In MAUD, the peak shape broadening algorithm described by N. C. Popa was employed. [34, 35] There are dozens of available settings that can be fixed or refined during the iterative solver portion of the Rietveld refinement. Since the goal of the study is analyze the phase fraction amounts for both NIST alumina and 6H SiC, the parameters specific to those phases that vary between samples must refine, such as crystallite sizes for NIST alumina and 6H SiC. The height of a sample above the sample holder plane is known as Z-displacement must be refined due to the 2θ angle geometry of the instrument. Even a few dozen microns can shift the peak positions. Similarly, any mechanical 2θ offset must be accounted for as a source of instrumental variability. Sample file and background file multiplicative scaling factors must also be allowed to vary. A variety of polynomial coefficients can be set to refine, although for the model system only the a₀ and a₁ terms, or “Polynomial_zero” and “Polynomial_one” in MAUD, were allowed to refine, see Figure 12. This affects the calculated fit versus the background file scaling factor. Unit cell parameters were allowed to refine to account for small strains in the manufactured powders. A glass peak was added to the background function instead of using higher
order polynomial factors to approximate at the shape of the glass peak. After applying known values for the FHWM of a standard amorphous glass peak, the peak height and position were allowed to refine. All other available settings were set to not refine, or “fixed”, specifically: other sample and instrument geometry factors, plus reflectivity, surface, and thermal character factors.

The analysis range of 2θ was set to 10° through 85° to capture the main peaks for both SiC and alumina, with the two notable exceptions. The 2θ angle ranges of 24.5° to 27° and 32° to 47° were excluded from the refinement range due to multiple refinement challenges. Because small shifts in position and intensity were observed for the lowest angle alumina peak at approximately 25.5°, this peak was omitted from Rietveld. The inconsistencies in this were attributed to the greater influence of z-displacement effects on lower angle peaks. The angle range of 32° to 47° contains the peak associated with the close packed plane where faulting occurs for both 3C and 6H silicon carbide. The nature of faulting in SiC is discussed at length by Pujar et al. [36-38] However, modeling of faulting in SiC is not straightforward. Features caused by SiC faulting could not be accurately accounted for in MAUD using either Ufer or Warren based faulting models. [24, 39] There is a large alumina peak in this same range that directly overlaps the SiC peak again complicating the refinement. This tightly overlapping peak region can be seen in Figure 12 below. When attempting to include this peak region, the resulting poor fits in this angle range created wide variation in phase fraction results. In summary, some low angle portions of the scan were retained to facilitate consistent fitting of the background and only higher angle peaks were used to fit crystalline phases, thereby avoiding several fitting issues.
In the production sequence of generating all of the phase fraction values, individual data files were consecutively loaded into earlier templates. This method worked well for creating an analysis file (.par) for each experimental data file, but each newly saved file .par retained some of the refinement values from the prior phase fraction refinement solution. A method was devised for controlling this history dependence. This method was coined “zeroing” and required that several parameters were reset to zero before applying a refinement to a given experimental file. This zeroing is noted in the following refinement process description.

Figure 12 – MAUD XRD refinement window

In the Rietveld refinement, two phase models were used to account for the silicon carbide signal. This was chosen to account for the bi-modal crystallite size distribution of the SiC material in some samples as evidenced by the “witch hat” nature of the SiC peaks in some samples. These models were coined “Large-Alpha” and “small-alpha”. Using the
Popa algorithms, the refinement parameters most closely representing crystallite size were set differently for Large-Alpha and small-alpha. Large-Alpha was set to a large crystallite size to represent the sharper Lorentzian peak contribution while small-alpha was set to a small crystallite size to represent the shorter Gaussian contribution.

The factors that perpetuate through the save process are listed above; the refined and fixed parameters, the excluded angle ranges, and the dual phase description for SiC. The experimental file must of course be applied for each refinement, but there were multiple repetitive steps used within MAUD to generate each refinement. The first was setting the Large and small alpha crystallite manually to a reasonable value, usually near 800 and 20 respectively, then fixing those values and then running the first refinement. This initial refinement was only the first of several. The next step was to manually adjust the values of the background file, poly-0, and poly-1 to drive the refinement plot line to overlap the experimental pattern plot line. Figure 12 shows a typical MAUD refinement window where the parts of a refinement have been color coded. Poly-0 is shown in blue and poly-1 in purple. The background pattern is in orange and the glass peak is the light gray hump above the orange, centered at about $32^\circ$. This light gray should not be confused with the darker purple-gray overlay of the excluded region, which is semi-transparent to show the peaks being excluded. The actual peaks used for refinement are shown as follows; red is alumina, green is Large-Alpha and yellow is small-alpha. The black line in the small window below the peak window is the error between the calculated and experimental values.

At this point, the refinement produced the lowest residual ($R_w$) values when the parameters for poly-0, poly-1, and the background file were locked; the z-displacement
zeroed; the phase fractions reduced by >50%; and small-alpha’s crystallite size set to 20 before refining again. The goal of reducing the phase fractions by such a large amount was that MAUD produced more consistent results refining by filling the peaks from the bottom up than from the top down. Typically 5-10 refinements were required to reach convergence. The art of science was most notable during the final phase of the refinement process. During subsequent refinements to lower the Rw values (indicating a good fit), the Rw tended to normalize near a value. But, using small changes to the crystallite size values for NIST alumina and both SiC phases the calculated plot line could still be manually adjusted to visually improve the fit with the experimental plot line. During this final adjustment stage the values for z-displacement were zeroed and the phase fractions were again reduced by >50% between each refinement. The final phase fractions generated by this refinement are then used in the Spike-In equations to generate the amorphous fraction of each sample.

2.3 Results and Discussion

As outlined in section 2.2.1.1 Samples and Processing, Set 1 consisted of mixtures with ratios as follows; the \((\text{Al}_2\text{O}_3 + \text{SiC} : \text{Glass})\) ratio equivalent to 10:1. Amorphous content amounts were compared to known glass masses using volume fraction values obtained from MAUD Rietveld analysis. The average of the volume fraction the four samples for each mixture showed a statistical \(R^2\) equal to 1 for correlation between calculated and known amorphous values as a function of alumina concentration. Set 2 consisted of mixtures with ratios as follows; the \((\text{Al}_2\text{O}_3 : \text{SiC} : \text{Glass})\) ratio was equivalent to \((5:5:x)\), where \(x\) values are listed in Table 2. Table 2 also shows initial results from phase fraction analysis of the model system.
Table 2 – Quantification of amorphous content using the Spike-In equation with raw data from the Rietveld analysis

<table>
<thead>
<tr>
<th>NIST Al₂O₃ wt%</th>
<th>α-SiC wt%</th>
<th>Amorphous wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass XRD</td>
<td>Mass XRD</td>
<td>Glass Mass XRD</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>49.8</td>
</tr>
<tr>
<td>47.6</td>
<td>47.6</td>
<td>46.8</td>
</tr>
<tr>
<td>45.5</td>
<td>45.5</td>
<td>45.5</td>
</tr>
<tr>
<td>33.3</td>
<td>33.3</td>
<td>33.4</td>
</tr>
</tbody>
</table>

Phase pure α-Al₂O₃ <1µm Avg.
Crystalline Content: 99.02 % ± 1.11%
Adv. Chemical α-SiC, <1µm Avg.
99.9% purity
SiO₂ (Highly Amorphous)
Corning 118 WAG/E Infrared Reflective

Amorphous content amounts were compared to known glass masses using Rietveld calculated volume fractions. The four-sample volume fraction averages were used to generate the amorphous content values. Figure 13 shows the diffraction patterns for both set 1 and 2 for comparison, where the crystalline peaks changing with concentration of alumina and SiC can be seen in the left image. In the right image of Figure 13, the concentration of glass is increasing with each successively lower XRD

Figure 13 – (Left) Sample Set 1: XRD pattern comparison of fixed glass content with varying Alumina:SiC ratio, (Right) Sample Set 2: XRD pattern comparison of fixed Alumina:SiC ratio with varying glass fraction
pattern. What is remarkable about this progression of patterns is that there is only a small change in the apparent glass content as evidenced by the lack of a wide amorphous peak/hump centered around 24° 2θ. [12]

To determine the most effective amount of the NIST Al₂O₃ spike-in agent to use, the amorphous content results from Set 1 (Table 2) were assessed as a function of the NIST Al₂O₃ to α-SiC ratio and compared to the known glass content and the total amorphous content within the spiked samples. The NIST 676a Al₂O₃ standard reference material contains 0.98wt% amorphous content. [25] By subtracting this amorphous content from the known mass of the NIST Al₂O₃ and renormalizing the weight fractions, its contribution was completely removed from the assessment of amorphous content (Figure 14). When examining the total amorphous content within the model samples, any amorphous content native to the α-SiC must be considered along with the glass content.

To determine the amorphous content of the α-SiC, both sets of data from Table 2 were

![Figure 14](image)

**Figure 14** – Plot of weight fraction of NIST Al₂O₃ and α-SiC as measured by mass and quantitative Rietveld analysis of diffraction patterns.
analyzed from the perspective of the relative masses of NIST Al₂O₃ and α-SiC. Thus the mass of the glass was ignored and the known mass of the NIST Al₂O₃ was corrected for the 0.98 wt% amorphous content. The relationship between the known mass and the weight fraction derived from the XRD patterns was fit with a linear equation. The weight fraction of NIST Al₂O₃ by XRD was then calculated from this fit for a sample containing 50 wt% NIST Al₂O₃ and plugged into the Spike-In equation, revealing that the α-SiC contained 1.6 wt% amorphous content. This amorphous content plus the glass content are reflected in Figure 15 as a function of composition by the line labeled “Amorphous Content (Glass + SiC)”. To examine individual measurement error on the amorphous content, an error effect was calculated by altering the predicted Al₂O₃(XRD) wt% values by ±0.75 wt%. Measurement error curves were plotted and found to encompass all of the data points. Analyzing Figure 15, the spread of the observed glass content for spiked samples tends to converge as the fraction of NIST Al₂O₃ increases. This is consistent with the reduced impact that a given measurement error would have on the Al₂O₃(mass) wt% to Al₂O₃(XRD) wt% ratio in Eqn 5. Concurrently, as the fraction of α-SiC + glass decreases relative to the fraction of NIST Al₂O₃, small deviations from the known glass content for spiked sample should translate in to larger errors in the perceived amorphous content of the model sample consisting of α-SiC + glass. To find the point where the total error is minimized, the difference between the known amorphous content and that due to a hypothetical 0.75 wt% measurement error should be divided by the mass of the sample (α-SiC + glass). This total error is minimized when equal parts of α-SiC and the NIST Al₂O₃ are present (Figure 15). Thus, samples where the weight fraction of the NIST Al₂O₃ spike-in agent and the crystalline portions of the sample are equivalent should
produce the most precise and accurate results. When the amorphous content is unknown, the use of 50 wt% spike-in agent is most likely to generate the best assessment of the amorphous content and the use of this concentration of spike-in agent is consistent with research done on other systems [12] [40-42].

Corrections were made to account for a native amorphous silicon dioxide layer on the silicon carbide powder as well as a listed amorphous layer on the surface of the NIST alumina powder, as shown in Table 3.

Figure 15 – Measured amorphous content (green circles) relative to the known Glass Content and Amorphous Content (Glass + SiC) and error curves, where the 0.98 wt% amorphous content of NIST Al₂O₃ was taken into account.
Table 3 – Quantification of Glass content using the Spike-In equation where corrections for the amorphous content of NIST Al₂O₃ and α-SiC have been applied

<table>
<thead>
<tr>
<th>NIST Al₂O₃ wt%</th>
<th>α-SiC wt%</th>
<th>Glass wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>XRD</td>
<td>Mass</td>
</tr>
<tr>
<td>50.2</td>
<td>50.2</td>
<td>49.8</td>
</tr>
<tr>
<td>47.7</td>
<td>47.7</td>
<td>47.4</td>
</tr>
<tr>
<td>45.6</td>
<td>45.6</td>
<td>45.2</td>
</tr>
<tr>
<td>33.3</td>
<td>33.3</td>
<td>33.1</td>
</tr>
</tbody>
</table>

Some portion of the error present in the perceived amorphous content of the model samples created using NIST Al₂O₃ spike-in agent could be due to variability in humidity. To examine the possible contribution of variable humidity for samples made over many days, the mass loss of dry and humid NIST powder were measured in a TGA, as described above. While it was shown that the mass loss difference on heating to 600°C between dry and humid NIST alumina is 0.35wt%, the error in model system using this powder is <0.5wt% amorphous. This error in the amorphous content is large enough to include the variable contribution of humidity/moisture pickup of the powders. The mass loss shown in Figure 8 for dry NIST alumina is also within the listed amorphous value on the certification for this powder. NIST alumina is certified as containing crystalline alumina: 99.02 % ± 1.11 %, where the upper error cannot exceed 100%. [25]

2.4 Conclusions

The Spike-In method was used to calculate amorphous content by quantifying the relative amounts of the crystalline phases within a given spiked sample and comparing them to the known mass of the spike-in agent. The Spike-In agent should have a similar linear absorption coefficient and be added in equal mass to the crystalline phase(s) in the sample to ensure accuracy. When working with an ideal system consisting of well
crystallized phases and completely amorphous material, the amorphous content can be quantified to within 0.5 wt%. This rapid and highly cost effective technique has the potential to be a viable screening tool for quantification of batch-to-batch variation of amorphous content in commercially available SiC fibers. [12]

3 Characterization of As-Received Commercial Fibers

3.1 Introduction

It is important to understand the properties and limits of commercially available fibers that are to be used in high temperature applications. There are multiple commercially available fibers, each made with unique precursors and processes. Understanding variation in amorphous content across these fibers is important to understanding their bulk properties in their end stage application.

3.2 Experimental

3.2.1 Fibers

Five commercially available fibers are the subject of this study; Hi-Nicalon, Hi-Nicalon Type-S, Tyranno-SA3, Cef-NITE, and Sylramic. Some of the properties of these fibers are summarized in Table 4, as well as the identifying spool marks from each manufacturer. [4, 20, 43] Hi-Nicalon is a second generation fiber made using a process that involves electron radiation in helium atmosphere to cross-link a polycarbosilane (PCS) preceramic polymer. This produces a green-state fiber which is then undergoes high temperature pyrolysis. Hi-Nicalon Type-S is a third generation fiber and is made
using Hi-Nicalon fiber that is taken up to near 1500°C in an H₂ atmosphere to lower the carbon to silicon ratio. These two fibers are both made by NGS Advanced Fibers Co., Ltd., a joint venture of Nippon Carbon, GE, and Safran. Tyranno-SA3 and Cef-NITE are third generation fibers and share a common precursor, polyaluminocarbosilane (PACS). The “NITE” in Cef-NITE stands for Nano-Infiltration by Transient Eutectic. This may refer to the action of aluminum during grain growth diffusion. Since the PACS precursor is the same in both fibers, the “transient eutectic” effect of grain refining should occur similarly. Tyranno-SA3 is manufactured by Ube Industries, Ltd and Cef-NITE is manufactured by the Institute of Energy Science and Technology, using the Tyranno-SA process under license from Ube. Sylramic is also a third generation fiber and is based on Tyranno Lox-M produced by Ube, which is based on polytitanocarbosilane (PTC). COI Ceramics, Inc. improves the properties of the Lox-M fiber by subjecting it to additional processing; decomposing the fiber to remove excess O and C, incorporating B as a sintering aid, followed by sintering at over 1800°C. [20, 43]

<table>
<thead>
<tr>
<th>SiC Fiber</th>
<th>Gen.</th>
<th>Mfgr.</th>
<th>Composition (wt%)</th>
<th>Tensile Strength (Gpa)</th>
<th>Elastic Modulus (Gpa)</th>
<th>Lot</th>
<th>Batch or Bobbin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi-Nicalon</td>
<td>2</td>
<td>NGS</td>
<td>Si: 62 C: 37 O: 0.5</td>
<td>2.8</td>
<td>270</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hi-Nicalon Type-S</td>
<td>3</td>
<td>NGS</td>
<td>Si: 69 C: 31 O: 0.2</td>
<td>2.6</td>
<td>420</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tyranno-SA3</td>
<td>3</td>
<td>UBE</td>
<td>Si: 67 C: 31 Al: &lt;2 O: &lt;1</td>
<td>2.6</td>
<td>380</td>
<td>S1F08PX</td>
<td>9930</td>
</tr>
<tr>
<td>Cef-NITE</td>
<td>3</td>
<td>UBE, IEST</td>
<td>Si: 67 C: 32 Al: &lt;2 O: &lt;1</td>
<td>2.1</td>
<td>380</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sylramic</td>
<td>3</td>
<td>UBE, COIC</td>
<td>Si: 67 C: 29 Ti: 2.1 B: 2.3 N: 0.4</td>
<td>3.2</td>
<td>~400</td>
<td>167-8244</td>
<td>06C</td>
</tr>
</tbody>
</table>
3.2.2 Samples & Processing

Each of these five commercially available fibers were prepared for three types of characterization, X-ray diffraction, TEM, and SEM. These SiC fibers arrive from the manufacturer with a sizing that must be removed before any processing takes place in order to minimize the effect of this protective layer on measurements. The X-ray diffraction samples were prepared for the Spike-In method; each fiber was mixed and ground with the NIST alumina standard. In the interest of controlling process quality, length of grinding time effects on XRD patterns were analyzed. TEM fibers were prepared singly in a FIB. SEM fiber samples were prepared in bundles with maximum electron conduction in mind.

Each fiber type arrives from the manufacturer on cardboard or paperboard spool, wrapped in padding and protective plastic to minimize damage. All fibers in this study were coated with water soluble PVA polymer, so fibers were desized by boiling twice in deionized water. For this process 2 meters of fiber were wound onto a nichrome wire spool shaped to hold fiber away from the bottom and edges of the 3L Pyrex beaker used for boiling and desizing. Care was taken to minimize contact with the fiber at every step, which can lead to inter-fiber friction and degradation of strength from handling damage. Curvature around the corners of the spooling wire, during winding for desizing, was also controlled to minimize damage. Each batch of desized fiber was then weighed and stored in air in polymer zip-closing bags.

Like the Spike-In validation powders, the fiber Spike-In mixtures were ground in a boron carbide mortar and pestle under isopropanol for 15 minutes until well-mixed and stored in air in glass vials. NIST 676a α-alumina was again used as the Spike-In agent.
All fiber samples were prepared using a 50/50 ratio of sample to Spike-In due to the determination described in the Spike-In validation above. Four samples of each fiber type were prepared to gain the statistical benefit of multiple data points. Fibers were weighed in fiber form before grinding, minimizing surface area for water to adhere. Additional contribution to the XRD pattern by humidity adsorption after mass measurements was presumed to be inconsequentially small in the phase fraction calculation.

Samples intended for characterization in TEM were prepared using Focused Ion Beam (FIB) milling in a specialized SEM (LYRA). Fiber segments 2mm long were affixed to posts on a molybdenum Omniprobe TEM grid using a 5-minute setting epoxy for each type of fiber to be studied. Each sample was placed in a specialized TEM-grid holder designed for use in a FIB-SEM and milled according to the following process. “Segments of the commercial SiC fibers, 2 mm in length, were each affixed to an Omniprobe TEM grid. To thin the fibers for imaging, a Lyra3 SEM with focused ion beam (FIB) (Tescan USA, Inc. Warrendale, PA) was used to mill small rectangular sections that were further thinned to produce a tapered and electron transparent section. A 1040 Nanomill (E.A. Fischione Instruments, Inc, Export, PA) was used to remove any amorphous damage layer induced by the focused ion beam.” [12]

SEM fiber samples were cut into short lengths, gold coated, and then set in epoxy with nickel filler and cured. The resulting fiber and epoxy mini-composite was then set again in epoxy and cured to make a large enough sample to polish. Each fiber was polished to a 1μm finish and then placed with standard carbon adhesive dots on aluminum SEM stubs.
3.2.2.1 Effects of Grinding and Sample Holder

Because fibers analyzed with powder XRD had to be reduced by grinding during the mixing process, the effect of mixing/grinding was examined for any impact on the XRD data. A sample was progressively mixed in a boron carbide mortar and pestle in 15 min. increments to 60 min. XRD scans were taken after each 15 min. mixing/grinding increment and are shown in Figure 16. The scans are statistically identical.

![Image of HiNic-S samples](image1)

![Image of HiNic-S + NIST samples](image2)

**Figure 16 – Effects of grinding time on powder appearance and XRD signal**
Homogeneity was achieved after 15 min. of grinding and mixing; no change in relative peak intensity was observed and the relative intensities were consistent with a random polycrystalline powder sample. There are a few slight variations in peak heights between grinding times, but these variations are consistent with the magnitude of variation from the model system. Grinding for more than 15 min. did not observably modify the fiber microstructure as evidenced by a lack of discernable change in peak width. Based on these results, spiked samples were mixed/ground for 15 minutes. The same 4-digit balance, mixing tools and vials were used as those of the Spike-In validation. Grinding time does not have a significant impact on total signal because average sampling depth is adequate regardless of how long the fibers are pulverized.

Due to the geometry of the sample holder, the overall signal is a function of the illuminated area of the X-ray beam. This factor was not relevant in the model system due to using a 1-dimensional Lynx-eye detector, which has very good signal to noise ratio. When switching to the 10-sample rotating stage in the Ultima IV (for efficient scanning) and monochromator-scintillator detection method (for simpler low angle analysis) the sample holder well diameter becomes a factor. In the penetration depth discussion outlined above the depths proposed represented a 2D section of a conical beam. To account for the impact of illuminated area, an experiment was devised comparing standard Rigaku well sizes. The XRD pattern in Figure 17 shows a narrow range in a sample scan of SiC fiber + NIST where XRD scan parameters and powders were identical but zero-background holder well size was varied. After these patterns were normalized for noise level, there is a clear dependence on well diameter for maximized signal-to-noise ratio. Sample holders with wells of 10mm and 7mm diameters well were
used for all fiber XRD measurements.

![Intensity vs. 2θ](image)

**Figure 17 – Sample holder well size impact on Monochromator-Scintillator XRD**

### 3.2.3 Characterization

#### 3.2.3.1 X-Ray Diffraction

For the commercial fibers, a Rigaku Ultima IV was used to collect all diffraction patterns. The Ultima IV’s 10-sample carousel was used for unattended data collection of multiple samples. This Rigaku also contained multiple hardware attachments that enabled scanning using either a scintillator or 1-dimensional (D-tex) detector, both using Bragg-Brentano hardware geometry. The signal to noise ratio was better for D-tex but the monochromator-scintillator had much less direct beam scatter resulting in a lower and less complicated intensity tail at low angles. Several scan setting variables had to be defined for each run. Each run was to capture the 10-100° 2θ angle range, which captures the important peaks necessary to perform Rietveld. Based on analysis of the model
system, the step size was set to 0.02°. The scan rate was set such that the peak-to-background ratio was near 100:1 for the (111) peak of the NIST alumina standard, which required 0.25°/minute.

The MAUD Analysis performed on the fiber was generally the same as described above in the model system description, with a few notable exceptions. The Large_Alpha and small_alpha phases were removed and in their place Large_Beta and small_beta were added. The glass peak feature was removed from the parameter set for all fibers since there was no longer a need to model the extra component. In the Hi-Nicalon analysis, only small beta was used, due to the extremely small grain size of this fiber. For Sylramic, an extra TiB₂ based phase was added to account for additional peaks only present in the Sylramic fiber. This extra phase is counted as crystalline in the spike-in difference equations, shown in equation 17, a modified version of equation 5. This also assumes Al₂O₃ is 100% crystalline with the combined fiber phases of SiC and TiB₂ containing amorphous material.

\[
\text{(Amorph.) wt\%} = 100\text{wt\%} - \left[ \frac{(\text{Al}_2\text{O}_3\text{(mass)})\text{wt}\%}{(\text{Al}_2\text{O}_3\text{(XRD)})\text{wt}\%} \cdot (\text{SiC}_{\text{XRD}} + \text{TiB}_2\text{XRD})\text{wt}\% \right] \quad [17]
\]

For the XRD crystalline components,

\[100\%_{\text{XRD}} = \text{SiC}_{\text{XRD}}\% + \text{Al}_2\text{O}_3\text{XRD}\% + \text{TiB}_2\text{XRD}\% \rightarrow \text{SiC} + \text{TiB}_2 = 1 - \text{Al}_2\text{O}_3 \quad [18]\]

Which results in the same simplification as equation 8 from the SiC only system.

\[
\text{(Amorph.) wt\%} = 100\text{wt}\% - \frac{(\text{Al}_2\text{O}_3\text{(mass)})\text{wt}\%}{(\text{Al}_2\text{O}_3\text{(XRD)})\text{wt}\%} \quad [19]
\]
3.2.3.2 SEM and TEM Imaging

An FEI Quanta SEM was used for imaging of fibers. Imaging was performed at 10kV and spot size 4 in Everhart-Thornley secondary electron detection mode. A Philips CM200 TEM was used for imaging in the submicron range. For each imaging session, a molybdenum Omniprobe sample as described above was loaded into a double-tilt TEM holder. Imaging was performed at 200kV in bright field mode.

3.3 Results and Discussion

3.3.1 X-Ray Diffraction

Looking at the raw XRD patterns for each fiber, mixed with NIST alumina, several observations can be made. Figure 18 shows three different sets of X-ray patterns. Figure 18A shows a waterfall stacking of one pattern for each fiber type on a selected range of the scan to show a detail view of both materials' highest peaks. This plot illustrates a variety of differences between the fibers that can be interpreted from subtle changes in features of each pattern. For Cef-NITE and Tyranno-SA3 there is a feature between 33.5° and 35° that coincides with degree and frequency of faulting as described by Pujar. [36, 37] This faulted region is less pronounced for Sylramic, Hi-Nicalon, and Hi-Nicalon-S. Sylramic is known to have TiB₂ present in small amounts. The contribution from this unique phase is visible as a very small peak in the Sylramic pattern at 34.1° in the SiC faulted region, and a second peak at 44.3°. [44] Figure 18B shows an overlay of all five patterns on the same selected range. The pattern-to-pattern statistical variability is visible in the two alumina peaks in this range, at 35.2° and 37.8° of Figure 18B. These small peak shape and area differences are one primary source of variability
when calculating integrated intensity. The grain size of each fiber is discussed at length in the next chapter, but in general, broader peaks suggest smaller crystallites, so the difference in crystal size among fibers is visible here as well. The legend is stacked in decreasing apparent crystal size, from top to bottom, with Cef-NITE having the largest crystals and Hi-Nicalon having the smallest. Figure 18C shows the full scan range of the

Figure 18 – Waterfall and overlay XRD patterns of as-received SiC fibers ground with NIST alumina
waterfall plot. Peaks from SiC crystals at 35.7°, 41.4°, 60°, and 90° show the peak broadening trend in each fiber for the length of the XRD pattern.

### 3.3.1.1 Amorphous content

Amorphous content for the as received fibers was calculated using the XRD patterns shown in Figure 18 and the Spike-In method with Rietveld described in the prior chapter. The amorphous content averages of 4 fibers are shown in Table 5. Four of the five fibers are under 10 wt% amorphous, with Hi-Nicalon having the highest amorphous fraction, and Cef-NITE having the lowest. These results are in line with the literature, where a larger fraction of amorphous content is expected in Hi-Nicalon as a Gen-II fiber. The others fibers are Gen-III and are supposed to be largely crystalline. [45] Although the amorphous contribution from SiOC should have a positive correlation to oxygen content, excess carbon and amorphous SiC may contribute more to the perceived amorphous content. This confirms the earlier argument that using oxygen as a proxy for amorphous content is unreliable.

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Amorphous Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi-Nic</td>
<td>15.2%</td>
</tr>
<tr>
<td>Hi-Nic-S</td>
<td>9.7%</td>
</tr>
<tr>
<td>Tyr-SA3</td>
<td>6.0%</td>
</tr>
<tr>
<td>Cef-NITE</td>
<td>5.4%</td>
</tr>
<tr>
<td>Sylramic</td>
<td>7.9%</td>
</tr>
</tbody>
</table>

### 3.3.2 SEM Imaging

Cross-sections of the five commercially available fibers are shown in Figure 19. The respective image sizes have been resized to show uniform circles for easy comparison of features, hence the lack of scale bar in the images shown in this figure. For reference the fiber diameters are on the order of 10-20 μm. Observing the individual
surfaces of the cross-sections, Hi-Nicalon and Hi-Nicalon-S appear uniform (although Hi-Nicalon exhibits damage consistent with insufficient polishing). Tyranno-SA3 and Cef-NITE show a non-SiC phase near the fiber center. Sylramic shows dark spots throughout the fiber, which are expected to be graphitic excess carbon and will also contribute to the amorphous content since graphite was not explicitly included in the analysis. Differences in fiber microstructure after heat treatment were visible in SEM and are discussed in the next chapter.

Figure 19 – SEM images of as-received fibers
Approximate fiber diameter is 10-20 µm
3.3.3 TEM Imaging

Several fibers were imaged using the CM-200 TEM. Hi-Nicalon Type-S, Tyranno-SA3 and Cef-NITE were selected for TEM imaging to observe the amorphous content in detail. As suggested by the peak broadening in the XRD patterns, there is indeed a wide variation in visible grain size across fibers.

Looking at TEM images one must remember that the image is generated by electrons passing completely through the sample. Several phases of material can overlap, complicating identification of individual features. This is evident in Figure 20, where the lighter, thinner regions of the wedge-shape are near the top of the fiber and the darker, thicker regions below allow less penetration. To discuss the features present in the TEM images a diagram has been prepared to simplify some of the complex features.

Figure 20 – Thickness variation in FIB-prepped fiber

Figure 21A shows a TEM image of a Tyranno-SA3 as-received fiber and Figure 21B shows a sketch of this same image with features simplified and colorized for comparison. The large green shapes represent grains of silicon carbide and the yellow gradations
behind the grains represent the amorphous content. There are two separate phases in the yellow area; the lighter yellow cellular shapes are primarily the glassy SiOC and the dark yellow cell-wall structures represent graphitic/turbostratic carbon. Comparing these color features to the TEM image, grayscale contrast is created by these different phases.

In Figure 22, these features are present in each fiber type, although in varying amounts. Graphically comparing the crystalline and amorphous for Hi-Nicalon, it is clear that Hi-Nicalon contains very small grains, which is confirmation of the broad peaks noted in the XRD pattern analysis above. The Hi-Nicalon-S grains are larger than the Hi-Nicalon, but smaller than the other three fibers, similarly predicted by the peak overlay plot in Figure 18. The Tyranno-SA3, Cef-NITE, and Sylramic fibers are all much larger grained, but specific size comparisons among them are difficult to make.

Quantification of these grains was performed, see next section.

There are many large faulted grains and pockets of amorphous material for each of the Gen-III fiber types. Without knowing the thickness of each sample wedge, or
deconvoluting the interlocking grains, quantifying either the amorphous fraction or the grain size from images like these is problematic. Two images presented in Figure 22 for these fibers are from Osborne et al. [46]

![TEM images of as-received fibers](image)

**Figure 22 – TEM images of as-received fibers**
*Photo credit for Hi-Nicalon and SyrRamic: Osborne*

The distribution of amorphous content varies substantially across the three fibers shown in Figure 23; Hi-Nicalon-S, Tyranno-SA3, and Cef-NITE. Figure 23A shows a 3D model of the amorphous material in Hi-Nicalon-S fiber. (This image was created at AFRL using Model-Based Iterative Reconstruction (MBIR, www.openmibr.org). The tomographic reconstruction was based on an image series obtained on a 300 kV FEI Titan High Angle Annular Dark Field-Scanning Transmission Electron Microscope (HAADF-
Figure 23A and B both show the homogenous distribution of grains and amorphous in Hi-Nicalon-S. Figure 23C and D show the difference composition of the center of the fiber versus the core. Comparing these images to the SEM images above, the secondary phases seen during polishing were consistent with the location of the amorphous material in the fiber. Figure 23E shows the same center-to-core variation in composition for Cef-NITE. The NIST-JANAF thermochemical tables report that the “heat of formation and equilibrium data indicate that β-SiC is more stable up to 1700°C,” [31, 48] but faulting is present throughout these three fibers (Hi-Nicalon-S, Tyranno-SA3, Cef-NITE, and Sylramic), confirming that these fibers have been exposed to temperatures over 1700°C at some point during the manufacturing process.
High-resolution TEM and TEM-EDS were analyzed to confirm the phases present in the amorphous content. Hi-Nicalon-S is shown in Figure 24. The left and right images show two different resolutions, where the right hand image is a magnification of a region near the center of the left image. Looking at the right-hand image, this image is atomic scale resolution and, crystal lattice fringes can be observed. The phase between the SiC grains, about 5nm wide was determined by TEM-EDS to be turbostratic carbon, a two-dimensionally ordered analog of graphite. The disordered phase surrounding the graphitic layers was confirmed to contain silicon, oxygen and carbon, inferring amorphous SiOxCy.

![Figure 24 – Turbostratic carbon on the surfaces of SiC grain, surrounded by SiOC](image)

Image credit: Randall Hay

### 3.3.4 Grain size

Table 6 shows a comparison of grain size values obtained from XRD, TEM, and the literature. The technique used to determine the grain size from XRD measurements is
described in the next chapter. The TEM values were determined using a limited number of circular approximations of grains in the TEM images. The literature values presented were obtained from Yun and DiCarlo [49], except for the Cef-NITE value from Kohyama *[50]. XRD values were typically on the order of half the value extracted from the TEM micrographs. These TEM values were close to published grain size values, with the exception of Sylramic fibers, which were somewhat larger than published. The difference between XRD and TEM values is likely due to faulting, which subdivides grains into platelet shaped diffracting domains thereby reducing long range order.

### Table 6 – Average grain size for as-received fiber, ordered by size

<table>
<thead>
<tr>
<th>Fiber</th>
<th>XRD</th>
<th>TEM</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiNicalon</td>
<td>3</td>
<td>7</td>
<td>5 (XRD)</td>
</tr>
<tr>
<td>HiNicalon-S</td>
<td>16</td>
<td>25</td>
<td>22 (XRD)</td>
</tr>
<tr>
<td>Sylramic</td>
<td>58</td>
<td>166</td>
<td>~100 (TEM)</td>
</tr>
<tr>
<td>Tyr-SA3</td>
<td>69</td>
<td>178</td>
<td>&gt; 150 (TEM)</td>
</tr>
<tr>
<td>Cef-NITE</td>
<td>80</td>
<td>182</td>
<td>~100 (*)</td>
</tr>
</tbody>
</table>

#### 3.4 Conclusions

The raw X-ray diffraction patterns show differences across the five fibers; apparent differences in grain size from peak broadening, an extra phase in Sylramic, as well as visual proof of statistical variation from scan to scan. The differences in the amorphous values calculated by Rietveld and the Spike-In technique, as tabulated in Table 5, were in line with expected values based on literature. The amorphous content amounts were qualitatively validated by the images seen in TEM. What cannot be seen by X-ray diffraction is the nanoscale distribution of amorphous content. This distribution
was shown in SEM and TEM to be different for the Hi-Nicalon-S fiber vs. the Tyran-no-
SA3 and Cef-NITE fibers. Quantified grain sizes were comparable to TEM and literature.

4 Characterization of Heat Treated Commercial Fibers

4.1 Introduction

Since state-of-the-art SiC fibers are not fully thermodynamically stable, it is
important to understand how fiber microstructure changes over time at elevated
temperatures, particularly because these fibers are intended for use in high temperature
applications over long periods of time. This instability comes from the oxygen containing
materials that, according to research by Kakimoto and Rocabois [51, 52], will evolve CO
and SiO gaseous species. Oxygen leaving the SiO$_x$C$_y$ amorphous grain boundary material
will leave behind SiC, as shown in Figure 1. So changes in mass, amorphous content, and
microstructure are expected. Thermally activated densification and grain growth is
expected at these temperatures as well. These effects should lead to an increase in
crystallinity and a drop in amorphous content. Heat treated fibers were characterized by
XRD, TEM and SEM to verify these predictions. An understanding of changes in silicon
carbide fibers during heat treatment is necessary to understand creep behavior and fiber
limitations at extreme temperatures. In pursuit of this goal, heat treated fibers were
investigated in the range of 1400-2000°C.
4.2 Experimental

4.2.1 Fibers

Heat treatments were applied to the same five commercially available fibers described in chapter 3 and summarized in Table 4.

4.2.2 Samples & Processing

Fiber handling and preparation was identical to the as-received fibers in chapter 3. Fibers were unwound, desized, and stored in air in polymer zip-closing bags. The heat treated commercial fibers and Spike-In mixtures were prepared for X-ray diffraction in the same manner as the as-received fibers in chapter 3, ground in a B₄C mortar and pestle in isopropanol for 15 minutes until well-mixed and stored in air in glass vials. NIST alumina was again used as the Spike-In agent. All fiber samples were prepared using a 50/50 ratio of sample to Spike-In based on the determination of optimal mixture ratio described in the Spike-In validation above. The same equipment was used throughout the heat treated fiber study as that of the as-received fiber study; glovebox, mass-balance, sample holders, etc. The same FIB technique was used to prepare fibers as well.

Two furnaces were used for fiber heat treating; a larger graphite furnace with approximate interior hot zone size of 12”x12”x12” (Materials Research Furnaces, F-14x14x14-GG-2500-VM-G), and a smaller graphite furnace with approximate interior hot zone size of 3”(dia.)x8” (Materials Research Furnaces, F-4x8-Top-Load-GG-2500-VM-G). Several atmospheres were considered before deciding on argon. Argon is fairly inexpensive, inert, generates needed pressure for very high temperatures, and can flow with slight positive pressure to purge outgassing species. Argon atmosphere was used in
both furnaces for all experiments. Fibers masses were taken before and after heat
treatment on the same balance used for the model system, with ten-thousandths of a gram
accuracy. The masses were matched for fiber and NIST to within 0.2% accuracy.

Different containers and surfaces were tested to find a minimally reactive platen
on which to heat treat the fibers. An effort was made to melt silicon onto bulk graphite to
determine the feasibility of converting the crucible base to SiC. In order to make this SiC
substrate a third furnace was used – a 2” alumina tube furnace (CM, Inc., Rapid Temp
Furnace, 54434-910770-1) with a graphite loading platform. A small 1” diameter by
0.25” thick disc of graphite (POCO) was placed in a tube furnace with a chunk of silicon
placed on top and heated to 1850°C. This did yield a SiC surface, but was determined to
be silicon rich and this approach was abandoned. Silicon powder was also reacted with
the graphite foil to create the SiC surface. This yielded a usable SiC substrate which was
used in the base of the small graphite furnace crucible described below.

The first heat treatments were conducted in the small graphite furnace. A graphite
(POCO) crucible with dimensions 3” OD and 2.25” ID, and lid with dimensions 0.375”
by 3” diameter, were designed and constructed specifically to maximize the volume
available to hold fibers in the hot zone of the furnace. In order to have the cleanest
possible environment for heat treating, the graphite crucible and lid were heat treated in
the small graphite furnace at 2100°C for 2 hours in argon. Given that the highest
experimental temperature the fibers would see would be 2000°C any compound that
might volatilize at 2000°C is assumed to have volatilized during the 2100°C bake-out.

Three arrangements of fiber tows were devised to determine the optimal geometry
for placement in the crucible. Hi-Nicalon-S fiber, which is nominally 10 µm in diameter
filament and bundled together in a tow of ~500 filaments, was used for this test. One tow was placed flat, parallel to the ground, on the converted graphite foil SiC sheet described above. Another tow was wound around the base of the crucible interior in a ring shape, incorporating three turns of the diameter. A third tow was placed vertically and leaned against the interior wall of the crucible. These three arrangements are shown in Figure 25. The crucible was loaded with these three arrangements, then placed in the small graphite furnace (SGF) for 20 hours at 1500°C. Upon cooling and removal from the furnace, the leaning and curled fiber tows showed substantial deformation. The tow that was lying flat on the converted SiC foil had partially fused to the SiC surface.

A graphite foil box was devised to hold the fiber vertical during heat treatment to counter the problems seen in the first crucible test. A tow of Hi-Nicalon-S fiber was hung in this box and placed in the SGF for 20 hours at 1500°C. Unfortunately, a great deal of foreign metal contamination was found on SGF samples during SEM/EDS study. The form factor of the crucible, the limitation of single fiber heat treatments, and contamination problems led to the conclusion that the heat treatments would be better performed in the large graphite furnace (LGF). The larger hot zone of the LGF,
measuring 1 ft³, was also capable of heat treating multiple fibers at once, which greatly expedited data collection.

To protect the fibers during heat treatment, another graphite foil box was designed to prevent airborne settling contamination and direct contact with the hot zone table stand. An upper and lower box half were each cut and folded to contain 2” fiber tow segments without touching the box edges. An extra sheet of graphite foil was cut to fit in the bottom of the box and was rounded slightly to prevent fiber movement during loading of the furnace. The fibers only contact during heat treatment was with this sheet of carbon foil which was replaced for every furnace run corresponding to each 100°C increment heat treatment. Similar to the small graphite furnace pre-treatment of the graphite crucible and lid, the graphite foil boxes prepared for the large graphite furnace were heat treated in at 2100°C for 2 hours in argon to volatilize possible contaminants.

### 4.2.2.1 Heat Treatments

Sets of five fiber samples were heat treated as listed in Table 7. Two different heat treatment groups were performed. The first treatment held time at temperature and environment constant while varying temperature with each sample set. The second held temperature constant and varied time. Each of the five commercial fiber types were heat treated as follows; ramped by 5°C per minute up to temperature, held there for either 2 or 20 hours in a flowing argon atmosphere, ramped back to room temperature at the maximum allowable cooling rate for the furnace. As discussed in the SEM imaging section below, the starred temperatures in Table 7 (1900°C and 2000°C) resulted in fibers that were transformed to a point that they no longer physically resembled fibers. As such, they were excluded from all XRD and TEM analysis.
The fiber specimens were laid flat on disposable graphite foil sheets inside graphite foil boxes prior to heat treatment. The large graphite furnace had space for all 5 fiber boxes to be heat treated simultaneously in the hot zone (isothermal region) of the furnace. While this may have introduced a small risk for cross contamination between fibers it ensured that the fibers all saw identical processing conditions, specifically heat ramp rate, time at temperature, and any fluctuations in the process.

The second treatment held environment and temperature constant while varying time at temperature for the set of five fiber types. The five commercial fiber types were again ramped by 5°C per minute up to 1500°C, in a flowing argon atmosphere, held for 20 hours, then ramped back to room temperature at the maximum allowable cooling rate for the furnace.

### 4.2.3 Characterization

#### 4.2.3.1 X-Ray Diffraction

For quantifying the amorphous content in the heat treated commercial fibers, the Rigaku Ultima IV was again used to collect all diffraction patterns. The 10-sample carousel, Bragg-Brentano hardware, scan setting variables of 10-100° 2θ angle range, step size of 0.02°, and scan rate were set the same as with the as-received fibers.
primarily for experimental consistency. For grain size, one additional scan was performed on each fiber using the D-tex detector. This detector has very good signal to noise ratio, >1000:1, and as such was used obtain the smoothest possible peaks and high angle peaks necessary to create a thorough Williamson-Hall plot. Scan settings for the D-tex runs were; 10-140° 2θ angle range, step size of 0.02°, and scan rate of 1°/minute. Grain size XRD patterns were all performed on the same device, same run settings.

4.2.3.2 SEM and TEM Imaging

An FEI Quanta SEM was used for imaging of fibers. Imaging was performed at 10kV and spot size 4 in both Everhart-Thornley secondary electron detection and back-scattered electron modes. The SE images have better signal and discernable surface geometry, but the BSE images provide atomic number contrast. A Philips CM200 TEM was used for imaging in the submicron range. For each imaging session, an Omniprobe was loaded into a double-tilt TEM holder. Imaging was performed at 200kV in bright field mode.

4.2.3.3 Grain size

Bruker’s TOPAS software was used to generate the full-width-half-maximum (FWHM) values needed to calculate grain size. TOPAS was chosen for its ease of use and reputation as an outstanding peak fitting tool. MAUD has a function for finding the needed values, but the interface for this function is cumbersome and not as efficient as TOPAS. Some concerns when fitting an X-ray diffraction file for FWHM are outlined by Lutterotti. [13] He suggests that users do not preprocess their data before profile fitting. Specifically, users should not smooth the data, remove the background, or strip Kα2
peaks. Additionally, as few peaks as possible should be visible during peak fitting, plus some background. The stability of the refinement will be improved if only the necessary variables are unconstrained when fitting peaks.

In line with Lutterotti’s advice, patterns were not preprocessed. A Pseudo-Voigt peak shape was selected in the software settings. Approximate peak positions were selected for each fiber to supply the refinement software with the number of peaks present in each XRD .raw data file. To refine as few peaks as possible patterns were fit in ranges of 30° 2θ; 20-50°, 50-80°, 80-110° and 110-140°. These ranges were selected based on low intensity points in the pattern where no peaks crossed the dividing points. There are many peaks overlaps in all patterns. To account for additive positions in the pattern where peaks do overlap the ranges could not realistically be subdivided further.

TOPAS will skip into different minima during the peak matching refinement, the same as MAUD, but to a lesser degree. This is evidenced by small jumps (<10%) in the Rw value when cycling the refinement, where at least 10 cycles are necessary to reach convergence. The value in the tenths place will drop suddenly on the 8th or 9th cycle when a fit has seemingly converged in the thousands place. An instrument profile for the Ultima IV Dtex configuration was not preloaded into TOPAS prior to peak fitting for the FWHM values. The peak shape was corrected for instrument broadening offline in Excel using a NIST 1976a calibration comparison.
4.3 Results and Discussion

4.3.1 Mass Loss

Kakimoto directly observed evolution of gaseous species in Si-Ti-C-O fibers, a similar composition to Sylramic. [51] Rocabois observed CO and SiO evolution during heat treatments of Si-O-C fiber. [53] T. Ishikawa and H. Oda noted on the importance of CO evolution during in Si-Al-C-O fiber processing [54], where they contend that the “strictly controlled” partial pressure of CO in the fiber heat treatment chamber will affect the rate of CO evolution. The reactions and thermodynamic calculations at work, as proposed by Ishikawa and Oda, are as follows and are shown in Figure 26.

\[
\begin{align*}
\text{A: } \text{SiO}_2(s) + 3\text{C}(s) &= \text{SiC}(s) + 2\text{CO}(g) \quad [20] \\
\text{B: } \text{SiO}(g) + 2\text{C}(s) &= \text{SiC}(s) + \text{CO}(g) \quad [21] \\
\text{C: } \text{SiO}_2(s) + \text{C}(s) &= \text{SiO}(g) + \text{CO}(g) \quad [22]
\end{align*}
\]

A is thermodynamically favorable over 1522°C and B is thermodynamically favorable for the entire range of 1200°C and 2000°C. All three reactions are favorable over ~1750°C. The primary resulting gas from this set of reactions is CO. However,
between 1750°C and 2000°C, if some SiO volatilizes (Eqn. 18) the SiO should form SiC\textsubscript{(s)} and CO\textsubscript{(g)} (Eqn. 17), assuming there is a source of free carbon. So some mass loss was expected for all temperatures based on fiber composition and the thermodynamics of CO and SiO formation. Additionally, as more reactions become favorable more mass loss should occur. Since the fibers were heat treated in flowing argon with minimal CO atmosphere, the CO evolution should be expected to be near maximum.

The charts in Figure 27 show data and trends of the mass loss for both experiments, isothermal and isochronal. Only one batch of each fiber was heat treated, so there is only one data point for each measurement. Each fiber lost progressively more mass as heat treatment temperature increased. The data point for Hi-Nicalon-S 1600° was removed as an outlier, believed to be user error during mass measurement. Mass loss does not exceed 1% until 1700°C and 1800°C heat treatment. Hi-Nicalon-S consistently lost the most mass, followed by Hi-Nicalon. Tyranno-SA3, Cef-NITE and Sylramic are nearly indistinguishable until 1800, where Tyranno sees a larger increase in mass loss. As implied by the thermodynamics above, mass loss trends increase with temperature. There

Figure 26 – Thermodynamic equations and plots for CO and SiO behavior
Adapted from T. Ishikawa and H. Oda

![Gibb's free energy vs. Temperature for Si-O-C system](image)

![Gibb's free energy vs. Temperature for Si-O-C system](image)
is a sharp increase in mass loss at 1800°C for all fibers (except Sylramic) where equation 22 is activated.

4.3.2 X-Ray Diffraction

Looking at Figure 28, the raw XRD patterns for each 1800°C heat treated fiber plus NIST alumina mixtures, several changes are evident compared to Figure 18, the as-received fibers. Figure 28 shows three different sets of X-ray patterns. Figure 28A shows a waterfall stacking of one pattern for each fiber type from the scan range of 33-39°, again to show a detail view of both materials’ (111) peaks. The faulting feature between 33.5° and 35° is relatively unchanged from the as-received state. The statistical variability is again visible in the two alumina peaks, at 35.2° and 37.8°. The Sylramic TiB₂ peak at 34.1° is visually unchanged. Figure 28B shows an overlay of all five 1800°C heat-treated XRD patterns on the same selected range and the legend is still stacked in decreasing apparent crystal size, from top to bottom. There is a striking difference in most of the peak shapes that is pronounced in the overlay plot when compared to the
equivalent as-received plot in Figure 18. The crystal sizes are all much closer in apparent size now. The Hi-Nicalon has sharpened substantially, and all of the (111) peaks appear to be sharper. The quantification of the resulting grain size is discussed later in this chapter. Figure 28C shows the same full scan range of the waterfall plot. The peak broadening trend from the as-received fibers at peak positions of 35.7°, 41.4°, 60°, and 90° is no longer visible at this scale.

Figure 28 – Waterfall and overlay XRD patterns of SiC fibers ground with NIST alumina, after 1800° heat treatment
4.3.2.1 Amorphous Content vs. Temperature

Amorphous fractions for the heat-treated fibers were calculated using XRD patterns and the Spike-In method with Rietveld described in the prior chapter. The 25°C data points are the as-received data from the prior chapter. In general the behavior shown in these charts agrees with the expectations, based on mass loss from volatile species and grain growth. Figure 29A shows the amorphous calculation data points at each temperature for each of the four spiked mixtures. The averages of these points were used to create the plots in Figure 29 to show trends in the data. All five of the fiber types have an exponential trendline that was visually fit as a guide to the eye to declutter the appearance of the compact data spread, shown as dashed lines.

![Figure 29](image)

**Figure 29 – Amorphous Content of SiC fibers vs Temperature of heat treatment**
(A) Data, (B) Average at each temperature with trends

Hi-Nicalon has the highest starting amorphous content among all five fibers, in the as-received state as well as every heat treatment temperature. This is not surprising, since Hi-Nicalon is a Gen-II fiber, although amorphous content drops nearly in half from 15% to 8% at 1800°C. The 1400°C data does not appear to follow the trend of the other
temperatures. This could be due to error in sample preparation for this particular fiber since the other fibers for this temperature are all much closer to their respective trends.

Sylramic and Hi-Nicalon Type-S have very similar starting amorphous values at 8% and 10%, respectively. This is remarkable in that they have different compositions. Hi-Nicalon is nearly stoichiometric, with a carbon/silicon ratio of 1.03, where Sylramic contains both titanium and boron. This would suggest that the changes in amorphous content are independent of the presence of Ti and B. Some variation is visible between these two fibers at each temperature, and amorphous loss for Hi-Nicalon overtakes Sylramic at 1600°C. The Sylramic data appears to have significant variations at 1400°C and 1500°C, but this likely due to lack of statistics.

Tyranno-SA3 and Cef-NITE have 6% and 5% amorphous respectively in the as-received condition and drop to 1% and 0% at 1800°C. The trend of the Tyranno-SA3 data is smooth compared to its green visual fit dashed line. The Cef-NITE data point at 1400°C is rather anomalous compared to the rest of the data, although it is only ~1 percent point away from the trendline. What is remarkable about the Cef-NITE is that it appears to go to zero amorphous content. This is visually verified in the TEM imaging section below.

The amorphous content results for 1500°C are of particular interest bearing in mind the turbine engine application goal for SiC fibers. Even though the mass losses for 1500°C heat treated fibers are all well under 1 percentage point, the amorphous content decrease from as-received to 1500°C is 2 percentage point or more. This suggests significant fractions of the amorphous crystallized. This crystallization is discussed in more detail below.
These results can be supported by TEM images, both in this study and a similar study by Gosset. [7] Although the furnace conditions Gosset used were not identical, they were very close, 2 hours heat treatment in 100°C increments between 1400°C and 2000°C, in a flowing helium atmosphere. In the TEM imaging section below visual qualitative confirmation is discussed in more detail.

4.3.2.2 Amorphous Content vs. Time

In order to study the effect of prolonged heating near the turbine application use temperatures, the five commercially available SiC fibers were subjected to a 20 hour heat treatment at 1500°C. The amorphous content values presented in Figure 30 were calculated using the same technique described in the previous section. The data for the as-received fibers are shown as zero hours, and the data for the 2 hour mark is from the 1500°C data of the prior dataset. The only new data displayed here is from the 20 hour heat treatment. Values shown are again from the average of 4 samples.

Figure 30A shows the 0, 2, and 20 hours plotted with the amorphous content. There is an unexpected positive change in amorphous content between 2 and 20 hours. Based on the increased temperature data showing decreased amorphous, using longer times as an analog for high temperature, the 20 hour amorphous data should be lower than the 2 hour data, not higher. There was a flat change in mass between 2 hour and 20 hour treatments (Figure 27), suggesting nothing volatilized. There was also a flat change in grain size (Figure 34), suggesting amorphous did not crystallize. These two comparisons suggest a flat change in amorphous, not an increase. The remarkable trend is that the 20 hour values are off from expected by a similar amount. To simulate the expected flat response in amorphous, Figure 30B was generated to show a correction to
each fiber’s amorphous content as a dashed line, where all 20 hour data points have been reduced by 3.0%.

There are two possible sources for this discrepancy, experimental error affecting the sample material or error during the analysis process. With regard to the XRD data files, two mixtures of SiC fiber and NIST were made for each fiber type and two separate scans were made of each mixture, which occurred months apart. The patterns were compared in Excel and had significantly different magnitudes of signal. However, this varied set of XRD patterns produced the same amorphous result, within +/- 1% amorphous, which is not enough variation to account for the apparent increased level of amorphous content. Furthermore, refinement files for the 20-hour dataset were created from the 2-hour refinement files to minimize user error. Thus the error does not appear to be pattern or analysis dependent.

With regard to experimental error, any deviation from standard process would have had to affect all fibers nearly equally. For example, the argon gas bottle had to be exchanged during the course of the 20 hour. If this exchange allowed oxygen and
humidity into the furnace chamber there could have been an oxide scale form on the fibers, increasing amorphous content. This would require that SiC mass loss must equal SiO₂ mass gain and that grain size increase must equal grain size decrease from silica formation. Also unique to this 20 hour material, this heat treatment was the last use of graphite boxes, which could have been a source of unknown contamination. Since this heat treatment was singular, e.g. there was not a 10 hour or 100 hour run, further discussion is moot without other data to compare. Some possible remediation steps include; rerunning the same experiment with additional controls, adding different times at the same temperature, or adding other temperatures for comparison, such as a 1600°C 20 hour run. TEM validation would also show evidence of extra amorphous.

4.3.2.3 Grain Size

Two methods for analysis of fiber grain size were considered. The Williamson-Hall method and the Scherrer method. The Williamson-Hall method can account for strain broadening of peaks as well as grain size. There is a strain term (ε) present in the Williamson Hall equation (equation 15) which accounts for the slope seen in W-H plots.

\[
\beta = \frac{K\lambda}{L \cos \theta} + 4\varepsilon \tan \theta; \quad L = \frac{0.94\lambda}{\beta \cos \theta} + \frac{4\varepsilon \tan \theta}{\beta}
\]

Where β is the FWHM, K is known to be 0.94 for spherical crystals with cubic symmetry (such as the cubic 3C polymorph found in SiC fibers), the wavelength of the X-ray beam photons (λ) is 0.154278 nm for copper X-rays, θ is the Bragg angle, and L is the crystallite size. Solving for L allows quantification of crystallite size in nm, which is considered to be the cube root of volume. The Scherrer equation (Eqn. 24) is a simplified version of the Williamson Hall equation since it does not use the strain term.
\[
\beta = \frac{K\lambda}{L \cos \theta} = \frac{0.94\lambda}{L \cos \theta}; L = \frac{0.94\lambda}{\beta \cos \theta}
\]  \[24\]

Comparing equation 23 to the \([y = mx + b]\) equation for a line, the strain (\(\varepsilon\)) represents the coefficient \(m\). The overlay of the Williamson-Hall plot for each as-received fiber is shown in Figure 31. There are strain and faulting effects visible in the 200, 400, and 331 peaks that tend to incline the linear average of all peaks into a negative slope. [7] As such, the Williamson-Hall method is problematic for SiC fiber due to the effects of strain and faulting. So crystallite sizes for all fibers were obtained using the Scherrer equation and Williamson-Hall plots, but not the Williamson-Hall equation. [55-57] Specifically, the 200, 400, and 331 peaks are associated with smaller crystal lengths because of faulting. As such they were discounted from the grain size calculation. The seven peaks used in the Scherrer equation analysis for grain size were the 111, 220, 311, 222, 420, 422, and 511 peaks.

Hi-Nicalon is known to be a very finely grained fiber. These grains are on the order of a few nanometers, only consisting of a few unit cells. This is present in the XRD pattern where the FWHM for many peaks is very large. These large FWHM translate to the W-H plot as very tall peaks relative to the other larger grained fibers. The effect is so
pronounced that three of the fibers are stacked nearly on top of one another when Hi-Nicalon is included on the plot (Figure 31, left). To show the differences in the other fibers, Hi-Nicalon was removed (Figure 31, right). Based on how close the plot points are for Tyranno-SA3, cef-NITE, and Sylramic it might be expected that the grains sizes will be similar. However, since grain is inversely related to FWHM, the closer the FWHM value gets to zero the higher the grain size will be. (This can be seen in Figure 33 and Figure 34, where there is substantial difference in starting grain size among all the fibers.) There are substantial differences in the behavior of the fibers with regard to changes in heat treatment temperature shown in Figure 32. The as-received fibers are plotted in black, and the heat-treated fibers are plotted in increasingly darker shades of orange which correspond to increasing heat treatment temperature. Some qualitative assertions can be made about the evolution of the fiber microstructure based solely on the trends apparent in the W-H plots. The Hi-Nicalon sees a rapid change as low as 1400°C. Hi-Nicalon-S, Cef-NITE, Tyranno-SA3, and Sylramic are all fairly stable up to 1600°C, and then see rapid changes up through 1700°C and 1800°C. Another interesting result was the correlation of precursor behavior shown in the bottom-right of Figure 32. Tyranno-SA3 and Cef-NITE are known to use an identical precursor and similar processing route. The
Figure 32 – Williamson Hall plots for each fiber, before and after heat treatment and comparison of Cef-NITE as received and Tyranno-SA3 after 2 hrs, 1800°C

overlap of 1800°C heat-treated Tyranno-SA3 plot with the as-received Cef-NITE plot alludes to a correlation with Cef-NITE merely being a heat-treated processing variant of Tyranno-SA3. The grain size data points shown in Figure 33 and Figure 34 are based on the output of the Scherrer equation using the same peaks described above: 111, 220, 222, 311, 420, 422, 511.
The plots shown here prove out many of the qualitative suggestions above. There is some uptick in grain size for all fibers between as-received and 1400°C. While Hi-Nicalon’s value continually increases, the other four fibers are fairly from 1400°C to 1600°C. The notable exception here is that Cef-NITE appears to decrease in grain size, which could point to substantial nucleation of amorphous material during the 1600°C heat treatment that did not occur in the lower treatments. All fibers see an increase in grain size between 1600°C and 1700°C, and a stronger increase yet between 1700°C and 1800°C. The total relative change in grain size from as-received condition to 1800°C varies per fiber and can be summarized by simple multiplicative factor; Hi-Nicalon
increased the most with a 15x change, then Hi-Nicalon-S with a 5x change, and finally the other three fibers with roughly a 2x change each.

The effect of heat treatment at 1500°C in the large graphite furnace for 20 hours versus 2 hours is largely insignificant. Statistically, there are not enough data points to support any change in grain size for any of the fibers, although Hi-Nicalon appears to have increased in size the most of the five fibers. Since L in the Scherrer equation is considered to be the cube root of volume, the values for L will underestimate actual crystallite diameter as observed by TEM. If L^3 is used to generate a total volume this indicates a cubic volume, where equiaxed crystals will have a more spheroidal shape. Assuming a spherical grain, comparing cubic volume to spherical volume suggests an error of 24% from just the assumptions in Scherrer equation.

![Grain size vs. Heat-treatment Time](image-url)
4.3.3 Mass Loss vs. Crystallinity

To analyze changes in the amorphous material as a function of heat treatment temperature, the fiber mass loss data was compared with amorphous content values. During heat treatment, a fraction of the fiber mass volatilized in the form of CO and SiO. The fraction of the amorphous material that did not volatilize or remain amorphous must have crystallized. The formula used to generate the crystallized fraction of a given fiber is shown in equation 25; where $\Delta m$ is the initial fiber sample mass minus the fiber mass after heat treatment, $AC_o$ is the amorphous content of the as-received fiber, and $AC_T$ is the amorphous content after heat treatment. The $AC_T$ term is a percentage based on the fiber mass after heat treatment, so it must be normalized to the initial mass to create an accurate representation of a given sample’s fiber mass fractions.

$$Crystallized\ Fraction = AC_o - (\Delta m) - \frac{AC_T}{1 + (\Delta m)}$$

[25]

The resulting values are plotted in Figure 35 with linear trendlines. The chart only includes the calculations for 1500°C through 1800°C. The 1400°C amorphous content heat treatment data showed significant variability, making the crystallization fraction also vary significantly, for this reason this temperature was removed to show more realistic trends in the other temperatures. To show a more complete figure, the mass loss for Hi-Nicalon-S at 1600°C was interpolated from the 1500°C and 1700°C values.

The clear trend for all fibers shows positive correlation between crystallization fraction and increased temperature. The mass loss appears to show a non-linear increase with temperature (Figure 27), which should create a negative slope to crystallization fraction. The $AC_T$ term (Figure 29) must be diminishing more rapidly with temperature,
leading to an overall positive slope in crystallization fraction. The mass loss in the
denominator also contributes to the rapid reduction of this term with increasing
temperature. Hi-Nicalon and Hi-Nicalon-S consistently crystallized more than the other
three fibers, regardless of temperature, and have very similar crystallized fractions.
Tyranno-SA3, Cef-NITE, and Sylramic also show similar trends in crystallized fraction,
moving from ~1% to ~3% with increased heat treatment temperature. There appears to be
a clustering of trends here based on original fiber manufacturers. Hi-Nicalon and Hi-
Nicalon-S show similar crystallization fractions and are both originally Nippon fibers.
Similarly, Tyranno-SA3 is an Ube fiber, both Cef-NITE and Sylramic are based on Ube
fibers, and show similarities in crystallization fraction.

Figure 35 – Crystallized Fraction of Fiber vs. Heat Treatment Temperature
4.3.4 SEM Imaging

4.3.4.1 Cef-NITE

Imaging of fibers after heat treatment was not exhaustive, only a few select fibers were SEM imaged. Of particular interest was the Cef-NITE fiber, whose apparent amorphous content dropped to zero. Figure 36 shows four fracture-surface images of Cef-NITE. Panel A and B are the same fiber, in as-received condition. A is taken in back-scatter to show Z-contrast and B is taken in secondary to discern surface features. Similarly, panel C and D are the same fiber, in the 1800° heat treated condition. C is taken in back-scatter to show Z-contrast and D is taken in secondary to discern surface features. In the prior chapter, devoted to the as-received fibers, it was illustrated that Cef-NITE has a strong surface-to-core variation and amorphous content is more prevalent in the core of the fiber. The grains stand out in relief and the grain-boundary triple-points are recessed. In the back scatter images, the excess carbon in the amorphous material can be seen in black. These areas coincide with the slightly darker triple points in the secondary images.
In panel C there appears to be far less black in the center of the fiber for as-received compared to panel A. This implies that there is substantially less free carbon left in center of the fiber after heat treatment. This agrees with the thermodynamics of CO and the mass loss seen prior. There also appear to be fewer dark triple points in panel D compared to that of panel B. There does not appear to be much if any change in the surface appearance after heat treatment.
4.3.4.2 Hi-Nicalon Type-S

Hi-Nicalon-S is of particular interest to the CMC development community as a production fiber for turbine engine applications. It is of particular interest in this study as the fiber that lost the most mass during heat treatments, and it was the test fiber for the small graphite furnace. Figure 37 shows a fracture surface image of Hi-Nicalon-S heat treated at 1800°C captured in secondary mode. There is a porous appearance to both the cross section and the outer diameter surface. Gasses escaping the dense fiber would have an easier path if channels existed in the grain boundaries and triple points. With the uniform distribution of amorphous content in Hi-Nicalon-S, described in the as-received section, the amorphous content distribution is the same at the core and on the surface of the fiber. As the SiOC decomposes at high temperature to SiC and CO\(_{(g)}\), the surface amorphous would partially crystallize and partially volatilize, leaving behind a more dense structure, and a hollow region. As heat treatment time continues, this pore would continue to grow towards the center of the fiber unimpeded, since the amorphous
distribution is uniform and this is well below the temperature at which SiC is known to sinter or densify.

### 4.3.4.3 Extreme temperature transformation

At the outset of the heat treatment phase of this study it was decided that the upper limit of fiber heat treatment would be explored. Figure 37 shows two image results for 1900°C, 2000°C heat treatments. These two images show visibly transformed fibers which clearly cannot withstand these extreme temperatures. Probing these fibers further would not yield a representative picture of changes to a fiber, since there is no fiber left to speak of. As such, work on these fibers in XRD and TEM was not undertaken.

Image A shows Hi-Nicalon fiber after 1900°C heat treatment, as seen in secondary mode. The remnants of fibers can still be seen, but in general the fiber has completely transformed. The large recrystallized particles were probed by EDS and determined to be SiC. The fiber-shaped material remaining was nearly all carbon. After vaporization and redeposition of fiber material into the larger particles all that remained of the original SiC fiber was a weak carbon fiber.

Image B shows a Sylramic fiber heat treated at 2000°C, as seen in back-scatter mode. The overall columnar fiber shape is still visible, but otherwise this fiber is also completely transformed. Both phases seen were examined by EDS. The gray platelet objects in the column are SiC that has experienced dramatic grain growth, where some of the grains appear to have grown to 10µm. The white particles are TiB₂ particles that have also experienced significant grain growth.
TEM Imaging

TEM images of several fibers were taken to qualitatively confirm the results from the XRD amorphous content and grain size analysis. The three fibers chosen were Hi-Nicalon Type-S, Tyranno-SA3, and Cef-NITE. TEM allows not only confirmation of XRD values, but a visual cue to the evolution of the microstructure at extreme temperatures.

Below, in Figure 39, is an image of the final stage of a FIB prepared fiber sample in SEM and the same fiber at the same scale in TEM. The fiber shown is a Cef-NITE fiber heat treated to 1800°C. The grains are only visible in the SEM image where grains are preferentially oriented for electron channeling to occur. In the interest of qualitative validation of grain size, TEM is clearly needed over SEM.
Tyranno-SA3 saw changes in amorphous content from an initial value of 6% down to 1% at 1800°C heat treatment, as well nearly doubling in grain size. To gauge the validity of this amorphous value, TEM images were taken of both fiber conditions. Figure 40 shows one half of a fiber cross-section and a full fiber cross-section for the 1800°C fiber. The surface-to-core variation is visible in both images. The apparent concentration of amorphous in the center of the fiber decreases in the 1800°C fiber. Since both images use the same scale, the grain size increase is easy to discern, and has arguably doubled from the as-received to the high temp condition.

The appearance of these cross sections is somewhat misleading with regard to amorphous fraction. The apparent fraction of amorphous in the 1800°C image may seem larger than 1% in this image, but this represents a 2-dimensional slice of a 3-dimensional cylindrical fiber. Figure 41 shows an example of this effect using four graphics labelled A-D and the supporting example equations beneath. Panel A shows the TEM image as visually subdivided into rectangular areas with only one half of the section is considered.

Figure 39 – Scanning vs. Transmission electron microscopy in a SiC fiber
The numbers in the rectangles represent a visual estimate of the amorphous fraction, ranging from zero amorphous at the fiber surface to 4% in the fiber center. Each panel has a radius designated from the center of the fiber. This rectangle must be revolved 360° to represent the actual fiber, as indicated in panel B. This revolution yields a cylinder, with equation for volume indicated in panel C. This would create a series of concentric cylinders, all with a common height, h. The comparison can be shown with this common h divided out, shown in panel D. The areas of the remaining circles are multiplied by their respective amorphous fraction and the sum is divided by the total circular area. The result of this exercise is that for an apparent center amorphous fraction of 4%, the actual amorphous value for this fiber would be 1.2%. This analysis is specific to fibers with surface-to-core variation, such as Tyranno-SA3 and Cef-NITE.
Cef-NITE had a final amorphous value of 0% after 1800°C heat treatment. TEM images were taken of this fiber to confirm this result. To have a basis for comparison, two other fibers were imaged with amorphous values of just above 0%. Cef-NITE 1700°C and Tyranno-SA3 had amorphous values of 2% and 1% respectively, so these were chosen for imaging. The three fiber samples shown in Figure 42 are ordered top to bottom, 2%, 1%, and 0% amorphous. There is some amorphous content visible in Cef-NITE 1700°C. Those same general regions in Tyranno-SA3 1800°C appear somewhat darker, implying less amorphous content. The amorphous content is visually completely crystallized in Cef-NITE 1800°C, except for a few isolated regions. From a volume fraction perspective, these regions will not affect the XRD amorphous fraction value. Cracking is visible from change in density due to volatilization and crystallization of amorphous content.

Figure 41 – Comparison of rectangular image apparent amorphous fraction with more accurate circular amorphous fraction using a normalized fiber radius ($r_o$)

\[
A.C. = \sum_{i=0}^{4} \frac{A.C._i}{\pi r_o^2} = 1.2\%
\]

<table>
<thead>
<tr>
<th>$r_i$ (%)</th>
<th>A.C.$_i$ (%)</th>
<th>A.C.$<em>i$ = $0.00* (\pi r^2 - \pi r</em>{i-1}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.50%</td>
<td>$A.C._4 = 0.04*(\pi r_4^2)$</td>
</tr>
<tr>
<td>0.4</td>
<td>1.13%</td>
<td>$A.C._3 = 0.03*(\pi r_3^2 - \pi r_4^2)$</td>
</tr>
<tr>
<td>0.6</td>
<td>1.26%</td>
<td>$A.C._2 = 0.02*(\pi r_2^2 - \pi r_3^2)$</td>
</tr>
<tr>
<td>0.8</td>
<td>0.88%</td>
<td>$A.C._1 = 0.01*(\pi r_1^2 - \pi r_2^2)$</td>
</tr>
<tr>
<td>1.0</td>
<td>0.00%</td>
<td>$A.C._0 = 0.00*(\pi r_0^2 - \pi r_1^2)$</td>
</tr>
</tbody>
</table>
In a similar work, studying primarily grain size of SiC fibers (not amorphous content), Gosset et al presented TEM images of Hi-Nicalon-S and Tyranno-SA3. They presented TEM images of these fibers in both the as-received state and heat treated to 1600°C and 1800°C. [Gosset Figures 8 and 9, [7]] Their images of Hi-Nicalon-S show 

Figure 42 – TEM validation of 2%, 1% and 0% amorphous content values
the characteristic amorphous content and its presence reducing with higher temperature heat treatment. The Tyanno-SA3 images they show are also in line with the results of this work, where the amorphous is present in the as-received fibers, and diminishes markedly at 1600°C and yet more with 1800°C. From the perspective of amorphous distribution, it is unknown from which area of fiber the TEM samples were produced. This is problematic for a suitable direct comparison between the Gosset Tyranno-SA3 images and the Tyranno-SA3 images presented in this work.

4.4 Conclusions

During the characterization of heat treated SiC fibers, it was shown that changes in mass, grain size, and amorphous content are interconnected. XRD and the Spike-In technique with Rietveld refinement were used to quantify amorphous content as a function of both time and temperature. While varying heat treatment temperature, grain size and crystallized fraction increased with temperature, while mass and amorphous content decreased. Grain size was stable up to 1600°C then increased dramatically for 1700°C and 1800°C for all fibers. Amorphous content for all fibers trended with an exponential curve, with Cef-NITE seeing amorphous content go to zero. While varying heat treatment temperature, grain size and mass loss were statistically the same for 2 hours and 20 hours. The 20 hour heat treatment results for amorphous content proved to be unexpected and there is a suspicion of either error in the data analysis or flawed experimental sample. Crystallized fraction increased with heat treatment temperature for all fibers. SEM imaging showed intergranular vents on the surface Hi-Nicalon-S, and observable changes in carbon near the amorphous regions. These observations of gaseous escape vents and changes in carbon agree with the predicted thermodynamics of CO
volatilization. The cross-sectional appearance of a TEM image can be misleading, but features seen in TEM images of SiC fibers support the amorphous content, grain size, and crystallized fraction changes seen in XRD pattern analysis.

5 Conclusions

The model powder system Spike-In validation proved a good predecessor to the study of commercially available silicon carbide fibers. As proposed in the introduction, the faulted nature of silicon carbide played a large role in the XRD analysis of these SiC fibers, even if the presence of the faulting only meant the faulted peaks were removed from amorphous content analysis. The study of the as-received and heat treated forms of the fibers yielded largely self-consistent results, in line with thermodynamics and existing literature. The primary exception is the apparent error associated with the 20 hour heat treatment amorphous content results.

It is unclear if this approach to quantifying amorphous content has been refined enough for actual production usage. The error in the 20 hour fiber is problematic and must be addressed. However, trends in amorphous content can be observed as well as trends in grain size and crystallized fraction. It is important to note that this approach also requires the use of a well-defined, consistent process for the Spike-In technique with Rietveld refinement and that the material system under investigation is a highly crystallized system. This study has tied amorphous content to processing, and indirectly performance, but much more work is needed to complete the connection.

There are several avenues for this work to continue. The apparent systematic error associated with the 20 hour heat treatment amorphous content results needs further investigation; such as TEM verification, rerunning the heat treatment, or adding
temperatures to the test matrix. The defect control of SiC polycrystalline fiber synthesized from poly-alumino-carbo-silane is of primary interest to the manufacturers of Tyranno-SA3. [54] Since the evolution of CO is considered the primary mass loss route, an experiment could be devised to control the partial pressure of CO during heat treatment. There is a need to tie amorphous content, grain size, and other heat treatment behavior to performance, specifically correlation to mechanical properties, tensile strength and modulus using mechanical testing. With regard to the composition and distribution of amorphous content in SiC fibers EDS is needed to compare composition to these results. Finally, a deeper study of Rietveld refinement would be advantageous; using a second Rietveld tool, adding parameters (such as strain) to the process described above or creating software algorithms to allow better fitting of faulted regions.
6 References


