ABSTRACT: Silicon carbide (SiC)-based ceramic matrix composites (CMCs) are utilized for their refractory properties in the aerospace industry. The composition and structure of these materials are crucial to maintaining the strength, toughness, oxidation, and creep resistances that are desired of silicon carbide. This work analyzes the chemical composition of the matrix in batches of SiC/SiC (silicon carbide fiber-reinforced silicon carbide matrix) minicomposites that are processed by chemical vapor infiltration of the BN interphase and SiC matrix on single Hi-Nicalon Type S fiber tows using a range of processing parameters. The analysis was performed here to investigate the potential causes of variation in matrix tensile strength in the various batches of minicomposites. Six different morphologies present in the silicon carbide matrix were observed: smooth, nodular, rough nodular, bumpy, nucleated, and plate-like. It was found that high-matrix tensile strength minicomposite batches contained solely the smooth morphology, while low-matrix tensile strength minicomposite batches contained a variety of other morphologies. FIB/TEM was used to study the atomic and crystal character of each individual morphology. Smooth SiC is oriented by the (111) planes and is primarily SiC, while the other morphologies are randomly oriented and contain significant oxygen. These results match the tensile strength tests, which pointed to smooth SiC as the strongest matrix material.

1. INTRODUCTION

Ceramics have low density and thermal expansion combined with relatively high hardness and oxidation resistance at operating temperatures. These properties have led to the utilization of ceramic materials in a variety of industries, but the inherent brittleness and resultant lack of toughness limit the ultimate effectiveness.1 Ceramic matrix composites (CMCs) are a class of materials that pair the strength and refractory properties of ceramic materials with the toughness and durability of composites.2,3 CMCs consist of a ceramic matrix which is reinforced by ceramic fibers that run continuously through the matrix. If the matrix and fiber are strongly bonded, the composite will still exhibit brittle behavior, similar to a monolithic ceramic. The weak interphase, typically a thin coating of BN or C on each fiber of 200−1000 nm thickness, acts to debond the fiber from the matrix. This debonding facilitates load transfer, crack deflection, debonding, and sliding between the matrix and the fibers to enhance the toughness of the composite.4 There are many industries that employ CMCs for a variety of applications.5−7 To meet that demand, there are several different compositions that have been employed for CMC applications.8−17 Silicon carbide (SiC) matrix deposition on SiC fibers has been chosen for evaluation in this study because of the influence of matrix quality on strength, refractory properties, creep, and oxidation resistance of SiC/SiC CMCs.18−20 These properties are highly dependent on the quality of silicon carbide that is deposited. Impurities, such as oxidation, will degrade the SiC material and render it ineffective.21−23 This study aims to analyze pure and impure SiC deposited on SiC fibers via chemical vapor infiltration (CVI) and act as a reference for future identification of high quality SiC materials.

Previous studies from the UCONN Advanced Ceramics Research Laboratory have produced SiCf/SiC minicomposites using CVI at atmospheric pressure.24 However, minicomposites fabricated under presumed identical conditions yielded different materials.25 Scanning electron microscopy (SEM)
examination revealed a range of surface morphologies, varying from smooth to nodular. Tensile strength tests revealed that smooth SiC was better for minicomposite strength, while the other morphologies were significantly weaker. A method to both study the infiltration procedure and analyze the varied morphologies was required. The infiltration procedure, tensile testing, and fracture surface SEM can be found in Petroski et al. 25

The goal of this study was to understand the structural and atomic characteristics of each SiC morphology. Focused ion beam (FIB) microscopy was the technique chosen for analysis of these SiC minicomposite matrix coatings. The nodules and other surface features are on the micron scale, so techniques such as X-ray diffraction (XRD) and X-ray fluorescence cannot be used to determine differences in atomic and structural characteristics between morphologies. FIB is a process that can manipulate samples through the use of an ion source that can be localized with nanometer resolution. One such manipulation is the preparation of samples for transmission electron microscopy (TEM), called lamella, which are a few-micron-sized rectangular structures which are thinned to 30–100 nm to allow for TEM analysis. Pairing TEM analysis with energy dispersive X-ray (EDX) spectroscopy and selected area electron diffraction (SAED) offers the opportunity to study atomic and structural characteristics of highly localized areas. FIB preparation for TEM examination thus acts as a site-specific analysis tool that yields information at a scale unattainable by other available techniques. The combined techniques will point to specific atomic and structural differences between the SiC surface morphologies. Accomplishing this will not only yield structural information of high-quality SiC and impure SiC but also develop insight into the growth mechanism of SiC and how impurities may foster.

2. EXPERIMENTAL SECTION

2.1. Materials. The materials considered in this study are minicomposites composed of Hi-NICALON Type S SiC fibers (produced by NGS Advanced Fibers Co., Ltd. Toyoma, Japan.), a boron nitride (BN) CVI interphase, and an atmospheric CVI-applied SiC matrix. Methyltrichlorosilane (MTS, CH₃SiCl₃ 98%) was purchased from Gelest, Inc (Morrisville PA). Ultrahigh-purity nitrogen and ultrahigh-purity hydrogen were purchased from Airgas, Inc.

2.2. SiC Infiltration. Petroski et al. describes the process for SiC and BN infiltration in detail. 25 CH₃SiCl₃ (l) was loaded into a glass bubbler and H₂ (g) was flowed through the bubbler to carry the CH₃SiCl₃ (l) vapor into the reactor. 25 Temperature, CH₃SiCl₃ (l) depth, and H₂ (g) flow were all varied throughout the study of minicomposite batch fabrication. 25 Temperature ranged from 1000–1100 °C and the H₂ (g) flow ranged from 5–30 sccm. The depth of the CH₃SiCl₃ solution in the bubbler was the main determinant for the gas saturation and thus the concentration, of the CH₃SiCl₃ (l). The maximum CH₃SiCl₃ (l) depth utilized was 14 cm, and the minimum depth was 1 cm.

2.3. Characterization. SEM at UCONN was conducted on a Teneo low-vacuum scanning electron microscope (LVSEM) with 5 kV and 0.4 nA for accelerating voltage and current, respectively. Depth analysis at UCONN was performed using a Thermo Fisher Helios Nanolab 460F1 FIB equipped with a gallium-ion column, a Multi-Chem protective cap deposition, an Easy-Lift needle, and a scanning transmission electron microscopy (STEM) detector. The FIB was operated at 30 kV ion accelerating voltage and 7.7 pA to 2.4 nA ion current. Transmission electron microscopy (TEM) was performed at UCONN using a Talos F200X microscope with 200 kV accelerating voltage, equipped with an EDX detector and SAED capability. Auger depth profiles were determined with an RBD Instruments PHI 660 scanning Auger electron spectroscopy system.

2.4. FIB Lift-out Procedure. The whole process was performed under vacuum of ~10⁻⁶ Torr. Opening of the microscope chamber was only performed for sample loading and removal.

An area on the surface of the minicomposite that represented the desired morphology was located using the electron beam, and a protective platinum cap with dimensions 10 μm × 1 μm × 2 μm was deposited on the surface. The gallium ion beam was used to remove a 10 μm × 10 μm square of matrix material on both sides of the platinum deposition with a targeted depth of 5–10 μm. On the surface of the sample, there is now a ~1 μm-thick rectangle of isolated material, referred to as the lamella. A U-cut is then performed perpendicular to the sample, angled towards the lamella face and not the surface. The gallium ion source cuts out three rectangles shaped into a U, all with a width of ~0.8 μm and length of ~5 μm. The lamella is now only attached to the remainder of the sample by two corners on the lamella surface. The Easy-Lift needle is brought down in contact with the lamella surface and welded to the lamella with a platinum cap from the Multi-Chem needle. Once the lamella is connected to the needle, gallium ions remove the last attachments of the lamella to the sample, which allows removal of the Easy-Lift needle with the lamella attached.

While remaining under vacuum, the Easy-Lift needle is brought to the flip stage and brought into contact with the TEM grid. The lamella is then welded to the TEM grid using a platinum cap from the Multi-Chem needle, and then the gallium ion source mills away the connection of the lamella from the Easy-Lift needle. The Easy-Lift needle is removed from the area, and gallium ions are used to remove material from both sides of the lamella until the thickness reaches around 100 nm. The STEM detector is then inserted, and the lamella thinning is continued until the electron beam transmits through the lamella. The finished lamella is then removed from the FIB and brought to the TEM instrument for further analysis. A visual representation of this process is displayed in Figure 1.

3. RESULTS

3.1. Tensile Testing and Fracture Surfaces. Fast fracture monotonic tensile tests were conducted on the SiC/SiC ceramic matrix minicomposites at NASA to understand the effect of various processing parameters on the tensile behavior across batches of minicomposites. The plot of normalized acoustic emission energy of each tested minicomposite versus stress applied to each tested minicomposite is shown in Petroski et al. 25 The labels correspond to two different batches; batch 1 (AE 1) and batch 3 (AE 3), where each batch had multiple test replicates. Both batches were 8 in.-long, SiC/BN/SiC minicomposites but were fabricated in separate but similar processes. SEM revealed that the SiC matrix in batch 1 was composed of primarily smooth SiC, while nodular SiC significantly dominated the matrix in batch 3. Batch 1 and batch 3 had extremely different tensile behavior, despite identical constituent types and volume fractions. There
is a slight difference in tensile behavior within each batch, which can be attributed to the random porosity shape size and distribution in the minicomposite. However, there is still a clear difference in the overall damage initiation, progression, and ultimate failure of batch 1 and batch 3. Batch 1 had a smooth SiC morphology with an average SiC matrix cracking strength of 248 MPa and an average ultimate tensile strength of 541 MPa, whereas batch 3 had a nodular SiC morphology with an average SiC matrix cracking strength of 147 MPa and an average ultimate tensile strength of 226 MPa. Thus, batch 3 exhibits lower tensile behavior than batch 1, indicating the effect of smooth versus nodular SiC morphology.

SEM images of the fracture surfaces of batch 1 and batch 3 post tensile testing are also shown in Petroski et al.25 In batch 3, the majority of fractured fibers splintered at the nodules, indicating that those may structurally contribute to the weaker tensile strength. Additionally, smooth SiC displayed a columnar growth throughout the matrix, while nodular SiC displayed a much more randomly oriented structure. This effect may be correlated to the weaker strength, and this phenomenon is confirmed by the FIB & SAED work here.

3.2. Silicon Carbide Morphologies. SiC minicomposites from batch 1 and batch 3 were sectioned, inch-by-inch, and studied for any indications regarding their different tensile behavior. Batch 1 SiC minicomposites demonstrated smooth SiC with minimal porosity and uniform coating. Upon examination of batch 3 SiC minicomposites, six different morphologies were identified within the surface of the matrix. The morphologies were identified as smooth, nodular, rough nodular, bumpy, nucleated, and plate-like (Figure 2).

Each SiC minicomposite was 8 in. in length, and the bubbler depth of methyltrichlorosilane was varied to affect the gas saturation and methyltrichlorosilane concentration.22 The smooth SiC sample was taken from the 4th inch of the minicomposite, with a depth of 7 cm of methyltrichlorosilane. Nodular SiC was taken from in. 6, with a depth of 14 cm. Rough nodular SiC was taken from in. 2, with a depth of 13 cm. Bumpy SiC was taken from in. 5, with a depth of 13 cm. Nucleated SiC was taken from in. 2, with a depth of 12 cm. Plate-like SiC was taken from in. 3, with a depth of 13 cm. Each measurement is from the front of the reactor, as per the reactor setup.25

To examine the matrix thickness, fracture surface SEM images were taken (Figure 3). Each matrix has a minimum of 10 μm SiC surrounding the fibers, yielding more than a sufficient amount of material for FIB lift-outs.

3.3. Cross-Sectional Analysis. FIB lift-outs for TEM analysis were performed on all six SiC morphologies. The process to prepare TEM samples for all morphologies is detailed in the Experimental Section. Prepared lamellae were then analyzed under TEM, and high-angle annular dark field (HAADF) images of all six morphologies were taken (Figure 4).

Smooth SiC displays crystallites in the lamella and a platinum cap on top of the lamella. The thick areas on the edges correspond to non-thinned SiC material. This is the only lift-out that has such significant remnants of the platinum cap, and to be welded to the side of the TEM grid. However, the difference between smooth SiC and the rest of the morphologies is clear. Each following lift-out shows a darker feature below the surface, indicating a region with lighter atomic density.26

Rough nodular SiC shows a thick layer of the darker area around 0.5 μm below the surface. Nodular SiC shows dark circles 3–4 μm below the surface. Bumpy SiC displays a thin dark layer about 3 μm below the surface. Nucleated SiC shows two unique dark layers, 0.3 and 3 μm below the surface. Plate-like SiC has a dark layer around 1 μm below the surface. Despite these dark layers, the rest of the lamellae looks familiar to the smooth SiC lamella.
3.4. Morphological Oxygen Content. EDX maps were taken of all six lamellae to identify the atomic character of the darker area, relative to the majority of the lamella (Figure 5). The lamellae were studied for their silicon, carbon, and oxygen content. Smooth SiC showed minimal oxygen content, but all other morphologies displayed oxygen below the minicomposite surface. Each dark area in the lamellae was shown to have significant oxygen character relative to the rest of the sample. For all maps, green indicates silicon, blue indicates carbon, and red indicates oxygen.

Smooth SiC displayed minimal oxygen in the lift-out. Rough nodular SiC had a thick layer 1 μm below the surface that contained more oxygen than the remainder of the lamellae. Nodular SiC had circles 3–4 μm below the surface with oxygen located in that area. Bumpy SiC had a thin layer 3–4 μm below the surface where oxygen was present. Nucleated SiC displayed two layers where oxygen was contained, one at 0.5 μm, and another at 3.5 μm below the surface. Plate-like SiC contained a thin layer 1 μm below the surface with significant oxygen character.

Auger depth profiles were performed on two different CVI-SiC minicomposites, one containing rough nodular morphologies and another containing nucleated morphologies, to confirm the oxygen presence below the surface (Figure 6).

These Auger depth profiles were obtained on separate sections of the minicomposites than the ones analyzed in FIB lift-outs. The atomic percentage of silicon, oxygen, and carbon was graphed as a function of sputtering time in minutes. The depth profile for rough nodular SiC shows a rise in oxygen atomic percent around 120 min of sputtering, which is correlated with a sharp rise in silicon atomic percent and sharp decline in carbon atomic percent. The depth profile for nucleated SiC shows two increases in oxygen content, around 75 min and 150 min of sputtering. This matches the two oxygen-rich layers in the EDX map. In both cases, the silicon atomic percent drops and the carbon atomic percent rises when oxygen appears.

3.5. Morphological Crystal Structure. Electron diffraction patterns were collected from all six lamellae to investigate the crystal structure of each SiC matrix (Figure 7).

Smooth SiC displayed an ordered crystal structure with a d-spacing of 2.5 Å in each layer, which can be indexed to the (111) planes of cubic SiC, also referred to as β-SiC. There is a substantial difference between the smooth coating and the rest of the morphologies; while the smooth one displays a pattern of ordered diffraction spots correlating to a crystal structure, all other morphologies exhibit diffraction rings. The presence of diffraction rings indicates a randomly oriented crystal structure.27 There were degrees of this random orientation; rough nodular SiC displays the formation of rings from diffraction spots but bumpy SiC has clear rings and no intense spots. Additionally, while those randomly oriented patterns were all indexed to indices of β-SiC, different morphologies exhibit different indices. All exhibited the (111), (220), and (311) planes, but the (200) planes were only present in nodular SiC and plate-like SiC.

4. DISCUSSION

This work details a thorough examination of SiC matrix morphology. Investigation of the surfaces of SiC minicomposite...
sites discovered six different morphologies, with smooth SiC exhibiting higher tensile strength than the rest. A FIB lift-out procedure for TEM was used to analyze the individual morphological characteristics, specifically atomic percentage and crystal structure, as other techniques cannot yield similar information on the scale of the matrix morphologies.

EDX was employed to analyze the silicon, carbon, and oxygen content of each morphology lift-out. Each lift-out was greater than 5 μm in depth, thus yielding sub-surface information for each morphology. Smooth SiC displayed minimal oxygen content, which likely arose from removal from a vacuum atmosphere to transport the lift-out from FIB to TEM. Every other morphology exhibited an oxygen-rich matrix below the surface. Auger depth profiles confirmed the presence of oxygen in a layer in rough nodular SiC and in two layers in nucleated SiC.

Oxygen was likely introduced into the system either through the contamination in the CH₃SiCl₃ or halting and subsequent resumption of SiC deposition. The methyltrichlorosilane is 98% pure and can oxidize from atmosphere exposure. The higher concentration of methyltrichlorosilane saturation in the process led to a rougher morphology. The greater amount of methyltrichlorosilane in the system would increase the amount of methyltrichlorosilane contaminants that are present as well.

Thus, the more the methyltrichlorosilane injected into the system, the more the oxygen is present in the system as well. This would explain the corresponding link between a rougher morphology and increased methyltrichlorosilane injection. The arrangement of oxygen in layers that is present in all oxygen-rich minicomposites, excluding nodular SiC, indicates surface oxidation that is then deposited upon. On some occasions, minicomposite fabrication was halted by quenching methyltrichlorosilane flow and keeping the system under a nitrogen atmosphere. This would allow any oxygen from the methyltrichlorosilane contaminants to react with the SiC minicomposite surface, without competition from additional SiC deposition. The reaction for SiC formation from methyltrichlorosilane is shown below, contrasted with the oxidation of SiC to SiO₂ in the presence of oxygen.

\[
\text{CH}_3\text{SiCl}_3(l) \rightarrow \text{SiC}(s) + 3\text{HCl}(g)
\]
\[
\text{SiC}(s) + 2\text{O}_2(g) \rightarrow \text{SiO}_2(s) + \text{CO}_2(g)
\]

The Auger depth profile for rough nodular SiC shows an increase in silicon content and a decrease in carbon content with the appearance of oxygen around 150 min of sputtering. This indicates the presence of SiO₂ along with SiC. The depth profile for nucleated SiC shows a decrease in silicon content and an increase in carbon content for both appearances of oxygen, the first at 75 min of sputtering and the next at 150 min. This points to a much lower presence of SiO₂ than rough nodular SiC, and the oxygen is tied to the carbon content. The SiO₂ character originates from the protective oxidation formed on the surface of SiC when interacting via oxidation. However, while that oxidation occurs, the infiltration process of SiC is still occurring, which causes coating on top of the
surfaces. SiC is an extremely strong refractory material, but nodules act as stress concentrators compared to smooth surfaces. 

If methyltrichlorosilane is decomposing and methyltrichlorosilane or degraded byproducts present in the carbon-rich oxygen area may be caused by impurities of the methyltrichlorosilane or degraded byproducts present in the boundary layer. If methyltrichlorosilane is decomposing and diffusing through the boundary layer that is now containing oxygen, there are many compounds besides SiC that could form and find a way into the matrix.

The various morphologies and the oxygen content appeared to affect the tensile strength and are the probable cause of the strength difference. The presence of surface features such as nodules contributes to closed porosity in a densified matrix, and nodules act as stress concentrators compared to smooth surfaces. SiC is an extremely strong refractory material, but a limitation of SiC is the loss of strength when oxidized below the passivating SiO2 layer. The oxidation of the SiC matrix in the nodular batch of SiC minicomposites, compared to the smooth batch, weakened the material by lowering the density of CVI SiC in the total material. To obtain maximum strength in these minicomposites, crack deflection at the fiber/matrix interface is required. Debonding of the fiber/interphase and interphase/matrix interfaces leads to crack deflection, but the presence of SiO2 instead of SiC in the matrix is going to interfere with the debonding. Thus, the SiO2 matrix character is responsible for weakening the toughening mechanisms in the minicompone. This presence of strength loss with the presence of oxygen in SiC would explain the link between rougher morphology and weaker cracking strength.

The diffraction pattern for smooth SiC is extremely ordered and crystalline, while the patterns for the other morphologies exhibit randomly oriented ring patterns. The ring patterns are indexed to the phase β-SiC and all display the (111), (220), and (311) planes. Nodular SiC and plate-like SiC also display the (200) planes. There is preferential ordering within all the ring patterns, indicated by the intensity of the (111) planes in all patterns. Additionally, while there are rings present in all these diffraction patterns, there is a trend of random orientation. Rough nodular SiC displays the most ordering, followed by nodular, plate-like, nucleated, and then bumpy SiC. The smooth SiC pattern exhibited multiple layers of the (111) planes of β-SiC. The fracture surfaces of smooth SiC and nodular SiC match the diffraction patterns; smooth SiC displays a columnar crystal growth around the fiber, while the nodules do not exhibit any visible crystallinity in the fractured matrix. The FIB process uses gallium ions to mill and manipulate the sample, and that has been shown to alter the crystal structure, commonly causing amorphization of previously crystalline samples. However, in this particular case, no amorphization has been detected, and EDX did not discern any signal for gallium.

The diffraction patterns for each morphology yield insight into how SiC is grown in this process. The ideal orientation involves the (111) planes, indicated both by the ordering of smooth SiC and the preferential ordering of the ring patterns. The presence of the oxygen may have led to some of the random orientation; however, diffraction patterns were taken both above and below the oxygen character and no difference was observed. Each nonsmooth SiC morphology formed at CH3SiCl3 depths at 12 cm or larger, indicating that an increased CH3SiCl3 concentration led to the diffraction patterns; smooth SiC displays a columnar crystal growth around the fiber, while the nodules do not exhibit any visible crystallinity in the fractured matrix. The FIB process uses gallium ions to mill and manipulate the sample, and that has been shown to alter the crystal structure, commonly causing amorphization of previously crystalline samples. However, in this particular case, no amorphization has been detected, and EDX did not discern any signal for gallium.

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5. CONCLUSIONS

CVI of SiC/SiC minicomposites at atmospheric pressure produced materials with varying surface morphologies. Six unique morphologies were identified. They were labeled smooth, nodular, rough nodular, bumpy, plate-like, and nucleated. Tensile tests were performed on a minicomposite batch with predominately smooth SiC present in the matrix and a batch with significant nodular SiC present in the matrix, with smooth SiC matrix samples displaying higher strength than nodular matrix samples.

To examine each individual morphology, various microscopy techniques were employed. SEM studies of smooth and nodular fracture surfaces indicated an ordered columnar crystal structure for smooth SiC and a randomly oriented structure for nodular SiC. FIB was used to lift out the material from each surface in nonuniform formations.22 The presence of oxygen also correlates with the random orientation in diffraction patterns. The presence of SiO2 suppresses the growth of the (111) SiC plane. The diffraction patterns reveal that given the ideal CH3SiCl3 concentration, that CVI SiC will preferentially grow along the (111) planes. If the concentration is not ideal, or there is oxygen present, the CVI SiC will not be ordered and oriented in the preferred direction, leading to weaker strength and lower toughness.
morphology, and TEM was used to examine that lift-out. EDX was used to analyze the atomic character of each morphology lift-out, and SAED was performed to investigate the crystal structure of each morphology lift-out.

Smooth SiC is the only lift-out that does not have significant oxygen character in the matrix. Smooth SiC also solely exhibits all four intense peaks from cubic SiC. Thus, the randomly oriented crystal structure and the presence of oxygen are contributors to the weaker strength of those morphologies compared to smooth SiC.

This study has quantified the relationship between the processing of various CVI SiC morphologies and the resulting chemical composition and microstructure. These results can be used as a fundamental input when processing advanced durable CMCs with optimized microstructure for safe implementation in various applications, including gas turbine engines and nuclear fuel cladding.

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Notes
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